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Qualitative near infrared spectroscopy, a new tool to recognize past vegetation signature in soil organic matter

Damien Ertlen [a, *], Dominique Schwartz [a], Didier Brunet [b], Jean-Michel Trendel [c], Pierre Adam [c], Philippe Schaeffer [c]

[a] Laboratoire "Image Ville Environnement", UMR 7362 CNRS-Université de Strasbourg, 3 rue de l'Argonne, 67083 Strasbourg, France
[b] IRD (Institut de Recherche pour le Développement), UMR 210 Eco&Sols, Montpellier SupAgro, Bâtiment 12, 2, place Viala, 34060 Montpellier Cedex 2, France
[c] Laboratoire de Biogéochimie Moléculaire, Institut de Chimie de Strasbourg, UMR 7177, Université de Strasbourg-CNRS, E.C.P.M., 25 rue Becquerel, 67200 Strasbourg, France

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ABSTRACT

Previous studies (Ertlen et al., 2010) have shown that near infrared (NIR) spectroscopy of soil organic matter (SOM) can be used successfully to discriminate between SOM from topsoils under forest vs. grassland following establishment of a referential. We have now extended this referential of topsoils, and the derived model was used to characterize SOM within three soil profiles in order to test if vegetation changes throughout these profiles can be detected using NIR spectra from buried soil organic matter. Comparison between the results from this new proxy based on NIR measurements and other historical and pedoanthracological data documenting soil occupation shows no major contradiction in terms of vegetation cover and its evolution with time. These promising results will need further development in order to provide a new palaeoenvironmental tool that is far less time consuming and easier to handle than other methods like pedoanthracology or soil lipid analysis.

1. Introduction

Soil organic matter (SOM) presents a great diversity of organic molecules (Andreux, 1979; Kögel-Knabner, 2002). This diversity is a consequence of the biodiversity and biochemical complexity of plants and of the variety of degradation/stabilization processes in the soils. As a result, the amounts, chemical structures and properties of organic molecules biosynthesized by plants are highly variable between soils covered with different vegetation assemblages (Guggenberger et al., 1994; Saiz-Jimenez et al., 1996; Trouvé et al., 1996; Marseille et al., 1999; Nierop et al., 2001; Rumpel et al., 2002; Otto et al., 2005). Several studies have highlighted plant-specific or ecosystem-specific signatures in SOM (Schwartz et al., 1986; Koerner et al., 1997; Bull et al., 2000; Trendel et al., 2010). For example, soils from 18 sites could be classified according to the biomes they belong to by analysing 128 chemical compounds (Vancampenhout et al., 2009). Trendel et al. (2010) could also establish a clear correlation between the molecular signatures of lipid fractions and the nature of the vegetation cover in the case of a series of grassland and forest topsoils. At a more local scale, Dümig et al. (2009) found chemical differences in soils under different types of vegetation using ^{13}C NMR spectroscopy, lignin analysis, measurement of soil colour lightness and groupings of heavy organo-mineral fractions according to their $^{13}C/^{12}C$ isotopic signature.

However, so far, all the methods used are time consuming and/or restricted to specific environments. For example, the use of $\delta^{13}C$ signatures that allows C3 vs. C4 vegetation to be distinguished is very limited in temperate environments since the vast majority of plants growing in such environments follow the C3 carbon fixation pathway.

We have recently developed a novel approach aimed at identifying ecosystem-specific signatures based on near infrared spectroscopy (NIRS; Ertlen et al., 2010). NIRS has the advantage of being a fast and cost-effective tool that has been intensively used for several decades in various industrial sectors (Wetzel, 1983; Burns and Ciurczack, 2001) and in soil science for the simultaneous prediction of various chemical, physical and biological quantitative parameters from a single spectral measurement (Coûteaux et al.,

* Corresponding author. Tel.: +33 (0)3 68850918.
E-mail address: damien.ertlen@live-cnrs.unistra.fr (D. Ertlen).

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2003; Viscarra Rossel et al., 2006; Barthès et al., 2008; Stevens et al., 2008; Cécillon et al., 2009).

Our initial approach (Ertlen et al., 2010) was based on the concept of fingerprinting (Palmborg and Nordgren, 1996) and consisted in discriminating the NIR spectra of SOM according to the vegetation cover. It could be concluded based on a large set of soil samples from 11 sites that SOM from grasslands can be clearly discriminated from that of soils under forests based on their NIR spectral signature (Ertlen et al., 2010). In the present study, we have first extended the referential of NIRS spectra from the initial surface horizon sample set to 14 sites, notably in order to confirm that grassland soils can be clearly distinguished from forest soils. Then, the NIR signatures from topsoils before and after lipid extraction (i.e., after removal of the organic solvent-soluble organic matter) were determined in order to evaluate the potential influence of lipids on discrimination of vegetal sources of SOM by NIRS. Indeed, some constituents of the lipid fractions are source-specific and allow the different vegetal sources of SOM to be discriminated (e.g. Trendel et al., 2010). Consequently, we have envisaged that the NIR signature of lipid constituents of SOM, often considered as a relatively recalcitrant SOM pool, could account, at least to some extent, for the specificity of the NIR signature of SOM.

A second part of the present article is devoted to the reconstruction of past vegetation based on the investigation of the NIR spectra of SOM within soil profiles. Indeed, SOM (geo)chemical analysis is potentially very useful to reconstruct past vegetation provided that recalcitrant and vegetation-specific organic fractions are preserved. However, to deduce chronological information, it is necessary to consider the turnover of SOM and its evolution with depth and pedological conditions. Many studies restricted to decade time scales do not take into account the deep soil horizons (Bernoux et al., 1998; Bird et al., 2002; Spielvogel et al., 2007), although these horizons contain, compared to topsoils, larger proportions of recalcitrant and potentially older organic matter originating from former vegetation covers (Rumpel et al., 2002). Given the presence of bioturbation and the lack of a stratified time scale in soils (Krull et al., 2006; Schwartz, 2012), a modelling approach of SOM "age" in soils is necessary. Several models, general or restricted to well-defined environments, have been proposed to predict the evolution of carbon stocks in soils (Smith et al., 1997). Most of them focus on topsoils, which have the highest organic carbon content. Others are modelling soil profiles down to one metre depth (Jenkinson et al., 2008). Some of them use partition into several soil compartments (Becker-Heidmann and Scharpenseel, 1992), and almost all of them include a stable or inert organic carbon pool. The different versions of RothC model (Jenkinson and Rayner, 1977; Jenkinson et al., 1990; Jenkinson and Coleman, 2008) and CENTURY model (Parton et al., 1989) use radiocarbon measurements to predict the evolution of carbon stocks in soils. The input data of the models are often from sites that have been monitored over the long term. However, follow-up periods rarely exceed a century (Smith et al., 1997) and what modellers call "long term" corresponds in fact to the very short term for paleoenvironmental studies over the Holocene period.

In the present study, we have investigated the possibility that NIRS could be used to reconstruct past vegetation considering that preserved organic matter with a high residence time in deep soil horizons might have a NIR spectral signature which can be associated to past vegetation. We have also hypothesized that the NIR spectral signature of organic matter related to a specific vegetal source is preserved through time and, thus, that vegetation changes can be detected based on NIR spectroscopy relying on the referential established on topsoils with well-characterized vegetation. To this aim, spectra from complete soil profiles were determined on three sites with a well known long term history. They were then compared with topsoil reference spectra in order to test first if the documented vegetation changes can indeed be detected using the NIR spectra from SOM with higher MRT. In a second stage, the NIRS profiles were interpreted in the frame of a soil organic matter turnover model adapted from Jenkinson et al. (1990) in order to evaluate the timing of the vegetation changes (if detected) and to compare the evaluated dates with those established according to the known history of the investigated profiles.

2. Material and methods

2.1. Characteristics of sites and soils

Thirteen sites from the Vosges mountains (North East France) (Fig. 1 and Table 1) and one site in the Beskidy mountains (Czech Republic; site code: SLF; Table 1) were chosen to investigate topsoils. The soils (Table 1) are mostly cambisols and umbrisols (WRB, 2006), except WHS (entic podzol) and RTH (leptosol). The main soil characteristics for initial eleven sites are described in Ertlen et al. (2010) and are summarised in Table 1, and the three additional sites EFA, BLH and SLF reported in the present study are developed on acidic bedrock. The organic-C and pH values of the latter are in the same range as those from the sites described in Ertlen et al. (2010). Organic-C content from the upper horizon (0–4 cm; Table 1) ranges from 4.5% (WHS) to 50.3% (RTH) and pH from 3.5 (DHS) to 5.0 (EFA).

The vegetation cover of the reference topsoils consists of grassland on six sites, beech or beech-fir forest on six sites (including a site with higher biodiversity that we call "mixed forest") and oak forest on two sites (Table 1). For each site, a detailed study of the forest history, including field observations and a review of ancient maps, is provided in Ertlen and Schwartz (2010). This review is mostly based on the Alsatian cadaster from 1760 at a scale of about 1/5000, the collection of maps drawn by the German army around 1890 (1/50 000), the registers of the French forest office (ONF) from 1840 until today and, for the twentieth century, the

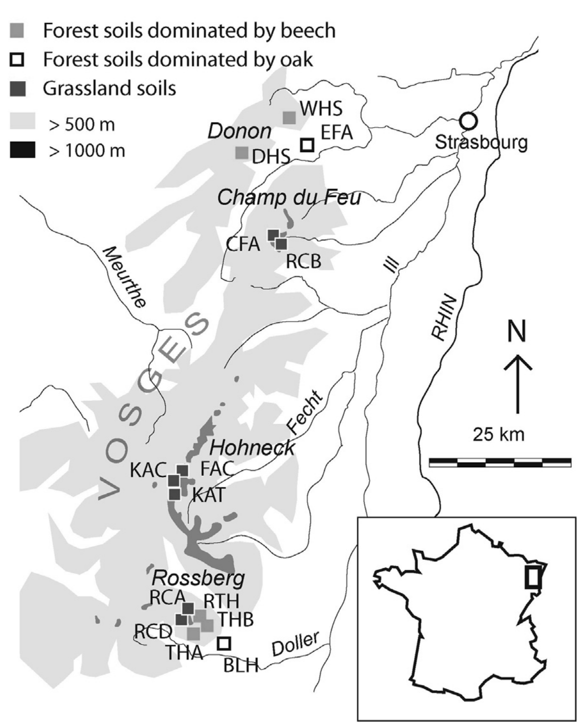

Fig. 1. Location of the sampling sites.