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Infrared spectroscopy as a useful tool to predict land use depending on Mediterranean contrasted climate conditions: A case study on soils from olive-orchards and forests

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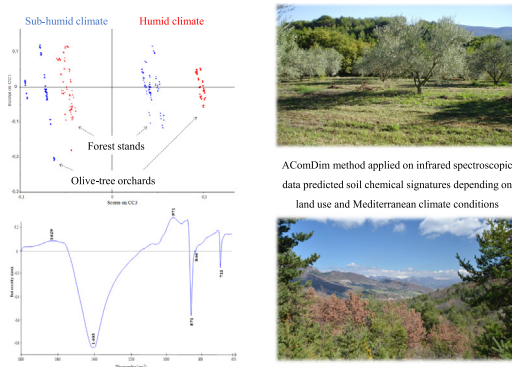
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HIGHLIGHTS

- FTIR-ATR was used to test land use effect on soil chemical properties.
- Soil chemical signature differs between olive-tree orchards and Mediterranean forests.
- Climate (Humid vs Sub humid, coastal vs inland area) also shapes soil properties.
- PLS modeling confirmed that FTIR-ATR is a useful tool to predict land use.

GRAPHICAL ABSTRACT



ABSTRACT

Soil chemical properties depend on various environmental factors such as above ground vegetation, climate and the parent rock substratum. Land use, and the associated management practices, is one of the major drivers which can deeply impact soil properties. To better understand the dynamics of soil chemical properties and to assess potential impact of land use, an improved monitoring of chemical signature in organo-mineral topsoils is necessary. Here, we explored how land use (forests or agrosystems i.e. olive-tree orchards) may shape soil chemical signature and whether it depends i) on the type of agricultural or silvicultural practices, ii) on contrasted Mediterranean climate conditions at different spatial scales. We measured variations in soils properties by FTIR-ATR (Fourier-Transformed Infrared – Attenuated Total Reflectance) spectroscopy and elemental concentrations. FTIR showed that the aromatic fraction of organic matter and CaCO_3 discriminated soils under different land uses (orchards or forests) and this depended on climate (sub-humid vs humid climate). Moreover, the chemical signatures of soils varied with the practices applied. For agrosystems, soils complemented with olive-mill wastes were characterized by aromatics compared to soils under natural grass or tillage. For forests, soils from *Pinus* spp. stands and *Quercus* spp. stands were discriminated by CaCO_3 and aromatics respectively. Contrasted climate conditions at local scale, i.e. northern vs southern slopes for forests and distance from the sea (coastal vs inland area) for agrosystems, had an effect on soil chemical signature. The AcomDIM interpretation of FTIR-ATR signals showed that factors “land use”, “practices” and “climate” and their interactions could

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1. Introduction

Soil organic matter (SOM) is composed of a great diversity of molecules from plant, animal and microorganisms, at different stages of decay, which defines soil chemical signature. This chemical fingerprint depends on various environmental biogeophysical drivers and their interactions (Coûteaux et al., 1995; Garcia-Palacios et al., 2016; Liu et al., 2019), mainly climate, above ground vegetation and the parent rock substratum. Soil chemical signature thus results from a combination of different processes linked to organic matter transformation i.e. degradation/stabilisation and their balance, which is subrogated to complex interactions of biological, chemical and physical processes in soils. The persistence and decomposition of SOM is known to be also influenced by the mineral fraction of soil and the proportion of the different components of this fraction depends on soil physico-chemical environment i.e. pH, redox potentials, temperature, humidity and soil parent material (Kleber et al., 2015). The physical and mineral composition of soil also contributes to its chemical signature as revealed for instance by spectroscopic and X-Ray diffraction techniques (Prandel et al., 2014).

Climate is one of the major factors controlling these processes. In the Mediterranean area, climate conditions are particularly drastic i.e. characterized by intense summer droughts and high temperatures. This stress linked to water potential is reinforced in coastal environments by wind regime and osmotic stress via sea spray exposure, hampering decomposition processes (Farnet et al., 2016; Qasemian et al., 2014).

Land use is also expected to have a strong effect on the quality and composition of SOM (Dhillon et al., 2017). In forests, vegetation assemblages are known to deeply impact SOM composition (Aranda et al., 2011; Brunel et al., 2017; Prescott and Grayston, 2013.). Broadleaved species, such as *Quercus* spp., enhance SOM quality, increasing easily-degradable compounds and thus enhancing microbial metabolism (Polyakova and Billor, 2007). Conversely, some vegetal species specific to the Mediterranean area such as *Pinus* spp. are particularly sclerophyllous (high amounts of recalcitrant molecules such as cutin or lignin) and poor in nutrients, which induces lower rates of decomposition (Iovieno et al., 2010). Agriculture and associated practices have a pronounced effect on soil chemical properties, such as nutrient content and balance, C/N ratio, pH and salinity (Gómez et al., 2011; Nieto et al., 2013). In the Mediterranean basin, olive trees (*Olea europaea* L.) and their cultivation have an important socio-economic role (Ferrise et al., 2013). Moreover, this type of culture can contribute to improve soil quality by favouring carbon sequestration in soils and limiting erosion depending on the practices applied i.e. natural grass but natural vegetation or use of cover-crop (Hernández et al., 2005; Marquez-Garcia et al., 2013).

SOM changes depending on various environmental factors can be successfully monitored by non-destructive techniques. FTIR spectroscopy is a rapid and non-destructive method well recognized for its ability to characterize the chemical composition of living plants (Fourty et al., 1996; Richardson et al., 2004) and plant litter (Farnet-Da Silva et al., 2017). Authors have shown that this technique discriminated soil depending on the vegetation cover i.e. grassland or forests (Ertlen et al., 2015; Vysloužilová et al., 2015), alternative rotations treatments or native prairie soil (Calderón et al., 2011). The impact of the drastic environmental conditions on soil properties was also revealed through Near and Mid-infrared spectral profiles (or a both combination) from semi-arid Mediterranean soils with different management practices (Aranda et al., 2014) or from insular Mediterranean soils (D'Acqui et al., 2010). Based on Near and Mid-infrared spectroscopic data, Partial

Least-Square Regression (PLSR) can rapidly discriminate soils depending on physical, chemical and microbial properties (total organic C, total N, CaCO₃, microbial biomass ...), which varied with above ground vegetation assemblages (Janik et al., 2007; Knox et al., 2015) or with land use change (Paz-Kagan et al., 2014; Madhavan et al., 2017).

However, to our knowledge, no study has compared the relative effects of different land uses on SOM profiles especially under Mediterranean climate conditions. Moreover, limited information is available about the effect of land use in interaction with climate conditions and with the practices associated to specific soil managements. Here, we aimed at identifying how land use (forest stands of *Quercus* spp. and *Pinus* spp. vs olive-tree orchards) shapes soil chemical signature. Moreover, we tested whether this relation depended on applied practices (monospecific or mixed stands for forests, tillage, natural grass or olive-mill waste (OMW) amendments for olive-tree orchards) and on the contrasted climate conditions of the Mediterranean area at various spatial scales (humid vs sub-humid Mediterranean climate, coastal and inland areas from the sub-humid Mediterranean climate, Southern vs Northern slopes from the humid Mediterranean climate).

Based on Partial Least-Square Regression (PLSR), our research will eventually provide a model relying on the interactions between climate conditions, land use and soil chemical properties. This model could be further used to better assess the effects of these environmental factors on ecosystem functioning since soil molecular composition is a major driver regulating microbial activities involved in C dynamics (i.e. either sequestration or mineralization) in soils.

2. Materials and methods

2.1. Study sites and sampling design

The study was conducted in spring 2013 in South Eastern France (Provence-Alpes Côte d'Azur), an area characterized by frequent and intense droughts and heat waves typical of the Mediterranean climate. The Provence's soil is characterized by carbonatic pedofeatures, such as fine calcareous silt clay loam (Luvisol in the inland area according to the IUSS Working Group (2006)).

We conducted our study in two distinct bioclimates i.e. sub-humid and humid (Table 1), corresponding to altitudinal arrangement of vegetation type i.e. Meso Mediterranean and Supra Mediterranean levels (Quézel and Médail, 2003). Sampling plots were selected in i) a 500 km² area from Sausset les Pins to Port de Bouc (43° 22'N, 5°3'E) for the sub-humid climate in coastal area (area 1), ii) a 700 km² area from the Massif de la Sainte Baume (43°21' N, 5°43'E) to the Massif des Alpilles for the sub-humid climate in inland area (area 2) and iii) in a 700 km² area from the Massif of Luberon to the Réserve Géologique of Digne les Bains (44°12' N, 5°59' E) for the humid climate (area 3). Different annual trends and mean monthly temperature and precipitation between these areas are shown in Table 1.

In area 1, five independent 20-year-old olive tree orchards for each practice (tillage, natural grass, OMW amendment) were selected with the same variety of olive trees. In each orchard, a sampling plot (400 m²) was delimited and for each plot, 10 bulk soil samples (10 × 10 × 10 cm) were cored at 1 m of olive tree trunk using a flat shovel. The ten samples of soils were combined to obtain a unique composite sample per plot.

In area 2, the same experimental design was used for soil sampling in olive tree orchards.

Table 1

Characterization of the two bioclimates and vegetation stages of the different areas under study (climate data from WorldClim dataset, 1950–2000, <http://www.worldclim.org/>, Hijmans et al., 2005).

Sampling area	Area 1	Area 2	Area 3
Bioclimates	Sub-humid	Sub-humid	Humid
Vegetation stages	Meso-Mediterranean	Meso-Mediterranean	Supra-Mediterranean
Location	43°22' N, 5° 3' E (coastal)	43°21' N, 5°43' E (inland)	44°12' N, 5°59' E
Mean altitude	30 m	400 m	1000 m
Main tree species	<i>Pinus halepensis</i>	<i>Quercus ilex</i> <i>Pinus halepensis</i>	<i>Quercus pubescens</i> <i>Pinus sylvestris</i>
Associated vegetation	<i>Quercus coccifera</i> , <i>Pistacia lentiscus</i> , <i>Asparagus acutifolius</i> <i>Rosmarinus officinalis</i> , <i>Cistus albidus</i>	<i>Asparagus acutifolius</i> , <i>Helichrysum stoechas</i> , <i>Juniperus oxycedrus</i> , <i>Phillyrea latifolia</i> , <i>Quercus coccifera</i> , <i>Rhamnus alaternus</i> , <i>Rosmarinus officinalis</i> , <i>Rubia peregrina</i> , <i>Thymus vulgaris</i> .	<i>Amelanchier ovalis</i> , <i>Aphyllanthes monspelliensis</i> , <i>Buxus sempervirens</i> , <i>Crataegus monogyna</i> , <i>Hieracium murorum</i> , <i>Juniperus communis</i> , <i>Rhamnus saxatilis</i> , <i>Sanguisorba minor</i> , <i>Teucrium polium</i>
Annual precipitation	670 mm	755 mm	842 mm
Precipitation of the driest month	15 mm	18.2 mm	40.6 mm
Mean annual temperature	13.7 °C	13.00 °C	9.60 °C
Min temperature of the coldest month	3.5 °C	1.6 °C	–2.5 °C

Forest stands of around 60 ± 10 -year-old, which had not undergone forest management for 35 years were selected: 30 square plots ($20 \text{ m} \times 20 \text{ m}$) were chosen using GIS software (MapInfo professional 11.5 ®) and combining the French Geological Survey with the Forest Property Regional Center and the National Institute of Geography databases. For each of the three types of forest stand (*Pinus halepensis*, *Quercus ilex* and mixed stands 50/50), five square plots were selected on south-facing and north-facing slopes. Mixed stands (50/50) *Pinus/Quercus* were selected by measuring the basal area ($\text{m}^2 \cdot \text{ha}^{-1}$) of *Quercus* spp. and *Pinus* spp. of each sampling plot, determined from each tree diameter measured at 1.20 m from the ground. Within each plot, ten bulk soil samples were collected from 0 to 10 cm deep (A horizon) and combined to obtain a unique composite sample per plot.

In area 3, the same protocol as described above was used for sampling in olive tree orchards and in forest stands of *Pinus sylvestris*, *Quercus pubescens* and mixed stands 50/50.

All the plots (in forest or orchards) were considered to be true replicates as the distance between them exceeded spatial dependence ($>2 \text{ km}$).

The composite samples were transported to the laboratory at ambient temperature, sieved to 2 mm and stored at 4 °C. These composite samples were dried at 70 °C for 72 h and ground to obtain a powder using a bullet blender Retsch MM40 (Fisher Scientific, France).

2.2. Chemical characterization of soils by FTIR-ATR (Fourier-Transformed Infrared – Attenuated Total Reflectance)

Soil samples were directly deposited on the attenuated total reflectance (ATR) accessory (Bruker “Golden Gate”) equipped with a diamond crystal prism (brazed in only one tungsten carbide part), four mirrors and two ZnSe focusing lenses in to reflect the optical path. Soil sample was pressed on the crystal area with the pressure arm and positioned over the crystal/sample area. The recording of FTIR-ATR spectra was performed with a Thermo Nicolet IS10 spectrometer equipped with a MCT detector, an Ever-Glo source and a KBr/Ge beam-splitter, at room temperature. Data acquisition was done in absorbance mode from 4000 to 650 cm^{-1} with a 4 cm^{-1} nominal resolution. For each spectrum, 100 scans were co-added. A background scan in air (in the same resolution and scanning conditions used for the samples) was carried out before the acquisition. The ATR crystal was carefully cleaned with ethanol to remove any residual trace of the previous sample. Three

spectra were recorded for each sample. Spectral zone between 4000 and 1800 cm^{-1} was withdrawn since the spectral zone ranging 4000 and 3000 cm^{-1} presents a broad band representative of O—H, N—H vibrations with a lot of hydrogen bonding effects encompassing a part of aliphatic bands and the spectral region from 2400 to 1900 cm^{-1} presents bands of CO_2 and diamond absorption. This is why this part of the spectrum is usually deleted in the analyses of the data. Multiplicative Scatter Correction (MSC) was used to compensate for additive and/or multiplicative effects in spectral data for chemometrics treatments.

2.3. pH, elementary analysis and C-CaCO₃ content

Briefly, pH H_2O was determined in distilled water after 45 min under magnetic stirring at 600 rpm. Extractable phosphorus (P), was measured with Olsen method and available potassium (K), iron (Fe) and calcium (Ca) by flame photometry. Total C and N contents were measured using a C/N elementary analyser (Flash EA 1112 serie ThermoScientific) on the dried cylindrical soil-core fraction $<2 \text{ mm}$. Determination of calcium carbonate (CaCO_3) in samples is based on the volumetric analysis of the carbon dioxide CO_2 , which is released during the application of hydrochloric acid solution HCl 4N and was performed using volumetric calcimeter Bernard modified method (Hulseman, 1966; Muller and Gatsner, 1971). Carbon proportion of CaCO_3 was then calculated using the molar mass: $\% \text{C-CaCO}_3 = \frac{11.991}{100} \times \% \text{CaCO}_3$. Then, organic carbon was calculated by the difference between total C content and C- CaCO_3 content (Wang et al., 2012).

2.4. Statistical analyses

The AComDim (Anova Common Dimension) method is a multi-block analysis highlighting the influential factors (and their interactions) by a simultaneous analysis of all data. This method is based on the same concept as ANOVA-PCA (also called APCA) and its description can be found in Amat et al. (2010) and Bouveresse et al. (2011). AComDim decomposes the experimental data matrix into successive matrices and a multi-block PCA analysis of all matrices is performed in order to extract the “Common Components” (CCs) and their specific contribution, called salience, which make possible to find the significant factors. The block significance is afterward estimated with a Fisher test (student Fisher F -test with $n - 1$ degrees of freedom, where n is the number of blocks and an alpha level equal to 0.01) applied on the F -

values (F_i) calculated as

$$F_i = \frac{\lambda_{res}}{\lambda_i} \quad (1)$$

where λ_{res} is the salience of the residual block on CC1 and λ_i is the salience of the i^{th} block on CC1.

The blocks for which F_i is greater than the critical value (F_c) of the Fisher table are considered as being related to influential factors or interactions. By examining the calculated saliences, it is possible to determine which CC is related to which factor or interaction. In order to estimate the effect of the factor, it is possible to plot the sample scores on the informative CCs vs. CC1. Loadings show spectral bands discriminating samples for a CC and are used to understand sample projections on the score graphs (Gaston et al., 2017). All the spectral bands were assigned according to Socrates (2007). All computations were performed using Matlab 7.14 (R2012a). The AComDim procedure was adapted from the ComDim function in the free toolbox SAISIR (Cordella and Bertrand, 2014).

Partial Least Square regression (Geladi and Kowalski, 1986; Van Roon et al., 2014) is a concept of multivariate calibrations forms where variables data are divided into groups of response variables and predictor variables. Here predictor variables were spectral profiles and responses were land use, climate or practices, binary codified. A linear regression equation was established where reflectance at each spectral wavelength (X_i) was related to a response variable (Y):

$$Y_p = a_1X_1 + a_2X_2 + \dots + a_nX_n + b \quad (2)$$

where Y_p was the predicted value for the response variable, a_1 to a_n were the PLS regression coefficients for predictor variables (X_i) and b was the equation intercept. The objective of this regression was to extract "components" or latent variables (LV) responsible for the variation of the predictor variables and which best model the behavior of the response variables. The choice of extracted latent variables was done by cross-validation which consisted of constructing a calibration model on a subset of X data, then testing the model obtained on another subset of X data (not taken into account in the calibration model). A validation model was obtained for which the number of components was chosen so as to minimize the estimation error.

The quality of the calibration models was estimated by the standard error of calibration (SEC) (Eq. (3)) and the robustness of the model was evaluated by the standard error of prediction (SEP) (Eq. (4)).

$$SEC = \sqrt{\frac{\sum_{i=1}^N (Y_i - Y'_i)^2}{N-1-p}} \quad (3)$$

$$SEP = \sqrt{\frac{\sum_{i=1}^M (C_i - C'_i)^2}{M}} \quad (4)$$

where Y_i is the measured value of the response variable and Y'_i the calculated value from the calibration or validation equation. N corresponds to the number of samples used for the construction of the model, p to the number of optimal independent variables determined by cross-validation, and M to the number of samples used for the prediction. For the building of some PLS models, spectral data were averaged per sample.

The statistical significance of climate, land use and practices on soil chemical parameters was determined by three-way analysis of variance (ANOVA) and statistically significant ($P < 0.05$) main effects and interactions were analysed further using the Tuckey HSD post hoc tests. Data that were not normally distributed, or showing unequal variance were transformed prior to analysis, using log10 transformation.

Table 2
Studied factors, level factors and number of spectral data used for the different AcomDim studies.

Studied factors	Land use		Climate			Practice				Exposure						
	Levels	Olive-tree orchards	Forests	Sub-humid inland	Sub-humid coastal	Humid	No-tillage	Tillage	Olive-mill waste amendment	<i>Pinus halepensis</i>	<i>Quercus ilex</i>	<i>Pinus sylvestris</i>	<i>Quercus pubescens</i>	Mixture	South-facing	North-facing
First study	52	180	116			116	20	16	16	30	30	30	30	60	/	/
Second study	78	/	26	26	26	26	30	24	24	/	/	/	/	/	/	/
Third study	/	180	90	/	/	90	/	/	/	30	30	30	30	60	90	90

/ level not considered.

/: level not considered.

3. Results

We first tested the effects of land use (agrosystem vs forest), climate (sub-humid vs humid climate), the practices applied (agricultural, sylvicultural) and their interactions (first study) on soil chemical signature. Then, for each land use, the effect of specific climate factors and practices were determined. For olive-tree orchards, the effects of climate across a climate gradient (sub-humid coastal, sub-humid inland and humid climate), agricultural practices and their interactions were tested (second study). For forests, the effect of climate conditions at regional (sub-humid vs humid) and at local (Northern vs Southern slopes) scales, sylvicultural practices and their interactions were analysed (third study). For each study, the number of spectra for each factor is presented in Table 2.

3.1. Infrared spectroscopy reveals the effect of land use on soil chemical signature

To determine how land use ‘fingerprint’ and/or practices applied modified soil chemical properties and whether it depended on climate conditions, FTIR-ATR technique was used to characterize the two sets of soils from either forests or agrosystems from the sub-humid and

humid climate (Table 2, first study). The F-values (computed from the saliences on CC1) of the different blocks (Fig. 1a) were close to 1 but only block 4 (“climate-land use interaction”) was larger than the critical F-value ($F_c = 1.23$) of the Fisher table according to the alpha level ($\alpha = 0.05$ by considering 261 degrees of freedom). The significance of the three main factors (climate, land use and practice) was border line with F-values comprised between 1.15 and 1.20 for an alpha level of 0.05. The study of saliences confirmed the results obtained with the F-values (Fig. 1b). The effect of the interaction between climate and land use on FTIR-ATR spectra is shown by the projections associated to CC3 (related to block 4 “interaction climate-land use”) in Fig. 2a. The score plots of CC3 clearly shows a discrimination between soil samples depending on climate (humid or sub-humid) and land use (forests vs olive tree orchards). From the loading plot (Fig. 2b), the projections according to CC3 are positively explained by IR signals assigned to $\nu(\text{C}=\text{C})$ phenolic acid and $(\text{C}-\text{H})$ out of plane (CH_3) (Fig. 2b) i.e. 1630, 971 cm^{-1} . This indicates that the chemical signature of forests soils from sub-humid climate and orchards from humid climate can be clearly differentiated by compounds from lignin, while soils of orchards from sub-humid climate and of forests from humid climate are characterized by the presence of carbonate, a key component of soils on calcareous parent material. These results are in accordance with those found

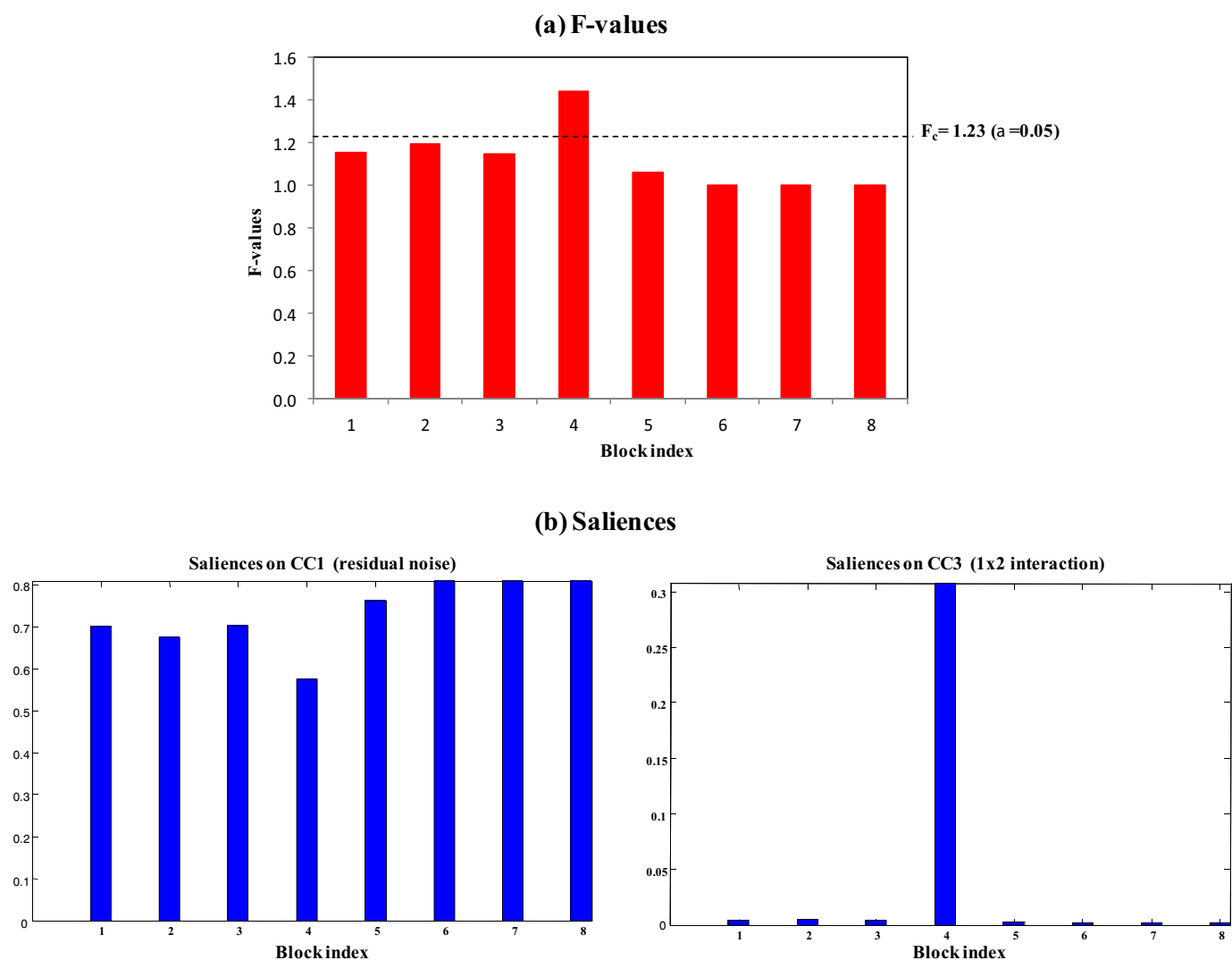


Fig. 1. AcomDim of spectral soil data from forest stands and olive-tree orchards: (a) F-values vs. block index, (b) saliences vs. block index for significant CCs. Block 1 “climate”, block 2 “land use”, block 3 “practices”, block 4 “climate-land use interaction”, block 5 “climate-practices interaction”, block 6 “land use-practices interaction”, block 7 “climate-land use-practices interaction”, block 8 “residual”.

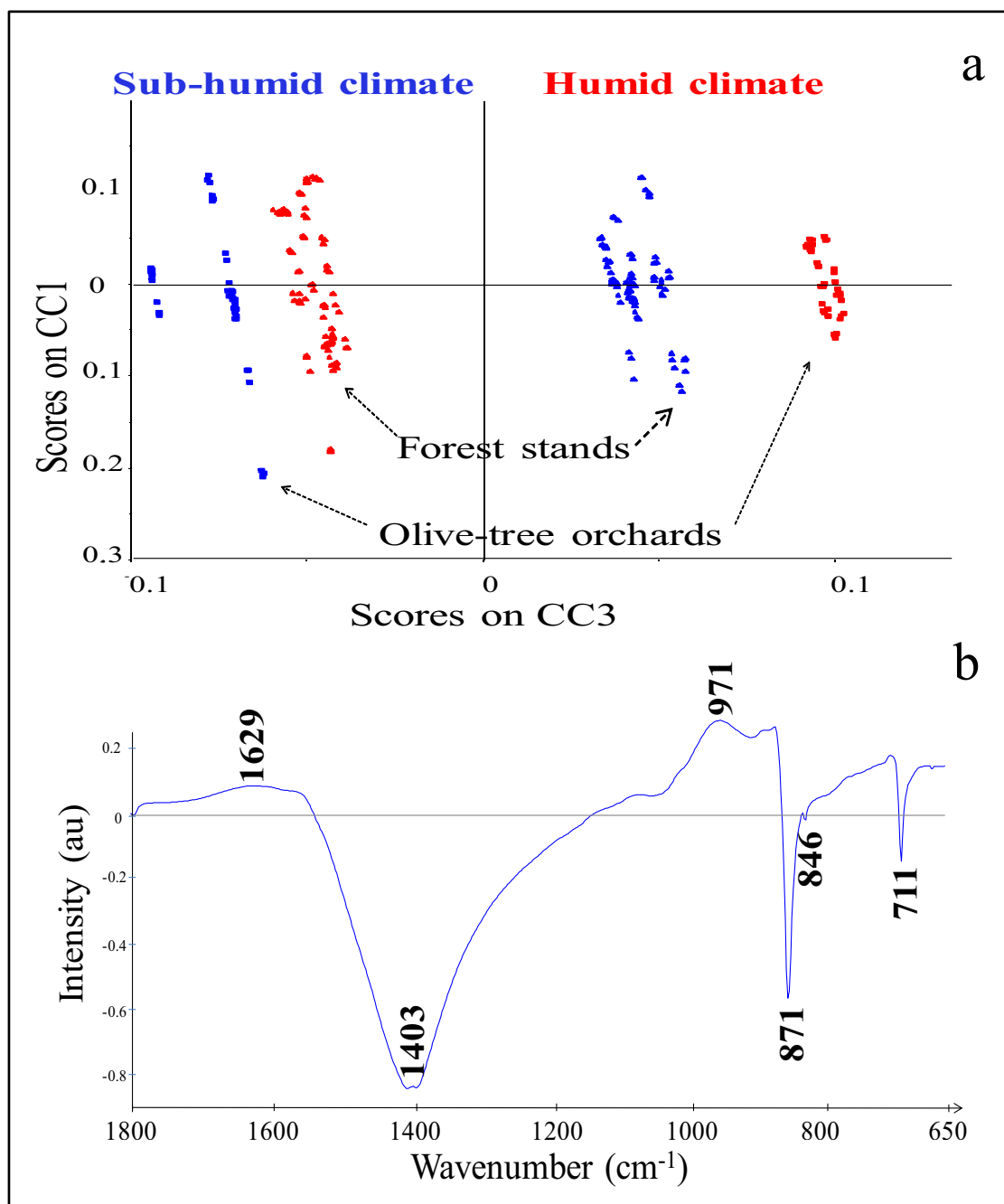


Fig. 2. AcomDim of spectral soil data from forest stands and olive-tree orchards: (a) CC1 vs. CC3 scores plots, (b) loading on CC3 corresponding to interaction "climate-land use".

with the other soil chemical properties analysed in this study. Higher amounts of C-CaCO₃ were found in soils of olive-tree orchards from sub-humid climate and of forests from humid climate and moreover, these forests had lower amount of Organic-C (Table 3).

Though FTIR-ATR spectra revealed that projections were discriminated for each type of land use the effect of practices appeared non-significant.

3.2. Infrared spectroscopy reveals the effect of practices applied for each land use

FTIR-ATR spectra were further analysed for each type of land use independently (Table 2, second and third studies).

For soils from olive-tree orchards (Table 2 second study), we thus tested the effect of climate (coastal and inland areas in sub-humid climate and humid climate) and of the practices applied (tillage, natural grass and OMW amendment). AcomDim analysis of spectral data of olive-tree orchards revealed that the critical F-value (F_c) was equal to 1.34. Under these conditions, only the first block, relative to the climate factor, had an F-value superior to F_c (plots of F-values and saliences versus block index not shown). The score plots of CC1 versus CC2 (Fig. 3a) showed that soils were clearly separated depending on climate. Projections of soils from the humid climate were explained on the positive part of the loading on CC2 (Fig. 3b) by signals at 1633, 1072, 973, 796 and 777 cm⁻¹ assigned to (C=O) vibrations (in carboxylic acids/esters) or (C=C) stretching (in aromatics), (C-H) out-of-plane deformation (CH₃) and (=C-H) out-of-plane deformation bands (in aromatics).

Table 3

Averages of soil chemical properties from forest soils ($n = 30$) and olive-tree orchards ($n = 15$) and p values from one-way ANOVA. Means with the same letter are not significantly different (Tukey's Test).

	p -Value	Sub-humid coastal climate	Sub-humid inland climate	Humid climate
Forest soils				
%N	<0.001	–	0.52 ± 0.10 a	0.39 ± 0.09 b
Organic C (%)	<0.005	–	9.90 ± 1.68 a	6.88 ± 0.89 b
C-CaCO ₃ (%)	<0.05	–	19.86 ± 5.81 a	28.84 ± 4.6 b
C/N	<0.05	–	25.83 ± 2.33 a	28.92 ± 3.21 b
Ca (g.kg ⁻¹)	<0.05	–	13.2 ± 3.1 a	16.4 ± 4.1 b
P Olsen (mg.kg ⁻¹)	ns	–	14 ± 2 a	15 ± 4 a
K (mg.kg ⁻¹)	ns	–	231 ± 81 a	203 ± 66 a
Fe (mg.kg ⁻¹)	ns	–	1.1 ± 0.2 a	1.8 ± 0.5 a
Olive-tree orchard soils				
%N	ns	0.17 ± 0.02 a	0.19 ± 0.04 a	0.19 ± 0.04 a
Organic C (%)	ns	2.80 ± 0.88 a	3.19 ± 0.80 a	2.59 ± 0.49 a
C-CaCO ₃ (%)	<0.05	27.88 ± 5.23 ab	35.20 ± 4.86 a	19.15 ± 4.11 b
C/N	ns	17.51 ± 6.24 a	17.05 ± 4.81 a	13.31 ± 0.81 a
Ca (g.kg ⁻¹)	<0.05	15.6 ± 2.2 ab	19.1 ± 1.1 a	12.8 ± 2.5 ab
P Olsen (mg.kg ⁻¹)	ns	8 ± 1	11 ± 3	10 ± 4
K (mg.kg ⁻¹)	ns	148 ± 78 a	202 ± 88 a	185 ± 95 a
Fe (mg.kg ⁻¹)	ns	2.1 ± 0.3 a	2.8 ± 0.5 a	1.8 ± 0.5 a

respectively. Soils from the coastal sub-humid climate were explained on the negative part by signals at 1400, 871 and 711 cm⁻¹, which can be assigned to the presence of CaCO₃. Soils from the inland area of sub-humid climate were centered on the origin of the two-dimensional plots (Fig. 3a). The effect of practices was non-significant using this set of data. On the other hand, when considering the coastal and inland areas from sub-humid climate, the effect of practices was revealed (Fig. 4). Thus, no discrimination of samples depending on the practices was actually possible when data from the humid climate were included in the analyses. The effect of practices was observed according to score plots of CC1 versus CC3: soils complemented with OMW amendment were discriminated from tilled and non-tilled soils (Fig. 4a). Projections assigned to OMW amendment were linked to positive signals of loading on CC3, pointed at 1083, 970 and 900 cm⁻¹ linked to C—O of various alcohol types, (=C-H) out-of-plane deformation bands (in aromatics). Soils under tillage and natural grass were explained by signals at 1409, 871 and 711 cm⁻¹ from CaCO₃. This has to be linked with the amounts of organic C which were significantly higher in soils complemented with OMW than in soils under tillage or natural grass ($F = 5.025$, $p < 0.05$, data not shown).

For soils from forest stands (Table 2 third study), we tested the effect of climate (sub-humid and humid), of the sylvicultural practices applied (monospecific stands of *Q. ilex*, *Q. pubescens*, *P. halepensis* or *P. sylvestris*, and mixed stands of *Q. ilex/P. halepensis* and *Q. pubescens/P. sylvestris*) and of exposure (Southern vs Northern slope). A critical F-value of 1.28 ($\alpha = 0.05$ by considering 180° of freedom) was found from ACOMDIM analysis and consequently factors “climate” and “practice” and interaction “land use - exposure” showed a F-value superior to F_c and can be considered as significant factors. The score plots of CC4 (corresponding to block 1 related to climate) showed discrimination of soils according to climate (Fig. 5a). Associated loading (Fig. 5b) characterized soils from humid climate by positive signals at 1411, 1164, 1122, 1083, 796, 777 cm⁻¹ assigned to C=C (Aromatic), ν_a (C-O-C) ester, C—H (Aromatic), γ (=C-H) out of plane aromatic, C—H out of plane (disubstituted aromatic ring), (Table 1) from phenolic compounds and cutins and by signals at 1394, 871 and 711 cm⁻¹ assigned to CaCO₃. These results are corroborated with the amount of CaCO₃ found in soils from humid climates which were higher than those from sub-humid climate (Table 3). The differentiation of samples from sub-humid climate was linked to signals at 1564, 908, 887, 727 cm⁻¹ (Fig. 5 b) on the negative part of CC4 loading, which can be assigned to C=C from aromatics, C—H out of plane (monosubstituted aromatic ring), C—H out of plane (disubstituted aromatic ring) from phenolic compounds.

The score plot of CC3 (corresponding to block 2 related to practices) (Fig. 5 c) showed that soils under *Pinus* spp. stands were gathered on the positive part of CC3 and were explained by the positive bands of CC3 loading at 1411, 871 and 711 cm⁻¹ i.e. from CaCO₃ (Fig. 5d). On the other hand, samples from *Quercus* spp. were projected on the negative part of CC3 scores plot and explained by negative signals at 1612, 977, 908, 794, 775, 744 cm⁻¹ related to ν (C=C) aromatic or conjugated, γ (=C-H) out of plane aromatic, ρ (HOH) from aromatics. Projections from soils of both *Quercus* spp. monospecific stands overlapped, while those of both *Pinus* spp stands were not strictly superimposed. Soils from both mixed stands (*Q. ilex/P. halepensis* and *Q. pubescens/P. sylvestris*) were centered at the origin of the two-dimensional plots, showing an equitable influence of the two tree species on soil properties.

The effect of exposure (northern vs southern slope) on the chemical signature of forest soils was found according to CC8, corresponding to block 6 related to interaction “practice - exposure” (Fig. 5e). Soils from either *P. sylvestris* and *Q. pubescens* stands were particularly discriminated depending on exposure compared to soils from *P. halepensis* and *Q. ilex* stands. Moreover, stand admixture has smoothen the effect of exposure as shown by projections gathered at the center of the two-dimensional plots. Soils under northern exposure of both stands from humid climate were linked to signals at 1394, 871 and 711 cm⁻¹ i.e. from CaCO₃ (Fig. 5f). Projections of South-exposed soils from the same stands were explained by signals at 906, 889, 777 and 720 cm⁻¹ assigned to γ (=C-H) out of plane aromatic, ρ (HOH) from aromatics and δ (CH₂) rocking (long chains).

3.3. Prediction of the environmental context (climate and land use) of soils

Regarding the ability to differentiate the two types of land use considered, the quality of the PLS predictions using entire FTIR profiles and a binary codification to differentiate forest and olive-tree orchards was significant (Table 4). Calibration performed on averaged spectral data gave an R² value of 0.99 and a low SEC. Parameters of the validation model showed that land use can be predicted (SEP equal to 0.24). The first regression coefficient (data not shown) confirmed the discrimination of the two land uses on the bases of specific spectral bands. These bands were pointed at 1400, 1162, 1087, 870 and 711 cm⁻¹ for olive-tree orchards and 3300, 1602, 973 and 908 cm⁻¹ for forests, characterizing the presence of carbonates or aromatic compounds respectively. Here, the implication of carbonate content in olive-tree orchards has a positive effect on the accuracy of PLS models to differentiate land use.

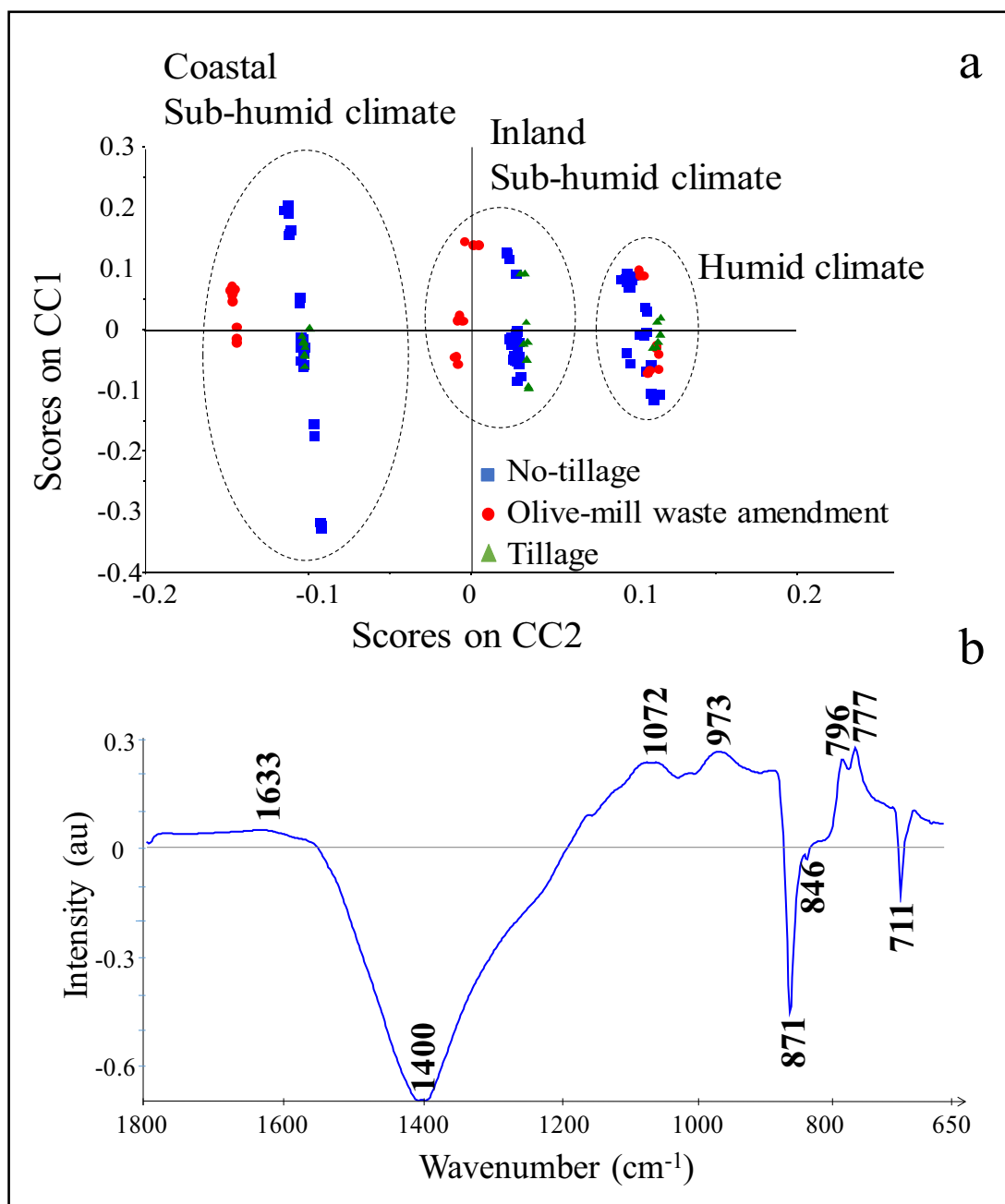


Fig. 3. AcomDim of spectral soil data from olive-tree orchards: (a) CC1 vs. CC2 scores plots, (b) loading on CC2 corresponding to factor "climate".

For climate prediction, cross-validation PLS resulted in a standard error of 0.28 and an R^2 equal to 0.86 and can thus be considered as significant. The first regression coefficient brought out the same spectral bands previously identified to discriminate sub-humid (3259, 1371, 870 and 711 cm^{-1}) from humid climate (1083, 796, 777 and 700 cm^{-1}). PLS cross validation performance was poorly improved by separating data per land use and without spectral data average.

4. Discussion

To our knowledge, few studies aimed at deciphering how the chemical signature of SOM differed depending on factors acting at various spatial scales. Here, we tested the effects of land use and of the associated practices under contrasted climate conditions at regional (sub-humid vs humid climate, coastal vs inland area) and local (southern vs

northern slopes) spatial scales. Though previous studies proposed models to predict SOM content and composition under agricultural or forested land use (Janik et al., 2007; Madhavan et al., 2017), authors underlined that specific calibrations should be realised considering main drivers of soil chemical signature such as climate and practices.

4.1. Land use shapes soil chemical signature depending on climate conditions as revealed by FTIR –ATR

This study clearly revealed a discrimination of soils under different land uses based on the chemical signature of both organic matter and mineral fractions of soil using FTIR technique. It has to be mentioned that CaCO_3 was found as the part of the mineral fraction which was involved in the discrimination of soils. This goes in line with the mineral composition of the calcareous soils studied here, with very low

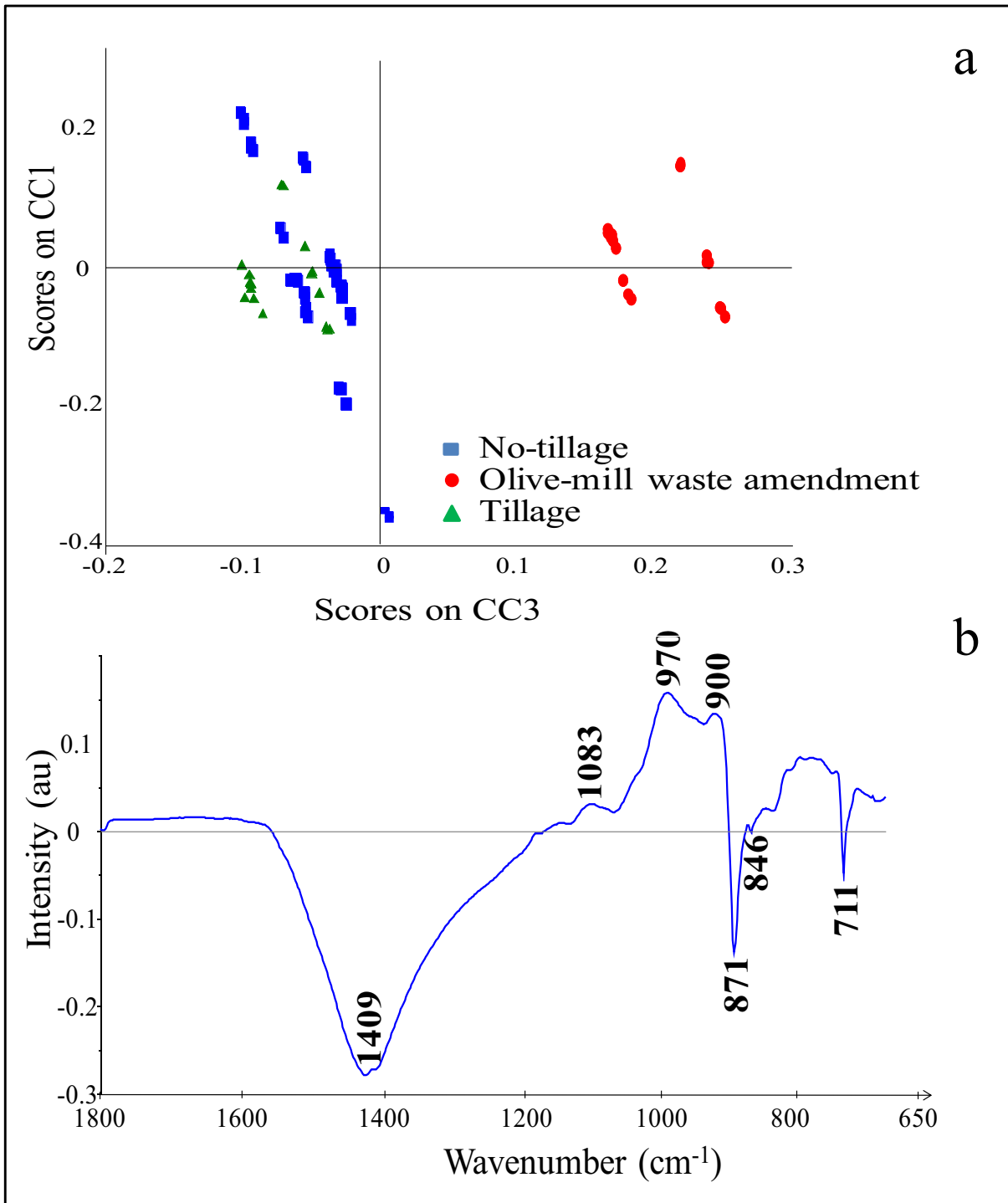


Fig. 4. AcomDim of spectral soil data from olive-tree orchards under Sub-humid climatic conditions: (a) CC1 vs. CC3 scores plots, (b) loading on CC3 corresponding to factor “practices”.

concentrations in iron and potassium compared to calcium (10^4 fold less) linked to CaCO_3 . Interestingly, this differentiation depended on the bioclimate considered: forest soils from humid climate and orchard soils from sub-humid climate were characterized by CaCO_3 . This is corroborated by the higher CaCO_3 amounts found in these soils. These results can be explained depending on the ecosystem considered. For forest stands, this is in accordance with our previous study: Brunel et al. (2017) found that concentrations in CaCO_3 in forest soils of *P. sylvestris* and *Q. pubescens* (from Humid climate) were higher than those from *P. halepensis* and *Q. ilex* (Sub-Humid climate). For olive-

tree orchards, a soil chemical signature linked to CaCO_3 may reveal a poor soil quality. Comino et al. (2018), indeed showed that in agricultural soils with low organic matter, contribution of the mineral fraction to FTIR spectra was strong. Consequently, they discriminated soils richer in SOM but with low carbonate concentrations from those with opposite trends considering these chemical characteristics. On the other hand, forest soils from sub-humid climate and orchard soils from humid climate were characterized by aromatics. Several previous studies underlined the specific effects of tree species on forest soil properties through above- and below-ground soil inputs, which modified organic

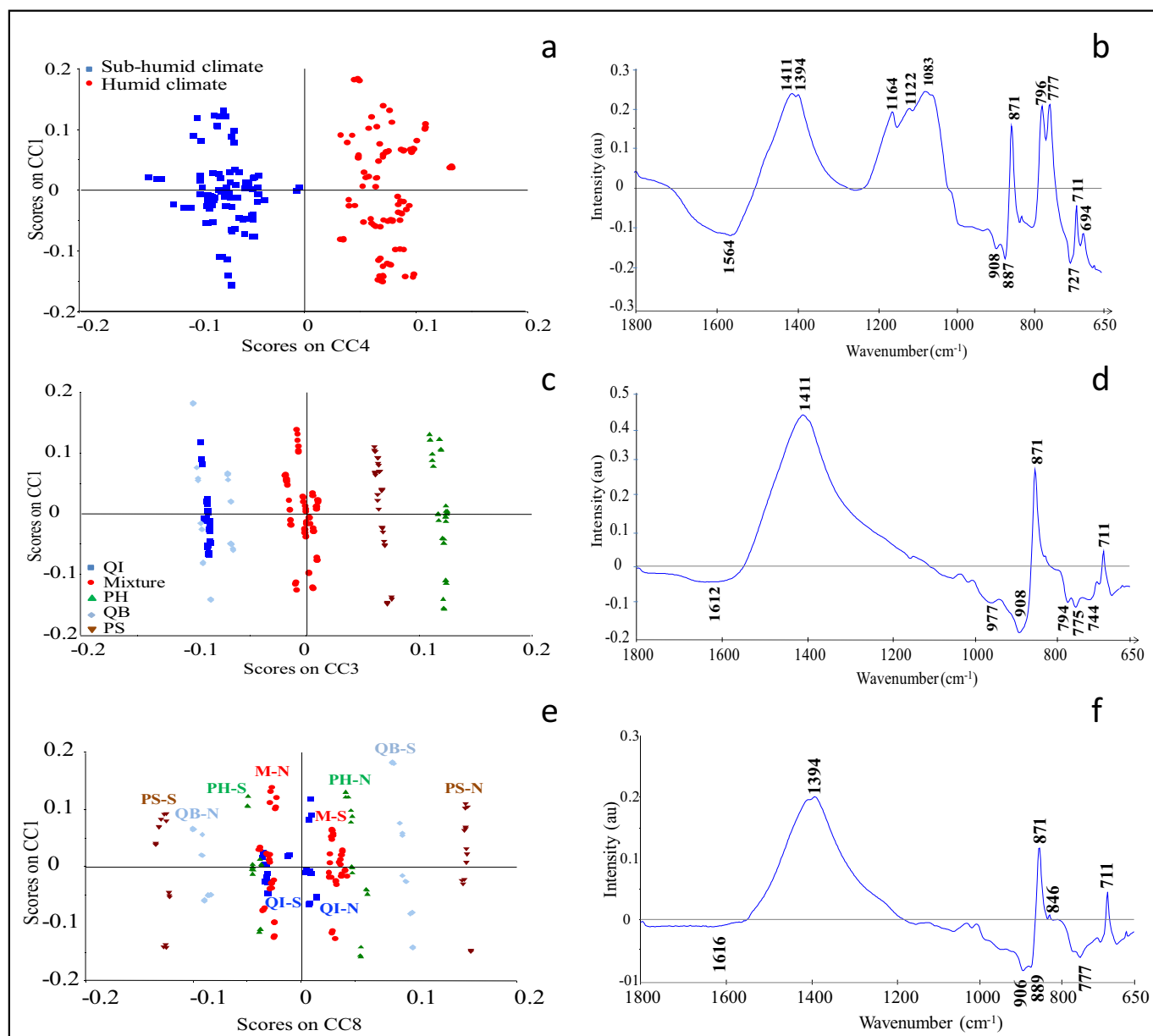


Fig. 5. AcomDim results on spectral soil data from forest stands: (a) CC1 vs. CC4 scores plots, (b) loading on CC4 corresponding to factor "climate", (c) CC1 vs. CC3 scores plots, (d) loading on CC3 corresponding to factor "land use", (e) CC1 vs. CC8 scores plots, (f) loading on CC8 corresponding to interaction "land use- exposure".

matter quality and quantity (Iovieno et al., 2010; Kara et al., 2008). *Q. ilex* is supposed to exhibit higher aromatic contents than *Q. pubescens* as described in our previous study using solid-state NMR of ^{13}C to

Table 4

PLS results for the prediction of land use and climate factors (considering soils from forest and olive-tree orchard together or separately).

	Calibration			Validation			
	Nb	R ²	SEC	LV	Nb	R ²	SEV
Land use (forest and olive-tree orchard data) ^a	58	0.99	0.07	15	29	0.88	0.23
Climate (forest and olive-tree orchard data) ^a	58	0.87	0.24	5	29	0.86	0.28
Climate (olive-tree orchard data) ^b	57	0.89	0.16	3	24	0.79	0.24
Climate (forest data) ^b	120	0.97	0.12	13	61	0.79	0.43

^a Averaged data.

^b Not averaged data.

qualify organic matter of Mediterranean tree species (Farnet et al., 2013). This also explained the differences in the chemical signature of forest soils depending on the climate considered (sub-humid vs humid climate). Concerning olive-tree orchards, the more favourable climate conditions in the humid climate may have limited the effect of conventional olive-grove agricultural practices, which often led to erosion producing a severe degradation of soil fertility (García-Ruiz et al., 2009). Here the aromatic signature found in olive tree orchards of humid climate can be linked to humification and organic matter aggregation that occurred in soils. Thus, FTIR showed that a soil chemical signature assigned to a land use also depended on climate revealing that climate conditions were another important factor structuring SOM. Aranda et al. (2014) also successfully differentiated soils from olive groves and forests of *Quercus* spp. in the Mediterranean area, though these authors did not consider the geographical location as a driving factor of soil chemical signature. It would be of huge importance to determine, under the Mediterranean context, whether this chemical differentiation is preserved as a chemical fingerprint "legacy" in the

deeper layers of soils since the history of land use can impact present soil structure and functioning (Oyonarte et al., 2008). Recently, Ertlen et al. (2015) have taken the first steps in deciphering the soil chemical signature of past land uses and the associated vegetation using NIR in soils from North Eastern France.

It has to be noted that the mineral fraction, here mainly assigned to CaCO_3 , is key to define soil chemical signature. Comino et al. (2018) indicated that the proportion of organic matter in soil can be particularly weak in agricultural soils and consequently mineral fraction is an important part of the origin of spectral variation. In bulk soils, carbonate can be found under different forms as calcite (CaCO_3) and/or dolomite ($\text{CaMg}(\text{CO}_3)_2$). Both calcite and dolomite can be present in different ratio depending on soil formation and geological background. FTIR profiles of pure calcite and dolomite showed few differences as described by Bruckman and Wriessnig (2013). Gunasekaran and Anbalagan (2006) confirmed that calcite and dolomite groups were characterized by infrared reflection band at 712 and 728 cm^{-1} respectively. In our case, AcomDim revealed the presence of calcite through specific peaks at 1400 cm^{-1} ($\nu_{\text{as}}\text{ CO}_3$), 871 cm^{-1} ($\gamma_{\text{as}}\text{ CO}_3$) and 711 cm^{-1} ($\delta_s\text{ CO}_3$).

4.2. Practices are determinant in defining soil chemical signature and it depends on climate conditions at various spatial scales

Considering soils from olive-tree orchards located in the sub-humid climate, our study revealed that FTIR spectra showed variations in the chemical signature according to the practices applied (tillage and natural grass vs OMW amendment). Boukhoudou et al. (2016) found that the effects of agricultural practices on soil properties were actually more pronounced in olive-tree orchards under more drastic climate conditions: the geographical location (coastal vs inland area) affected how agricultural practices influenced soil properties and the authors concluded that soil management should take into account certain specific environmental conditions. Here, OMW amendment, compared to tillage or no-tillage, provoked a change in FTIR spectra, revealing a chemical signature linked to aromatics. The study of Aranda et al. (2016), which analysed the long-term effect of OMW amendment on soil hydrophobicity and wettability, indicated that, though no change in mineralogy was observed, olive pomace addition induced an increase in organic carbon. Discriminating soils depending on the practices applied is a particularly important result since most studies using FTIR actually showed the effect of land use on soil chemical signature but few revealed the fingerprint of the practices applied. For instance, Comino et al. (2018) did not find any significant differences in olive grove soils under conventional or organic practices, though conventional management included tillage (at 20 cm depth, 3 to 5 times a year) and the use of herbicides and mineral fertilizers, which are known to have a great impact on soil properties.

In our study, soils from different forest stands were discriminated depending on the functional traits of tree species (coniferous vs broadleaved and evergreen species) and on their admixture. Traversa et al. (2008) successfully distinguished the plant covering fingerprint (from typical Mediterranean plant species from forests and shrublands) on dissolved organic matter in soils using FTIR. Tree species identity strongly modifies, via litter quality (C/N, lignin and tannin concentrations), soil microbial and chemical properties and thus the global rate of decay (Laganière et al., 2009; Moukoui et al., 2006). Our study indicated that forest composition, driven by silvicultural practices, had a great impact on soil chemical properties as shown before (Weand et al., 2010) and that this can be efficiently described using FTIR-ATR.

Northern or Southern exposure appeared to be determinant in defining soil chemical signature and it was particularly true for stands in humid climate. In a previous study, Pailler et al. (2014) examined the relative effects of climate conditions and tree species on soil properties in South-Eastern France and found that the 'climatic-geographic factor', defined by different variables i.e. distance from the sea, elevation, exposure, summer rainfall and mean annual temperature, together with tree

species strongly modified microbial catabolism. These modifications can consequently impact soil chemical signature at local scales as suggested here.

4.3. FTIR-ATR is a useful tool to predict the environmental context (climate and land use) of soils

The PLS prediction successfully distinguished soils depending on land use and climate under the Mediterranean context. This rapid and discriminating method could thus help provide referential data to further build model to forecast land use legacy (Ertlen et al., 2015) from deeper horizons of soils which is particularly relevant in the Mediterranean area. The surface and composition of European Mediterranean forests were indeed strongly structured by wildfires and human activities leading to agro-silvo-pastoral systems during the last century (Quézel and Médail, 2003). From the 1930s, abandonment of land previously devoted to agriculture promoted massive colonization by resinous species such as *Pinus halepensis* Mill. and *Pinus sylvestris* (Tatoni and Roche, 1994). Thus, forests of different historical continuity, which probably leads to different soil properties, can be found in Mediterranean area, and models built from FTIR data could help at integrating land use legacy to understand soil functioning.

5. Conclusion

This paper underlined that soil chemical signature from agrosystems or forests can be discriminated by mineral (CaCO_3) vs organic fractions (aromatics) of soil. Moreover, the effect of practices on soil chemical signature was also highlighted: in agrosystems, aromatics were linked to OMW amendment, in forests, CaCO_3 characterized *Pinus* spp. stands and aromatics, *Quercus* spp. stands. All these subtle variations depended on Mediterranean climate conditions at different spatial scales and were successfully revealed by FTIR. Thus, this technique combined with chemometric treatments (AcomDim and PLS methods) can easily discriminate soil identities depending on various environmental factors and predict land use depending on climate conditions. This preliminary study will be completed with other techniques such as X-rays or UV and fluorimetry to better explore soil spectral signature depending on climate and land use.

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