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Influence of soil forming factors on the molecular structure of soil organic matter and carbon levels

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Highlights

- Pyrolysis applied to soil samples reveals the impact of soil forming factors
- Vegetation and climate play the chief role in soil organic matter composition
- High soil C levels are associated with slightly transformed lignin in soil
- Low SOC levels are related with non-methoxylated aromatic constituents

Abstract

There is currently an active controversy about the variable influence of the factors involved in the total content and the quality of the soil organic matter (SOM), which translates into its resilience and stability against biodegradation, and importantly on the rates of release of CO_2 into the atmosphere. The aim of this work is to study the molecular composition of SOM in contrasting environments in order to evaluate the extent to which such conditions may affect SOM characteristics in addition to the levels of soil organic C (SOC). Up to 33 soils from different environmental scenarios of Spain were analysed by pyrolysis combined with gas chromatography mass spectrometry (Py-GC/MS). The 193 major pyrolysis compounds released from the soils were included in a chemostatistical study based in discriminant analysis to assess the impact of classical soil forming factors (i.e., climate, vegetation and geological substrate) in SOM content and composition. Improved van Krevelen diagrams were used to facilitate the recognition of different patterns in SOM composition dependent on soil forming factors. The results showed that the molecular composition of SOM varies systematically according to environmental factors with a decreasing influence in the order: climate > vegetation > geological substrate. In addition, the total levels of SOM were also different depending on the environmental scenarios on these soils, suggesting both qualitative and quantitative control of soil C sequestration.

1. Introduction

The factors involved in the transformation of soil organic matter (SOM) are extremely complex and responsible of its total levels and quality. While some authors highlight the importance of climatic factors in controlling the soil formation processes, others consider the effect of vegetation or geological substrate more important (Duchafour and Jacquin, 1975; Ganuza and Almendros, 2003; Jenny, 1994; Johnson et al., 2011; Towett et al., 2015). In addition, there is still no consensus regarding the quantitative influence of the factors that determine the fact that some soils store more soil organic carbon (SOC) than others, which results in important differences in their potential for sequestration of atmospheric carbon that is currently a subject of great interest (Lal, 2004). At this respect, it is also well known that organo-mineral interactions and microencapsulation of the SOM may play an important role on the physico-chemical protection of the SOM (Simonetti et al., 2017; Song et al., 2012; Spaccini et al., 2002). On the other hand, land use may also affect soil C sequestration processes (Hernández et al., 2019; Pizzeghello et al., 2017; Yazdanshenas et al., 2018). Apart of this and regarding soil C level, it is also relevant to point out that the chemical composition of the SOM may also be an important constraint in its recalcitrancy (Jiménez-González et al., 2017, 2018, 2019). This is traditionally taken into account when referring the melanization of soil horizons, which reflects the fact that, depending on the environmental conditions, the accumulation of humus is variable in quantity and quality (Bockheim and Hartemink, 2017; Di et al., 2019).

In this context, the use of analytical degradation techniques for molecular characterization of the SOM, such as Py-GC/MS, may represent a source of

semiquantitative data suitable to explore the molecular composition of the SOM. This technique has a series of advantages such as not requiring chemical pretreatments, or previous SOM isolation with alkaline reagents (Derenne and Quénéa, 2015; Schnitzer and Schulten, 1992). The composition of SOM may represent a reliable repository of environmental information about the influence of soil forming factors, such as climatic conditions, vegetation types and geological composition. Consequently, a major goal of this research is to assess the influence of the above factors on the humification processes, as reflected by the molecular composition of the SOM, but also to assess the biogeochemical meaning of the variability in the chemical composition of the SOM in terms of the different SOC levels.

2. Materials and methods

2.1. Study area

Topsoil samples (0–10 cm) were collected from thirty-three ecosystems (Fig. 1) with a large variability in local climatic conditions, vegetation and geological substrate. The soils were previously classified according to the IUSS Working Group WRB (2014) system (Table 1). The sampling sites were chosen to cover a large range in SOC content. Three sampling points were selected for each sampling area. The soil samples were collected from the A horizon after removing the litter layer (1–5 cm, depending on the morphology of the soil profile). The sampling was carried out under the canopy of the dominant species, to try to minimize interference from other species. In a second stage, a series of composite soil samples were prepared by mixing samples collected from three different points, and then air-dried and sieved (< 2 mm).

The soil textural analysis was carried out by using the densimeter method (Bouyoucos, 1927). The pH value was determined in soil-water suspension (1:2.5, w:w) with an XS pH meter model pH 7 (Carpi, MO, Italy). A 1*M* ammonium acetate solution at pH7 was used to measure the cation exchange capacity (CEC) which was measured according to Juo et al., (1976). The SOC concentration was determined by wet chemical oxidation with 1 *M* potassium dichromate (Nelson and Sommers, 1982; Walkley and Black, 1934) and the N by micro-Kjeldahl digestion (Prince, 1945).

2.2. Analytical pyrolysis

The molecular composition of the SOM was analyzed by Py-GC/MS using whole soil samples. Homogenized soil samples were prepared from 5 g samples grounded to fine powder (< 0.01 mm) with a planetary agate ball mill.

Pyrolysis was carried out at 500 °C with a PY-2020iD pyrolyser (Frontier Lab Ltd., Fukushima, Japan) coupled to an Agilent 6890 GC/MS system with a phenylmethylsiloxane column (Agilent HP-5MS 5%). Helium was used at a flow rate of 1 cm^3 min^{-1} as carrier gas. The GC oven temperature was set to 50 °C for 1 min, then increased to 100 °C at 30 °C min^{-1}; from 100 to 300 °C to a rate of 10 °C min^{-1}, and finally isothermal at 300 °C for 10 min. An Agilent 5973 quadrupole mass spectrometer detector was used, and mass spectra were acquired using 70 eV ionizing energy. The peak areas (total area counts) in the chromatograms were integrated for the different compounds and expressed as total abundances. Finally, cumulative values of the main families of compounds (viz. alkanes (A), olefins (O), fatty acids (F), phenols (P), methoxyphenols (M), *N*-compounds (N), alkylbenzenes

(B), polycyclic aromatic hydrocarbons (H), carbohydrate-derived compounds (C) were calculated to be used as independent variables in the discriminant analysis.

2.3. Statistical analysis

The influence of the different factors on the SOM composition was explored using discriminant analysis. In this treatment, the relative abundances of the different families of pyrolytic compounds were used as descriptors (independent variables). On the other hand, the dependent variables (classification pedogenesis factors) consisted of the different states that define the main soil forming factors (vegetation type, geological substrate and climatic conditions). These different qualitative sample descriptors for each of the soil forming factors were, for the geological substrate: igneous, metamorphic and sedimentary rocks. For the vegetation: Cupressaceae, Fagaceae and Pinaceae species, because most of the forest characteristic species could be included in these groups, and for the climate the Köppen classification (Kottek et al. 2006) was followed: Cfa, Cfb and Csa types. In a second stage, after performing the discriminant analysis and considering the results in the classification table, the soil samples incorrectly classified were discarded, then the average composition of the different 193 pyrolytic compounds was calculated for each soil group using only the samples correctly classified in terms of the results of the discriminant analysis. This fact let us to obtain the most representative composition of SOM under each factor due to the soils samples incorrectly classified were not used to calculate this average. This approach led us to obtain numerical arrays corresponding to average pyrograms of SOM samples formed under each factor, in order to subsequently prepare a series of plots based on the classical van Krevelen

diagram where these compositions of SOM are represented. Finally, the average SOC content was also calculated for the same groups of samples and the statistical significance of the differences between the average SOC values of the groups were checked at 90% ($P < 0.1$) using the Student's *t* test.

The compounds identified by analytical pyrolysis were essentially the same for all samples but with quantitative differences in their abundances between soils. For a simplified perceptual interpretation of the results we used plots based in the classical van Krevelen (1950) graphical-statistical method. Although this procedure has extensively been used to represent the elemental composition and transformation reactions of complex macromolecular materials such as coals or humic substances, this plot has proven to be useful to facilitate the interpretation of the complex assemblages of individual compounds released by different analytical methods (Almendros et al., 2016; Ikeya et al., 2015; Kramer et al., 2004). Essentially, the approach used for this study consists of plotting "surface density plots" built from the abundances of the individual pyrolysis compounds represented in the space defined by their H/C and O/C ratios (Almendros et al., 2018). For this purpose, the scores for atomic O/C and H/C ratios of the individual pyrolysis compounds are represented in the basal plane (*x,y* axes, i.e., the classical van Krevelen diagram). The vertical dimension (*z* axis) corresponds to the normalized abundances of the individual compounds (sum= 100). Using authors' own ad hoc computer program, the original *z* (*x, y*) data were transferred into a 50 × 50 matrix (suitable to reallocate the 193 individual compounds represented in the plane defined by the atomic ratios) by an agglomerative manner. When several compounds coincided in the same H/C and O/C range their abundances were aggregated, i.e. the case of olefins. From this matrix, an interpolated surface is obtained by applying the moving average algorithm

(i.e., averaging each cell value with those of its 4 orthogonal neighbour cells). The resulting plot shows a series of broad 3D peaks or compound clusters, whose size is proportional to the collective value of the abundances of the compounds with similar elemental composition and chemical nature (alkanes, olefins, phenols, etc). This method lets us, in a very perceptual way, to observe the different amounts of compounds which tend to accumulate in the SOM formed under the influence of the different factors (Almendros et al., 2018). In principle, the density surfaces, as the original van Krevelen plots (Fig. 3), are valid only to display the molecular composition of individual soil samples, which limits its usefulness to discuss differences among the 33 different van Krevelen graphs. For this reason, here we build up van Krevelen surfaces representing the average compound composition of a set of pyrograms from samples sharing a defined supervised characteristic i.e., the same environmental characteristic. Further refining is based on comparing additional plots representing subtraction values between the average pyrograms from soils developed under each environmental factor and the total average of the 33 pyrograms, which are shown as van Krevelen surfaces. These subtraction plots are useful to display the differential characteristics between the pedogenesis factors, showing positive or negative peaks depending on whether the corresponding compounds predominate or are in comparatively low proportions in the defined soil groups.

Finally, using the Student's *t* test for each compound, it is observed whether the above differences between compounds proportions in the soil groups developed under different formation factors, are considered significant or not. In this work, differences in $P < 0.1$ have been considered.

3. Results

3.1. Chemical analysis

In Table 1, the general analytical characteristics (pH, CEC, SOC) of the soils showed large variability between the samples studied. Soil samples showed pH values ranging between 3.9 and 7.7 and CEC values between 4.5 and 41.9 $cmol_c \cdot kg^{-1}$. The SOC content presented a wide range (18–157 $g \cdot kg^{-1}$). With the Py-GC/MS analysis it was possible to identify up to 193 different compounds in the whole soil samples (Table 2). The semiquantitative results for the pyrolytic compounds normalized as percentages (considering 100% the sum of all peaks identified) were grouped into different families and used as descriptors to perform the discriminant analysis using these reduced variables set. Table 3 shows that the main families of pyrolytic compounds had a large variability in their total abundance among the soils. The proportions of methoxyphenols, which are typical pyrolysis products from lignin, ranged between 0.1 and 27.8 %. Other aromatic compounds as phenols and alkylbenzenes were also abundant with percentages of 5.1–17.7 % and 11.1–46.4 %, respectively. Aliphatic compounds included alkanes (0.1–17.0 %), olefins (3.3–20.8 %) and fatty acids (0.0–4.7%). *N*-compounds that are related with protein ranged between 6.9 and 21.1%. Polycyclic aromatic hydrocarbons (5.2–18.5%) and carbohydrates (5.1–17.9%) were present in similar levels. Finally, some steroids were identified in the chromatogram (0.1–5.8%).

3.2. Discriminant analysis

The results of the discriminant analysis showed that it is possible to identify the soil formation factors exclusively using the chemical information provided by analytical pyrolysis. At first sight (Fig. 2) it was observed that the different soil groups selected in each forming factor result in disjoint clusters in the plot; only in the case of geological substrate a somewhat higher overlap between the three groups was observed. Based on the number of samples correctly classified (also reflected as the sharpness of the clusters indicated with the size of the whiskers), it may be considered that most of the classification factors studied allowed to obtain an excellent value of samples correct classified (93.9% for climate, 91.7% for vegetation). In the case of geological substrate, the number of samples correctly classified was comparatively lower (57.6 %). When the above results were compared with those of the average SOC content of the groups, it was observed that the differences were significant between the soil groups under different environmental conditions for each soil forming factor.

When using climatic types as classification factor, the three groups were found to be significantly different in terms of its SOC content. Soils under Cfa climate had the highest SOC content, followed for Csa and finally by Cfb, with the lowest content. As regards the vegetation type, the differences were also significant ($P < 0.05$) in two of the groups (Cupressaceae and Fagaceae families), which showed significant differences in the SOC: the soils developed under the former vegetation showed higher SOC content that the soils under the latter. Concerning the geological substrate, soils on metamorphic and sedimentary substrates also had comparatively high SOC content than soils on igneous rocks.

3.3. Van Krevelen plots

In Fig. 4, the van Krevelen diagrams corresponding to subtraction values between the average composition under each factor and the general average from the whole samples studied are shown. The first factor studied was climate: soils under Cfa climate comparatively showed low proportions of alkanes, aromatic constituents (mainly short-chain alkylbenzenes, aromatic *N*-compounds and polycyclic aromatic hydrocarbons) and methoxyphenols, but comparatively increased proportions of phenols and fatty acids. The following climatic type in terms of SOC content was Csa, which corresponded to scores showing similar relative depletion in aromatic compounds including polycyclic aromatic hydrocarbons. Finally, the SOM under Cfb climate, with the lowest SOC content, characteristically had higher proportions of olefins, alkylbenzenes, aromatic *N*-compounds and polycyclic aromatic hydrocarbons, and lower proportions of methoxyphenols and fatty acids than the average.

Concerning vegetation types, the SOM under Cupressaceae showed comparatively low values of olefins, phenols, long-chain alkylbenzenes, aromatic N-compounds and polycyclic aromatic hydrocarbons. This group showed high proportions of fatty acids, short-chain alkylbenzenes and methoxyphenols, in particular guaiacyl-type. The same occurred in the Pinaceae group: in the subtraction plots alkanes, olefins, alkylbenzenes, aromatic *N*-compounds and polycyclic aromatic hydrocarbons had negative values. Phenols, and guaiacyl-type methoxyphenols had positive values, whereas syringyl-type presented lower values than the average. Finally, the SOM under vegetation of Fagaceae showed slightly lower proportions of

aromatic compounds, phenols, fatty acids and carbohydrate-derived compounds. Olefins, polycyclic aromatic hydrocarbons and syringols showed greater values than the average of the whole soil set.

Finally, the geological substrate was the classification criterion leading to the least number of samples correctly classified by the discriminant analysis. The SOM composition in the soils developed under sedimentary rocks released a comparatively low proportion of alkanes, short-chain alkylbenzenes and polycyclic aromatic hydrocarbons, conversely showing positive values for olefins and phenols. The metamorphic substrate was associated with SOM with high proportions of olefins but low of phenols, alkylbenzenes, aromatic *N*-compounds and polycyclic aromatic hydrocarbons than the average. The igneous rocks were associated to the soils with low SOC content. The subtraction values with respect to the whole set of samples displayed a compositional pattern with negative values for olefins, fatty acids methoxyphenols and carbohydrate derivatives, whereas the proportions of different aromatic compounds (alkylbenzenes, aromatic *N*-compounds) and polycyclic aromatic hydrocarbons were higher than the average.

4. Discussion

The application of discriminant analysis to the pyrolysis results demonstrated that the soil-forming factors considered in this research (vegetation, climate and geological substrate) exert a significant influence not only in the total SOC content but mainly in the SOM composition as reflected by analytical pyrolysis of whole soil samples. The climate and the vegetation showed the most outstanding effects, whereas the type of geological substrate is reflected to a lesser extent in the molecular composition of the

SOM. This fact may depend on the depth of the sampling; in this study the topsoil was selected, which is far from the parent rock and its influence may be less.

Other important variable under examination is the SOC content, which represents an indirect measure of the potential for SOC storage, and was found largely influenced by the soil-forming factors studied, probably due to the influence in the chemical composition of SOM. It is possible that the above qualitative and quantitative features of the SOM varying in terms of the forming factors could be causally related, an aspect that would deserve further detailed investigation. Nevertheless, it is clear that the results point to the fact that soils with significantly different C contents have also SOM with significantly different molecular composition, regardless of whether these differences in molecular composition are the cause or the effect of its stability or recalcitrance. This latter aspect is relevant with respect to the fact that soils with high SOC content are not necessarily soils where SOC is more stable or recalcitrant. This is clearly observed in the composition displayed in the van Krevelen diagrams (Fig. 4).

The van Krevelen diagrams illustrated how the SOM composition differs significantly in soil groups classified according to its common soil-forming factors. Considering the differences among the groups in terms of the SOC content, the most important difference was the tendency to accumulation of aromatic structures in soils with comparatively low SOC content. This fact has frequently been correlated with SOM recalcitrance, considering that aromaticity of the SOM often behaves as a surrogate of its chemical stability and resistance to degradation (Miralles et al., 2015; Tinoco et al., 2015). Despite its comparatively low SOC content, this may be more recalcitrant than in other soils with higher SOC values. In fact, C storage is usually carried out at expenses of labile fresh organic matter, which is reflected by the

dominance of lignocellulose (polysaccharides and methoxyphenols). A similar situation occurs with the alkanes; the proportions of alkanes showed a clear variation with the SOC content, in agreement with its chemometric potential in forecasting SOC levels described by Jiménez-González et al., (2018).

The differences depending on the geological substrate could be interpreted as the effect of a different nature of the organo-mineral interactions controlling the humification processes (Karimi Nezhad, 2019). This fact would also depend on the greater or lesser capacity of weathering of the different types of rocks and the mineralogy of the resulting clay fraction. The most characteristic pattern was observed under metamorphic rocks, where preferential accumulation of condensed alkyl constituents mainly olefins was observed, whereas aromatic products including phenols does not tend to accumulation. In the case of the sedimentary geological substratum—which included the soils on limestone—no large differences were observed in the methoxyphenol or carbohydrate region of the van Krevelen diagram: although the values of the former compounds may differ from those in the general average, the differences are not highly significant. These soils on sedimentary substrate show low proportions of aromatic compounds, especially of high condensation, which could correspond to a possible encapsulation effect by carbonates or active colloidal minerals, which are traditionally considered to delay the transformation of the SOM and its evolution towards more advanced forms (Duchaufour, 1970). Finally, SOM of the soils developed on igneous rocks apparently show a high transformation reflected by the significant depletion of oxygen-containing constituents compatible with an origin from both vegetation and microorganisms (all types of phenols in addition to lipid- and carbohydrate derivatives). The most

characteristic pyrolysis products consisted of alkylbenzenes, aromatic *N*-compounds and polycyclic aromatic hydrocarbons.

When comparing the SOM composition in soils under different vegetation types, it can be seen that in soils under Fagaceae the composition tend to accumulate more alkyl compounds than aromatic constituents, which point to high microbial activity (Dinel et al., 2012; Kögel-Knabner et al., 1992). In addition, carbohydrate derivatives and phenolic compounds are degraded comparatively, while the accumulation of low proportions of condensed aromatic compounds is significant. However, under gymnosperm vegetation, and in particular under pine trees, the SOM is comparatively less transformed, as constituents of lignocellulosic biomass such as methoxyphenols and carbohydrate derivatives predominate. Conversely, pyrolytic products characteristic for higher degree of transformation of plant biomass, e.g. alkylbenzenes, aromatic *N*-compounds and polycyclic aromatic hydrocarbons do not tend to accumulate in SOM. In general, the patterns in the van Krevelen diagram are quite similar in the two groups of gymnosperms, Pinaceae and Cupresaceae, but SOM quality would be lower in the case of the Pinaceae attending to the significantly higher proportions of syringyl type methoxyphenols (indicating preservation of the less-condensed, easily biodegradable lignin) and carbohydrate derivatives (Jiménez-González et al., 2017, 2019; Miralles et al., 2015).

When comparing the effect of climate simultaneously considering differences in moisture and temperature, it would be possible to describe the different SOM evolution depending on whether the climate tends to greater tropicality or to desertification. For instance, the coldest climatic type Cfb favour the accumulation of organic matter composed mainly of non-methoxylated aromatic compounds, in addition to alkyl and fatty acid type constituents, the proportions of which being

significantly higher as regards warmer climate types, Cfa and Csa (Fig. 4). In general, under warmer climatic conditions (both Cfa and Csa) the accumulation of aromatic, polycyclic aromatic hydrocarbons and alkyl constituents in the SOM is to lesser extent favoured, probably due to the wildfires (Jiménez-González et al., 2016) which have a high frequency under this climatic condition. Concerning the simultaneous increase in moisture and temperature, i.e., a tendency to tropicality that would correspond to an evolution from Cfa climate to Csa, Fig. 4 suggests changes in SOM consisting of a comparatively lower accumulation of alkyl compounds than in warmer and dry conditions (Csa). In the case of differences more typical for a trend towards desertification (from Cfb to Csa), the SOM showed accumulation of raw humus, where lignin-derived methoxyphenols prevail on condensed aromatic compounds. Considering the narrow climatic range amongst all soils studied under Mediterranean climate, it seems clear that a progressive climatic warming would lead to lower quality of the SOM at least defined as the extent to which the constituents of the biomass are preserved and are not replaced by more or less condensed aromatic products and fatty acids compatible with microbial reworking processes.

5. Conclusions

There is a clear distinction in the molecular composition of SOM as a function of the impact of different soil-forming factors. It was found that the transformation processes of SOM in the topsoil differed significantly in terms of vegetation, climate and, to a lesser extent, of geological substrate. In addition, significant differences in SOC levels depending on the environmental characteristics studied were also observed. For instance, soils under gymnosperm vegetation or developed on sedimentary

geological substrate had high levels of SOC and displayed prevailing soil C storage processes at expenses of preservation of slightly transformed lignin. Conversely, soils developed under Cfb climatic type or on igneous geological substrate had low SOC levels but the SOM showed high proportions of non-methoxylated aromatic compounds. This fact is related with high humification degree, suggested by its molecular composition indicating advanced transformation stages as regards the precursor biomass.

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References

Almendros, G., Tinoco, P., De la Rosa, J.M., Knicker, H., González-Pérez, J.A., González-Vila, F.J., 2016. Selective effects of forest fires on the structural domains of soil humic acids as shown by dipolar dephasing ^{13}C NMR and graphical-statistical analysis of pyrolysis compounds. J. Soils Sediments 18, 1303–1313. http://dx.doi.org/10.1007/s11368-016-1595-y

Almendros, G., Hernández, Z., Sanz, J., Rodríguez-Sánchez, S., Jiménez-González, M.A., González-Pérez, J.A., 2018. Graphical statistical approach to soil organic matter resilience using analytical pyrolysis data. J. Chromatogr. A 1533, 164–173. https://doi.org/10.1016/j.chroma.2017.12.015

Bockheim, J.G., Hartemink, A.E., 2017. The soils of Wisconsin. Springer. Madison. DOI: 10.1007/978-3-319-52144-2

Bouyoucos, G.J., 1927. The hydrometer as a new method for the mechanical analysis of soils. Soil Sci. 23, 343–353.

Derenne, S., Quénéa, K., 2015. Analytical pyrolysis as a tool to probe soil organic matter. J Anal. Appl. Pyrolysis 111, 108–120. https://doi.org/10.1016/j.jaap.2014.12.001

Di, X., Xiao, B., Dong, H., Wang, S., 2019. Implication of different humic acid fractions in soils under karst rocky desertification. Catena 174, 308–315. https://doi.org/10.1016/j.catena.2018.11.028

Dinel, H., Lévesque, P.E.M., Jambu, P., Righi, D., 1992. Microbial activity and long-Cchain aliphatics in the formation of stable soil aggregates. Soil Sci. Soc. Am. J. 56, 1455-1463. https://doi.org/10.2136/sssaj1992.03615995005600050020x

Duchaufour, P., 1970. Précis de Pédologie. Masson & Cie. Paris.

Duchaufour, P., Jacquin, F., 1975. Comparaison des processus d'humification dans les principaux types d'humus forestiers. Sci. Sol 1, 29–36.

Ganuza, A., Almendros, G., 2003. Organic carbon storage in soils of the Basque Country (Spain): the effect of climate, vegetation type and edaphic variables. Biol. Fertil. Soils 37, 154–162. https://doi.org/10.1007/s00374-003-0579-4

Hernández, Z., Almendros, G., Álvarez, A., Figueiredo, T., Carral, P., 2019. Soil carbon stabilization pathways as reflected by the pyrolytic signature of humic acid in agricultural volcanic soils. J Anal. Appl. Pyrolysis 137, 14–28. https://doi.org/10.1016/j.jaap.2018.10.015

Ikeya, K., Sleighter, R.L., Hatcher, P.G., Watanabe, A., 2015. Characterization of the chemical composition of soil humic acids using Fourier transform ion cyclotron resonance mass spectrometry. Geochim. Cosmochim. Acta 153, 169–182. https://doi.org/10.1016/j.gca.2015.01.002

Jenny, H., 1994. Factors of soil formation. A System of Quantitative Pedology. Dover Publications, inc. New York.

Jiménez-González, M.A., De la Rosa, J.M., Jiménez-Morillo, N.T., Almendros, G., González-Pérez, J.A., Knicker, H., 2016. Post-fire recovery of soil organic matter in a Cambisol from typical Mediterranean forest in Southwestern Spain. Sci. Total Environ. 572, 1414–1421. https://doi.org/10.1016/j.scitotenv.2016.02.134

Jiménez-González, M.A., Álvarez, A.M., Carral, P., González-Vila, F.J., Almendros, G., 2017. The diversity of methoxyphenols released by pyrolysis-gas

chromatography as predictor of soil carbon storage. J. Chromatogr. A 1508, 130–137. https://doi.org/10.1016/j.chroma.2017.05.068

Jiménez-González, M.A., Álvarez, A.M., Hernández, Z., Almendros, G., 2018. Soil carbon storage predicted from the diversity of pyrolytic alkanes. Biol. Fertil. Soils 54, 617–629. https://doi.org/10.1007/s00374-018-1285-6

Jiménez-González, M.A., Álvarez, A.M., Carral, P., Almendros, G., 2019. Chemometric assessment of soil organic matter storage and quality from humic acid infrared spectra. Sci. Total Environ. 685, 1160–1168. https://doi.org/10.1016/j.scitotenv.2019.06.231

Johnson, K., Harden, J., McGuire, A.D., Bliss, N.B., Bockheim, J.G., Clark, M., Nettleton-Hollingsworth, T., Jorgenson, M.T., Kane, E.S., Mack, M., O'Donnell, J., Ping, C-L., Schuur, E.A.G., Turetsky, M.R., Valentine, D.W., 2011. Soil carbon distribution in Alaska in relation to soil-forming factors. Geoderma 167–168, 71–84. https://doi.org/10.1016/j.geoderma.2011.10.006

Juo, A.S.R., Ayanlaja, S.A., Ogunwale, J.A. 1976. An evaluation of cation exchange capacity measurements for soils in the tropics. Commun. Soil Sci. Plant Anal. 7, 751–761. https://doi.org/10.1080/00103627609366684

Karimi Nezhad, M.T., 2019. Storage and drivers of soil organic carbon and nitrogen in a rangeland ecosystem across a lithosequence in western Iran. Catena 176, 245–263. https://doi.org/10.1016/j.catena.2019.01.018

Kögel-Knabner, I., de Leeuw, J.W., Hatcher, P.G., 1992. Nature and distribution of alkyl carbon in forest soil profiles: implications for the origin and humification of aliphatic biomacromolecules. Sci. Total Environ. 117–118, 175–185. https://doi.org/10.1016/0048-9697(92)90085-7

Kottek, M., Griese, J., Beck, C., Rudolf, B., Rubel, F., 2006. World Map of the Köppen-Geiger climate classification updated. Meteorol. Z 15, 259–263. https://dx.doi.org/10.1127/0941-2948/2006/0130

Kramer, R.W., Kujawinski, E.B., Hatcher, P.G., 2004. Identification of black carbon derived structures in a volcanic ash soil humic acid by Fourier transform ion cyclotron resonance mass spectrometry. Environ. Sci. Technol. 38, 3387–3395. https://doi.org/10.1021/es030124m

Lal, R., 2004. Soil carbon sequestration to mitigate climate change. Geoderma 123, 1–22. https://doi.org/10.1016/j.geoderma.2004.01.032

Miralles, A., Piedra-Buena, A., Almendros, G., González-Vila, F.J., González-Pérez, J.A., 2015. Pyrolytic appraisal of the lignin signature in soil humic acids: Assessment of its usefulness as carbon sequestration marker. J. Anal, Appl. Pyrolysis 113, 107–115. https://doi.org/10.1016/j.jaap.2014.11.010

Nelson, D.V., Sommers, L.E., 1982. Total carbon, organic carbon and organic matter. In: Page, A.L., Miller, R.H., Keeney, D.R., (eds) Methods of Soil Analysis: part 2,

Chemical and Microbiological Properties, 2nd edn. American Society of Agronomy, Madison, pp 539–579.

Pizzeghello, D., Francioso, O., Concheri, G., Muscolo, A., Nardi, S., 2017. Land use affects the soil C sequestration in Alpine Environment, NE Italy. Forests 8, 197. https://doi.org/10.3390/f8060197

Prince, A.L., 1945. Determination of total nitrogen, ammonia, nitrates, and nitrites in soils. Soil Sci. 59, 47–52. https://doi.org/10.1097/00010694-194501000-00007

Simonetti, G., Francioso, O., Dal Ferro, N., Nardi, S., Berti, A., Morari, F., 2017. Soil porosity in physically separated fractions and its role in SOC protection. J. Soils Sediments 17, 70–84. https://doi.org/10.1007/s11368-016-1508-0

Schnitzer, M., Schulten H.R., 1992. The analysis of soil organic matter by pyrolysis-field ionization mass spectrometry. Soil Sci. Soc. Am. J. 56, 1811-1817. doi:10.2136/sssaj1992.03615995005600060027x

Song, X., Li, L., Zheng, J., Pan, G., Zhang, X., Zheng, J., Hussain, Q., Han, X., Yu, X., 2012. Sequestration of maize crop straw C in different soils: role of oxyhydrates in chemical binding and stabilization as recalcitrance. Chemosphere 87, 649–654. https://doi.org/10.1016/j.chemosphere.2012.01.038

Spaccini, R., Piccolo, A., Conte, P., Haberhauer, G., Gerzabek, M.H., 2002. Increased soil organic carbon sequestration through hydrophobic protection by humic

substances. Soil Biol. Biochem. 34, 1839–1851. https://doi.org/10.1016/S0038-0717(02)00197-9

Towett, E.K., Shepherd, K.D., Tondoh, J.E., Winowiecki, L.A., Lulseged, T., Nyambura, M., Sila, A., Vågen, T-G., Cadisch, G., 2015. Total elemental composition of soils in Sub-Saharan Africa and relationship with soil forming factors. Geoderma Regional 5, 157–168. https://doi.org/10.1016/j.geodrs.2015.06.002

Tinoco, P., Almendros, G., González-Vila, F.J., Sanz, J., González-Pérez, J.A., 2015. Revisiting molecular characteristics responsive for the aromaticity of soil humic acids. J. Soils Sediments 15, 781–791. https://doi.org/10.1007/s11368-014-1033-y

Van Krevelen, D.W., 1950. Graphical-statistical method for the study of structure and reaction processes of coal. Fuel 29, 269–284.

Walkley, A., Black, I.A., 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37, 29–37.

World Reference Base for Soil Resources (2014) International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Yazdanshenas, H., Tavili, A., Mohammad, J., Shafeian E., 2018. Evidence for relationship between carbon storage and surface cover characteristics of soil in rangelands. Catena 167, 139–146. https://doi.org/10.1016/j.catena.2018.04.037

Table 1 General characteristics of the ecosystems studied

Sample No.	Geographical coordinates	SOC[a] ($g \cdot kg^{-1}$)	C/N	CEC[b] ($cmol_c \cdot kg^{-1}$)	pH	Vegetation	Vegetation family	Soil type IUSS Working Group WRB (2014)	Soil texture	Geological substrate
1	40°33'N 4°8'W	41	11.3	16.4	5.2	*Quercus pyrenaica*	Fagaceae	Dystric Cambisol (Humic)	Sandy loam	Granite
2	41°7'N 3°34'W	67	14.8	24.4	3.9	*Pinus sylvestris*	Pinaceae	Haplic Umbrisol (Hyperhumic)	Sandy loam	Gneiss
3	40°23'N 3°16'W	96	15.3	30.8	7.2	*Quercus ilex*	Fagaceae	Calcaric Cambisol (Humic)	Silt loam	Limestone
4	40°53'N 3°34'W	87	13.3	22.0	6.2	*Fraxinus angustifolia*	Other	Gleyic Cambisol (Humic)	Sandy loam	Granite
5	40°53'N 3°34'W	48	13.1	14.4	5.3	*Paeonia coriacea*	Other	Dystric Cambisol (Humic)	Sandy loam	Granite
6	40°44'N 3°42'W	18	16.0	4.5	5.2	*Quercus rotundifolia*	Fagaceae	Dystric Cambisol (Ochric)	Sandy loam	Gneiss
7	40°47'N 2°57'W	87	13.3	21.5	6.8	*Quercus rotundifolia*	Fagaceae	Leptic Kastanozems (Hyperhumic)	Clay loam	Limestone
8	41°14'N 3°24'W	32	16.4	11.6	5.7	*Fagus sylvatica*	Fagaceae	Leptic Podzol (Arenic)	Sandy loam	Schist
9	40°44'N 3°48'W	140	18.1	14.2	5.1	*Pinus sylvestris*	Pinaceae	Dystric Cambisol (Humic)	Sandy loam	Granite
10	40°21'N 3°56'W	117	26.7	13.9	4.9	*Pinus pinea*	Pinaceae	Dystric Cambisol (Humic)	Loamy sand	Sandstone
11	40°33'N 3°43'W	93	8.9	20.1	6.4	*Quercus rotundifolia*	Fagaceae	Dystric Cambisol (Loamic)	Loamy sand	Sandstone
12	40°54'N 3°28'W	134	12.1	19.8	7.0	*Juniperus oxycedrus*	Cupressaceae	Eutric Cambisol (Humic)	Sandy loam	Schist
13	40°52'N 3°34'W	104	18.5	22.2	6.5	*Juniperus oxycedrus*	Cupressaceae	Eutric Cambisol (Humic)	Sandy loam	Gneiss
14	40°58'N 3°37'W	81	16.9	17.1	6.0	*Pinus pinaster*	Pinaceae	Dystric Cambisol (Humic)	Sandy loam	Gneiss
15	40°54'N 3°53'W	55	18.0	15.9	5.7	*Quercus pyrenaica*	Fagaceae	Dystric Cambisol (Humic)	Sandy clay loam	Gneiss
16	40°51'N 3°44'W	39	13.0	13.8	5.6	*Pinus sylvestris*	Pinaceae	Dystric Cambisol (Colluvic)	Sandy loam	Granite
17	40°45'N 3°41'W	105	17.0	41.9	7.2	*Quercus ilex*	Fagaceae	Leptic Cambisol (Humic)	Loam	Granite
18	43°15'N 2°51'W	41	15.8	15.8	4.6	Pastureland for grazing: *Brachypodium retusum, Lolium perenne, Trifolium repens*	Other	Leptic Umbrisol (Loamic)	Loam	Sandstone
19	43°4'N 2°35'W	44	13.4	11.3	5.1	*Fagus sylvatica*	Fagaceae	Haplic Luvisol (Humic)	Silty clay loam	Limestone
20	42°34'N 2°38'W	57	13.9	32.8	6.9	Pastureland for grazing: *Brachypodium retusum, Cynosurus cristatus, Trifolium repens*	Other	Eutric Cambisol (Humic)	Clay loam	Limestone
21	43°15'N 2°51'W	27	17.0	13.3	4.2	*Pinus radiata*	Pinaceae	Haplic Umbrisol (Loamic)	Loam	Sandstone
22	42°28'N 8°53'W	133	31.0	32.4	3.5	*Pinus pinaster*	Pinaceae	Leptic Regosol (Humic)	Sandy loam	Granite
23	42°36'N 8°38'W	90	20.0	22.6	3.7	*Pinus pinaster*	Pinaceae	Leptic Regosol (Humic)	Sandy loam	Granite
24	43°4'N 8°22'W	132	18.0	31.7	4.2	*Pinus pinaster*	Pinaceae	Leptic Umbrisol (Hyperhumic)	Loam	Schist
25	28°26'N 16°29'W	22	12.0	18.3	7.7	*Euphorbia canariensis*	Other	Leptic Regosol (Arenic)	Clay loam	Volcanic
26	28°14'N 16°28'W	23	14.0	29.1	7.3	Fallow: *Solanum tuberosum*	Other	Leptic Regosol (Arenic)	Sandy loam	Volcanic
27	28° 9'N 16°38'W	105	27.0	20.2	6.4	*Pinus canariensis*	Pinaceae	Folic Umbrisol (Chromic)	Sandy loam	Volcanic
28	40°13'N 4°29'W	35	20.0	4.9	5.7	*Pinus pinea*	Pinaceae	Dystric Regosol (Arenic)	Sand	Sandstone
29	41°29'N 4°19'W	99	25.9	9.3	5.7	*Pinus pinea*	Pinaceae	Eutric Cambisol (Humic)	Sand	Limestone
30	40°18'N 4°38'W	46	16.8	12.8	5.4	*Quercus rotundifolia*	Fagaceae	Eutric Cambisol (Arenic)	Sandy loam	Granite
31	41°1'N 3°12'W	89	23.7	17.2	6.2	*Quercus rotundifolia*	Fagaceae	Eutric Cambisol (Humic)	Silt loam	Schist
32	40°58'N 3°44'W	157	21.6	18.0	6.6	*Juniperus thurifera*	Cupressaceae	Eutric Cambisol (Humic)	Sandy loam	Gneiss
33	40°56'N 3°41'W	92	13.9	25.9	7.4	*Juniperus thurifera*	Cupressaceae	Dystric Leptosol (Humic)	Loam	Limestone

[a]SOC: soil organic carbon; [b]CEC: cation exchange capacity

Table 2 Pyrolysis products identified in soils samples with an indication of the diagnostic value of each of the compounds with respect to the different formation factors studied

Compound	Environmental proxy value[a]	Compound	Environmental proxy value[a]	Compound	Environmental proxy value[a]	Compound	Environmental proxy value[a]
Alkanes		C_9-Alkylbenzene	++-	Quinoline	-+-	Methylphenanthrene IV	---
n-Alkane C_9	-+-	C_{10}-Alkylbenzene	+++	1*H*-Benzimidazole, 1-ethyl-	---	Methylphenanthrene V	++-
n-Alkane C_{10}	---	C_{11}-Alkylbenzene	+++	**Olefins**		C_2-Alkylnaphthalene I	+++
n-Alkane C_{11}	---	C_{12}-Alkylbenzene	+-+	*n*-Alkene C_9	---	C_2-Alkylnaphthalene II	---
n-Alkane C_{12}	---	C_{13}-Alkylbenzene	--+	*n*-Alkene C_{10}	+--	C_2-Alkylnaphthalene III	-++
n-Alkane C_{13}	---	C_{14}-Alkylbenzene	--+	*n*-Alkene C_{11}	---	Biphenyl	+++
n-Alkane C_{14}	---	C_{15}-Alkylbenzene	+--	*n*-Alkene C_{12}	---	Diphenylmethane	+++
n-Alkane C_{15}	---	C_{16}-Alkylbenzene	---	*n*-Alkene C_{13}	--+	Biphenyl, 3-methyl	+++
n-Alkane C_{16}	---	C_{17}-Alkylbenzene	---	*n*-Alkene C_{14}	---	Biphenyl, 4-methyl	++-
n-Alkane C_{17}	---	C_{18}-Alkylbenzene	---	*n*-Alkene C_{15}	---	Biphenyldiol	-+-
n-Alkane C_{18}	-+-	C_{19}-Alkylbenzene	---	*n*-Alkene C_{16}	---	Indane	++-
n-Alkane C_{19}	---	C_{20}-Alkylbenzene	---	*n*-Alkene C_{17}	--+	Methylindane	++-
n-Alkane C_{20}	++-	C_{21}-Alkylbenzene	---	*n*-Alkene C_{18}	++-	Indene	--+
n-Alkane C_{21}	+-+	C_{22}-Alkylbenzene	-++	*n*-Alkene C_{19}	---	Methylindene I	--+
n-Alkane C_{22}	++-	C_{23}-Alkylbenzene	--+	*n*-Alkene C_{20}	-+-	Methylindene II	--+
n-Alkane C_{23}	---	C_{24}-Alkylbenzene	--+	*n*-Alkene C_{21}	--+	C_2-Alkylindene I	---
n-Alkane C_{24}	---	C_{25}-Alkylbenzene	-++	*n*-Alkene C_{22}	---	C_2-Alkylindene II	-+-
n-Alkane C_{25}	---	**Fatty acids**		*n*-Alkene C_{23}	+--	C_2-Alkylindene III	---
n-Alkane C_{26}	--+	Decanoic acid	+++	*n*-Alkene C_{24}	---	C_2-Alkylindene IV	---
n-Alkane C_{27}	---	Dodecanoic acid	+++	*n*-Alkene C_{25}	---	C_2-Alkylindene V	--+
n-Alkane C_{28}	--+	Tetradecanoic acid	+++	*n*-Alkene C_{26}	-+-	Inden-1-one,2,3-dihydro	--+
n-Alkane C_{29}	--+	Hexadecanoic acid	+++	*n*-Alkene C_{27}	-+-	**Phenols**	
n-Alkane C_{30}	+-+	Octadecanoic acid	++-	*n*-Alkene C_{28}	--+	Phenol	+++
n-Alkane C_{31}	+-+	Eicosanoic acid	+-+	**Polycyclic hydrocarbons**		Cresol I	-+-
Benzene, alkylbenzenes		Docosanoic acid	+-+	Azulene	++-	Cresol II	-++
Benzene	-++	**Methoxyphenols**		Naphthalene	++-	Ethylphenol	---
Toluene	--+	Guaiacol	+++	Methylnaphthalene I	+++	4-Vinylphenol	+++
Styrene	-+-	Methylguaiacol	+-+	Methylnaphthalene II	+++	**Carbohydrate derivatives**	
Methylstyrene	++-	Ethylguaiacol	+++	C_2-Alkylnaphthalene I	--+	2-Furancarboxaldehyde	-+-
Dimethylstyrene	-+-	Vinylguaiacol	+-+	C_2-Alkylnaphthalene II	--+	Acetylfuran	---
Trimethyl styrene	-+-	Propenylguaiacol	+++	C_2-Alkylnaphthalene III	+++	2-Furancarboxaldehyde, 5-methyl	++-
Benzaldehyde	-++	Acetoguaiacone	+-+	C_2-Alkylnaphthalene IV	-+-	Benzofuran	++-
Acetophenone	+++	Syringol	++-	C_2-Alkylnaphthalene V	-++	Methylbenzofuran I	-++
Xylene I	-+-	Methylsyringol	+++	C_2-Alkylnaphthalene VI	-+-	Methylbenzofuran II	+++
Xylene II	++-	Ethylsyringol	+++	C_3-Alkylnaphthalene I	-+-	Dimethylbenzofuran	++-
Xylene III	++-	Vinylsyringol	+++	C_3-Alkylnaphthalene II	-+-	Maltol	+++
Propylbenzene	+++	Propenylsyringol	+++	C_3-Alkylnaphthalene III	++-	Levoglucosan	+++
C_3-Alkylbenzene I	+--	Acetosyringone	++-	C_3-Alkylnaphthalene IV	++-	**Steroids**	
C_3-Alkylbenzene II	+--	***N*-compounds**		C_3-Alkylnaphthalene V	-++	7-Dehydrodiosgenin	---
C_3-Alkylbenzene III	+-+	Indole	++-	C_4-Alkylnaphthalene I	++-	Ergosta-4,6,8(14),22-tetraen-3-one	+--

C_3-Alkylbenzene IV	---	1*H*-Indole, 7-methyl-	+++	C_4-Alkylnaphthalene II	++-	Ergosta-5,7,9-trien-3-one	---
C_4-Alkylbenzene I	++-	Pyridine	-++	C_4-Alkylnaphthalene III	+++	Sitosterol	-+-
C_4-Alkylbenzene II	-++	Methylpyridine I	-++	C_4-Alkylnaphthalene IV	+--	Hydroxydioxocholestenyl acetate	---
C_4-Alkylbenzene III	++-	Methylpyridine II	+++	Fluorene	++-	Stigmastan-3,5-diene	+--
C_4-Alkylbenzene IV	+-+	Dimethylpyridine	++-	Methylfluorene	++-	Stigmasta-3,5-dien-7-one I	++-
C_4-Alkylbenzene V	++-	Pyrrole	-+-	Pyrene	-+-	Stigmast-4-en-3-one	++-
C_5-Alkylbenzene I	++-	1*H*-Pyrrole, 1-methyl-	+++	Phenanthrene	++-	Stigmasta-3,5-dien-7-one II	++-
C_5-Alkylbenzene II	++-	1*H*-Pyrrole, 3-methyl-	++-	Anthracene	-+-	**Terpenoids**	
C_6-Alkylbenzene	+++	Pyrazole	--+	Methylphenanthrene I	---	Lup-20(29)-en-3-one	-+-
C_7-Alkylbenzene	++-	Benzonitrile	-++	Methylphenanthrene II	---	Friedelan-3-one	++-
C_8-Alkylbenzene	++-	Methylbenzonitrile I	-++	Methylphenanthrene III	--+	Neoleana-3(5),12-diene	--+

a: Key to its value as marker compound for the different formation factors: climate, vegetation, rock, respectively (Student's t test between soil groups ($P < 0.1$)).
Roman numbers indicate different isomers

Table 3 Total abundances of the principal families of compounds identified by analytical pyrolysis

Sample No.	Phenols (%)	Alkylbenzenes (%)	Methoxy phenols (%)	Alkanes (%)	*N*-compounds (%)	Polycyclic aromatic hydrocarbons (%)	Fatty acids (%)	Olefins (%)	Carbohydrate derivatives (%)	Steroids (%)
1	8.5	21.7	8.7	10.0	19.0	9.5	0.7	12.5	8.1	1.4
2	8.1	28.0	4.9	5.8	14.9	13.2	0.7	13.6	9.4	1.2
3	11.8	19.7	21.3	5.4	14.8	8.7	0.6	9.8	5.9	2.0
4	17.7	11.1	22.6	8.6	11.1	5.2	1.5	11.3	9.4	1.4
5	13.0	18.0	13.1	6.3	12.8	7.0	1.5	12.9	13.7	1.7
6	5.2	21.4	4.4	10.5	17.1	6.9	0.0	20.8	11.5	2.1
7	12.5	17.4	16.7	7.2	12.3	9.5	1.1	15.6	7.3	0.3
8	7.3	21.6	5.1	13.3	14.6	10.1	0.5	17.2	9.7	0.6
9	10.8	18.5	27.8	3.1	6.9	8.2	3.2	8.6	11.9	0.9
10	14.2	18.0	26.8	2.2	8.5	5.6	1.5	5.9	15.4	1.9
11	10.4	16.1	17.7	6.3	13.2	8.5	1.3	15.8	8.2	2.5
12	10.6	19.9	16.8	7.0	10.2	8.6	3.2	12.4	7.4	3.9
13	13.2	18.2	23.7	4.6	9.4	8.3	2.3	8.5	11.0	0.8
14	12.2	14.6	23.8	5.5	7.7	6.6	3.5	10.1	10.1	5.8
15	6.9	20.9	11.8	6.8	12.6	9.1	0.4	13.8	12.1	5.7
16	6.4	26.9	3.5	5.3	21.7	9.4	0.0	10.8	12.5	3.6
17	13.3	22.3	16.5	4.7	17.1	11.0	0.5	7.3	6.7	0.7
18	16.4	24.8	4.5	0.1	11.9	17.1	0.6	12.6	11.8	0.2
19	9.8	26.2	2.0	4.4	22.3	10.6	0.0	8.4	16.1	0.1
20	7.7	28.2	2.5	5.4	19.5	11.2	0.0	11.3	12.4	1.6
21	5.8	24.9	1.5	17.0	12.3	12.2	0.3	15.6	9.3	1.0
22	10.3	19.7	11.8	5.6	8.6	8.3	1.8	13.4	18.7	1.8
23	12.7	21.0	11.0	6.1	8.2	9.0	1.8	12.7	14.8	2.8
24	11.2	26.0	8.2	3.6	12.5	10.7	1.4	7.6	17.9	0.9
25	5.1	46.4	0.1	0.8	18.6	18.5	0.0	3.3	5.7	1.5
26	16.9	28.8	1.2	5.7	21.1	16.5	0.0	4.6	5.1	0.1
27	11.1	21.9	21.0	3.8	11.0	9.4	1.8	10.1	9.4	0.5
28	10.4	24.3	9.7	6.3	13.5	8.0	0.9	12.0	14.1	0.9
29	14.6	17.8	22.6	5.3	8.2	5.8	2.4	8.7	13.8	0.7
30	8.4	28.4	2.6	5.9	20.1	10.2	0.2	11.6	11.5	1.1
31	8.7	19.6	12.1	12.5	11.5	7.5	1.0	14.3	11.5	1.2
32	13.0	15.2	24.6	6.1	8.6	6.8	4.7	8.9	9.1	3.1
33	13.8	17.9	18.3	6.2	14.3	8.2	2.0	9.7	8.9	0.8

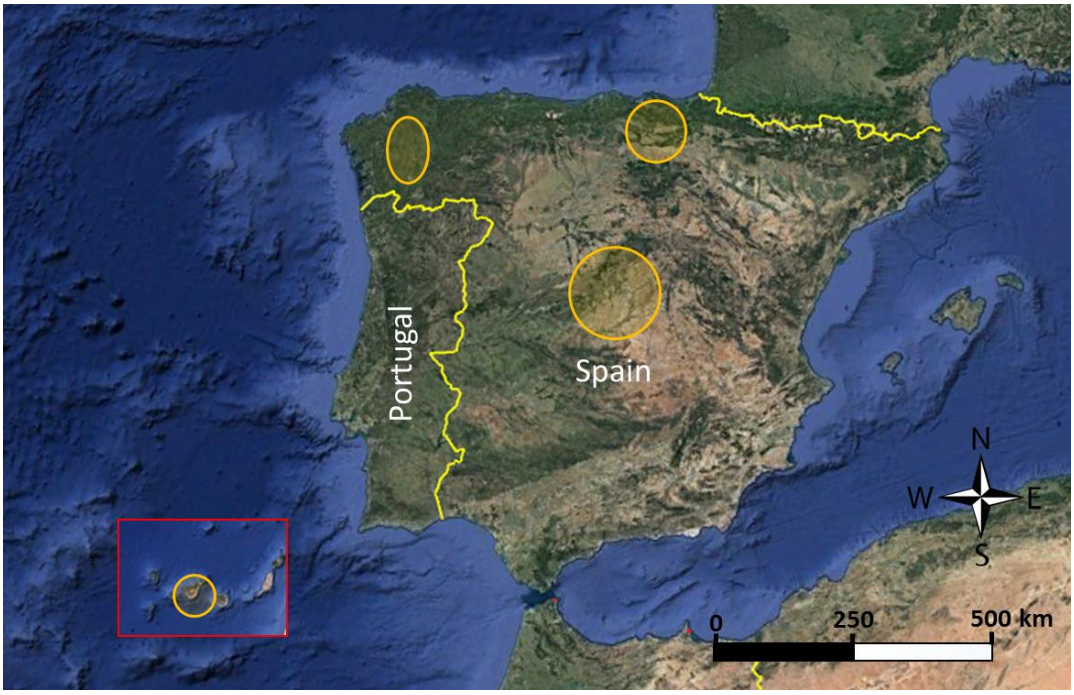

Figure 1 Location of the different sampling areas (marked in orange).

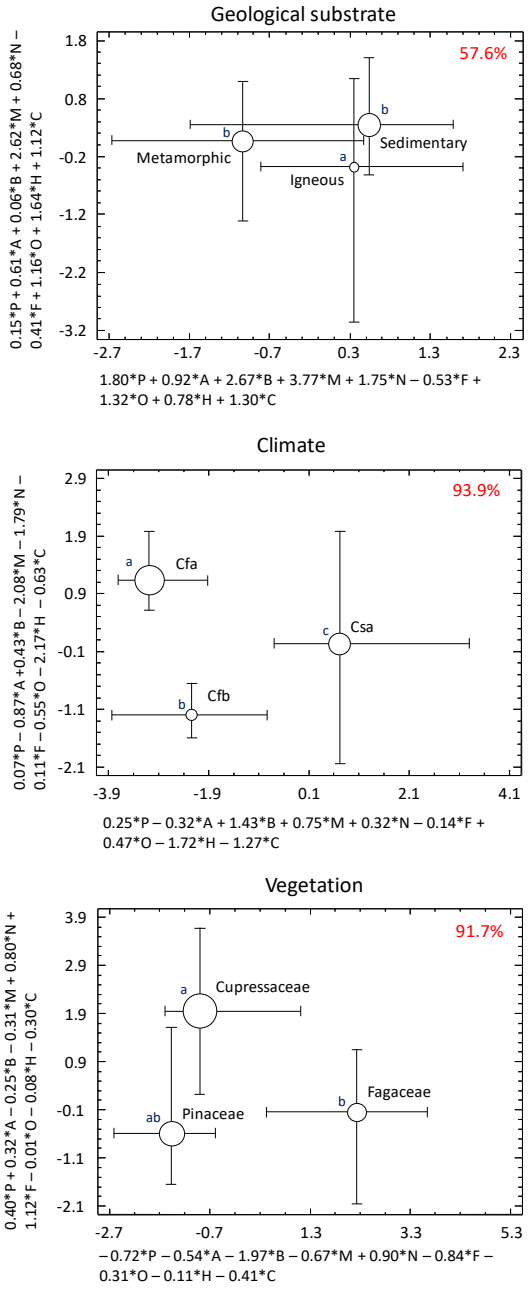

Figure 2 Results of discriminant analysis applied to the assessment of the relative importance of different soil forming factors in the molecular composition of soil organic matter and its total C concentration. For each soil group, the position of the centroid (circle) and the variability between the scores of the different soils (whiskers) are shown. Circles area is proportional to the average soil organic carbon for each group. The lower case letters close to the centroids indicate soil groups which are statistically different in soil organic carbon content according to Student's test at 90% ($P < 0.1$). The descriptors used for this analysis were the proportions (total abundances) of pyrolytic compounds: alkanes (A), olefins (O), fatty acids (F), phenols (P), methoxyphenols (M), *N*-compounds (N), alkylbenzenes (B), polycyclic aromatic hydrocarbons (H) and carbohydrate derivatives (C). The coefficients of the discriminant functions are shown on the axes. The percentage of soils correctly classified in the different groups is shown at the right upper corner (%).

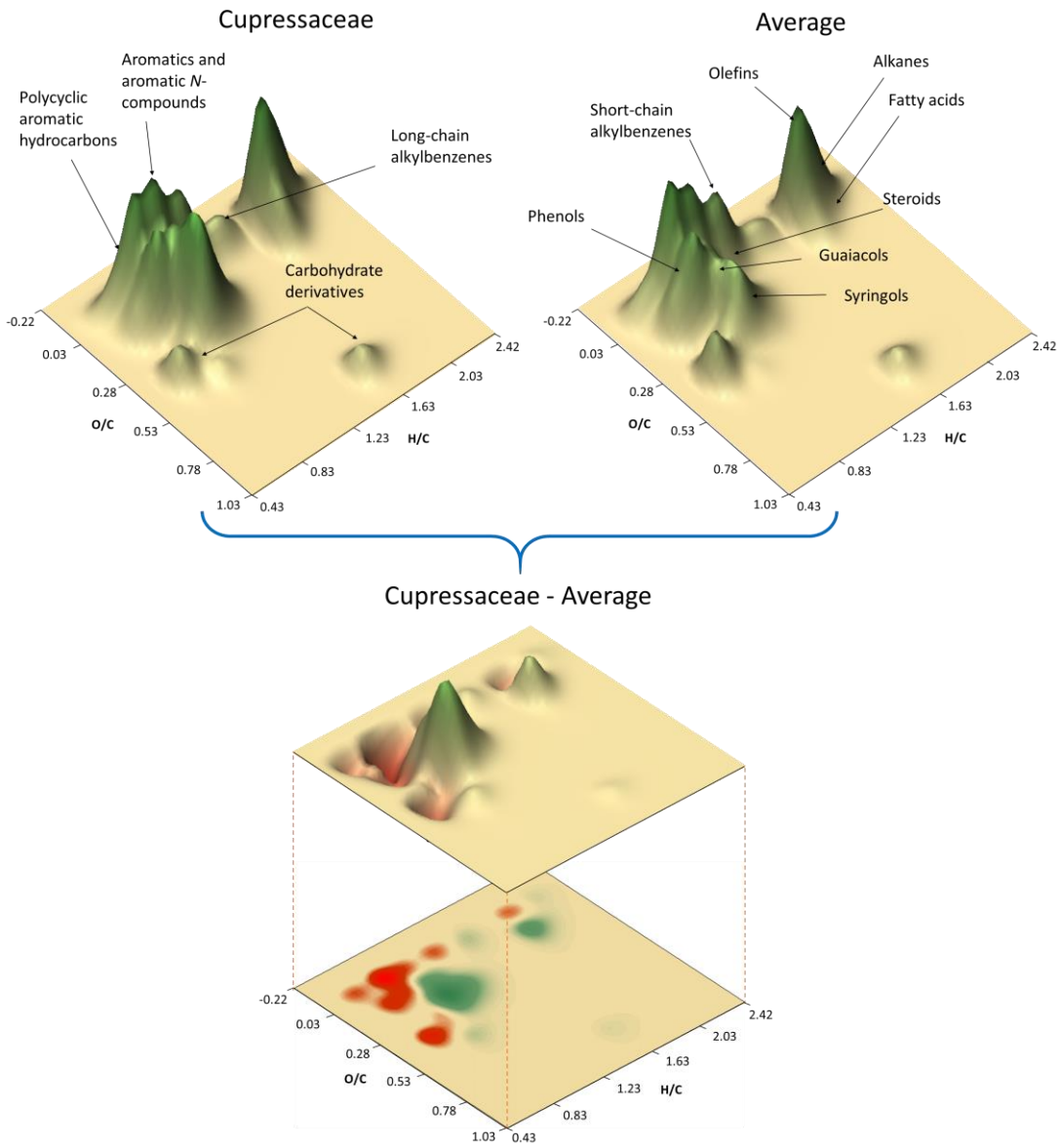

Figure 3 Example of van Krevelen diagrams obtained by subtracting average values of the abundances of the pyrolytic compounds from the whole set of soil samples (33 soils) minus the average values of the abundances of the same compounds in soils developed under vegetation of Cupressaceae. The subtraction plots, either represented as surface density plots or density maps, allows to easily detect the groups of compounds that differ in abundance between the two groups of samples. The compounds that are more abundant in the soils developed under Cupressaceae than in the general average of the 33 soils are shown in green colour, while those present in comparatively lower proportions are shown in red.

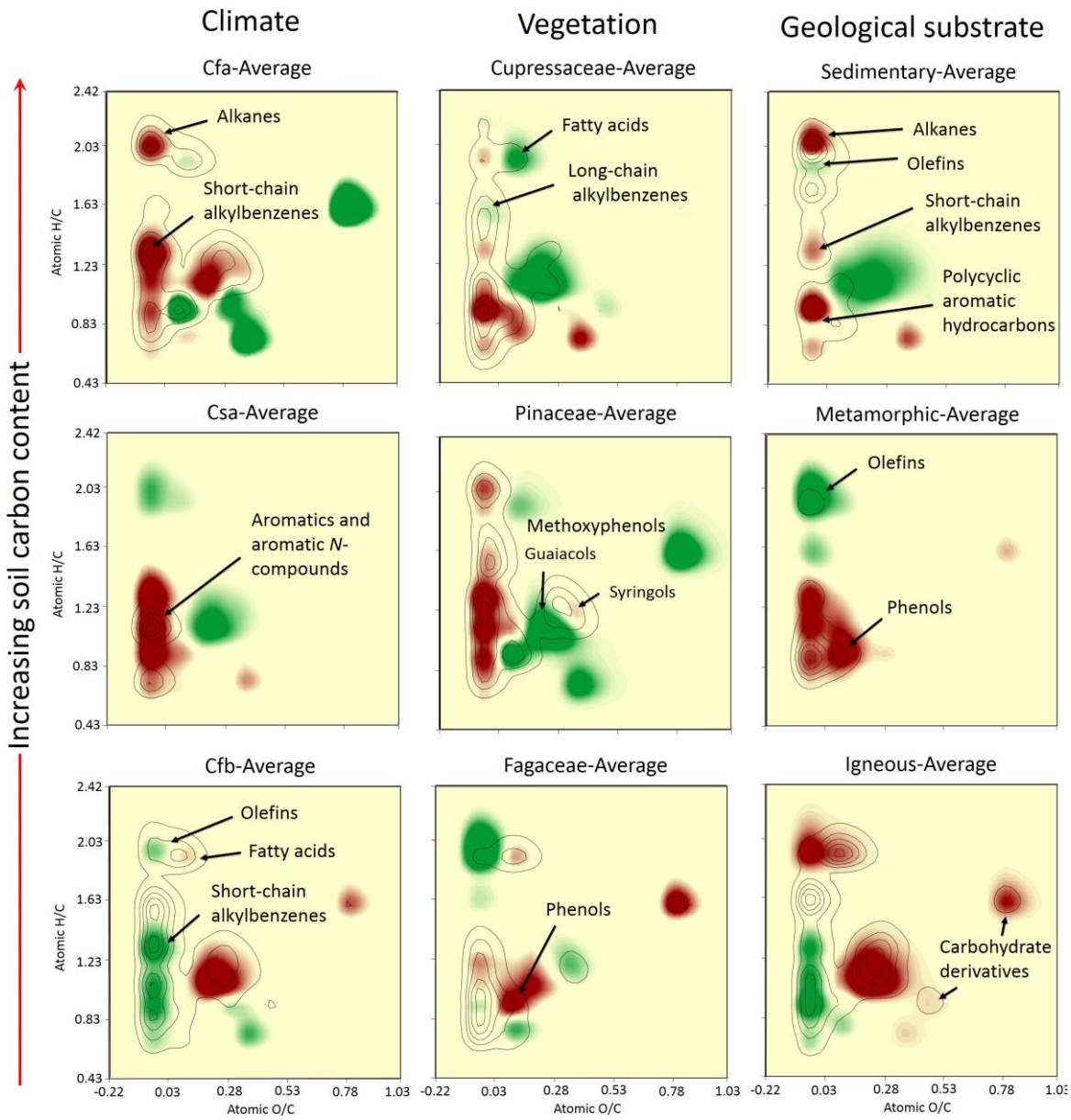

Figure 4 Van Krevelen diagrams obtained by subtracting average values of the abundances of the pyrolytic compounds from the whole set of soil samples (33 soils) minus the average values of the abundances of the same compounds in soil subsets (consisting of the soils developed under different soil forming factors, and correctly classified according to the previous discriminant analysis) and shown as density maps in the space defined by their H/C and O/C atomic ratios: molecular constituents of soil organic matter that prevail in soils developed under the corresponding formation factor (positive values after subtraction) are shown in green, whereas those present in lower proportions than in the general average are shown in red. The superimposed contour diagram shows the significance level of the difference between compounds abundances in the general average and the averages from the different subsets corresponding to individual forming factors (i.e., significance levels of the Student's *t* between each compound in the two soil sets, $P < 0.1$ in the external contour).