PYROLYSIS-GC-MS ANALYSIS OF ORGANIC MATTER FRACTIONS CONTROLLING SOIL WATER REPELLENCY

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Introduction

Soil water repellency is a property that reduces affinity for water and therefore infiltration capacity having a major impact on hydrological, geomorphological and geochemical soil processes (Jordán et al., 2013). Soil water repellency is widely observed in different climatic conditions, soil types and vegetation covers (Doerr et al., 2000). In the Mediterranean area, evergreen trees such as pines and oaks as well as shrubs are usually associated with the occurrence of soil WR (Doerr et al., 2000).

Soil water repellency is conditioned by different biotic and abiotic variables *i.e.* soil type, mineralogy, canopy, organic content, aggregation, seasonality, fire events, depth, etc (Mataix-Solera et al., 2013). It has been usually related with soil organic matter (SOM) content (DeBano, 2000; Doerr et al., 2000; Mataix-Solera et al., 2013; Zavala, 2014). However this relationship could be due to specific compounds within the SOM pool. The origin of natural WR has been attributed to organic compounds released from different plant species and sources (resins, waxes and other organic substances; Rumpel et al., 2004). In fact, soil lipids released by plants or microorganisms play a relevant role on the development of WR (Lozano et al., 2013).

This research attempts to enlighten the relationship between soil water repellency , soil organic matter content and the possible effects of the relative abundance and molecular assemblage of specific hydrophobic substances (n-alkane/alkene pairs and n-alkanoic acids) present in organic matter.

Methods

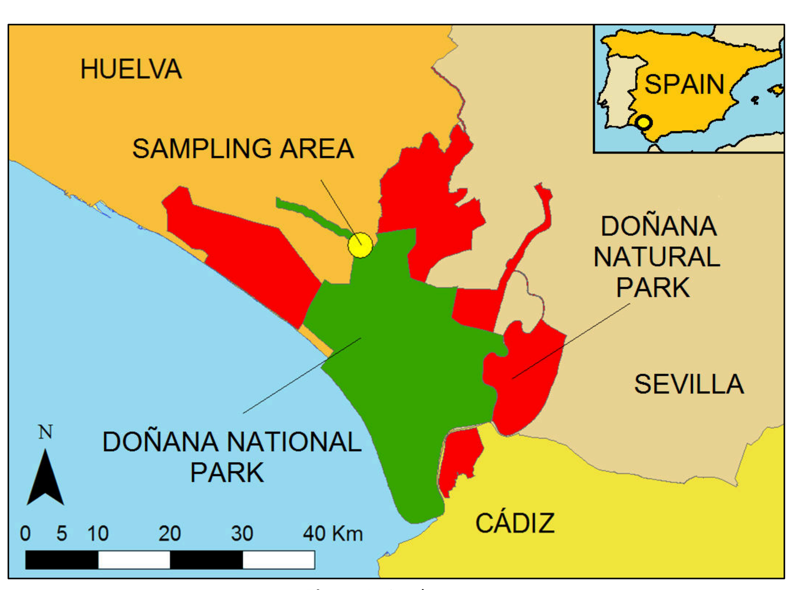

Figure 1. Study area.

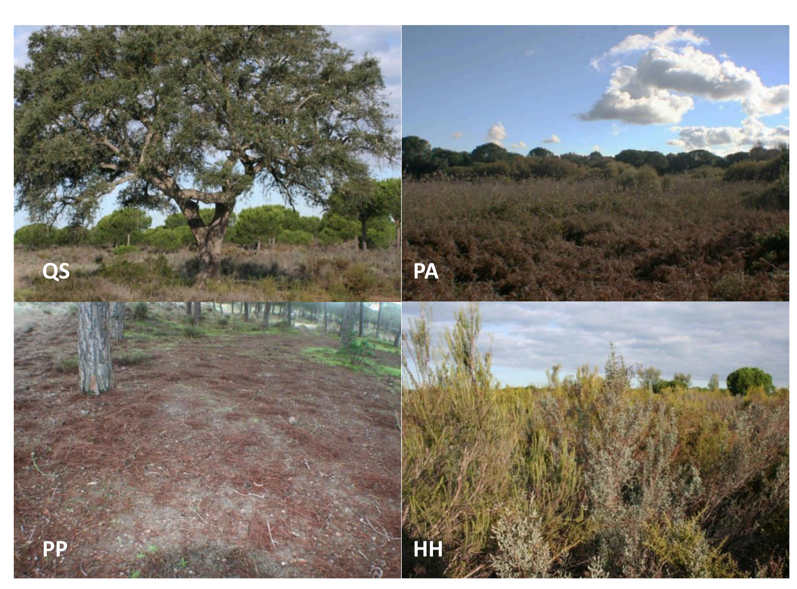

Figure 2. Details of sampling areas under *Quercus suber* (QS), *Pteridium aquilinum* (PA), *Pinus pinea* (PP) and *Halimium halimifolium* (HH).

Formulation of hypothesis and research proposal

- Search scientific articles related to the object of study

Sampling

- Sampling under Quercus suber (QS), Pteridium aquilinum (PA), Pinus pinea (PP) and Halimium halimifolium (HH)
- Air Dry
- Obtaining the fine earth fraction (<2 mm)
- Separation aggregate fractions (1-2, 0.25-1, 0.05-0.25, and <0.05 mm)

Laboratory tests

- Physico-chemical characterization
  - Physical properties
    - Texture analysis (Bouyoucos method)
    - Persistence of water repellency (water drop penetration time test)
    - Intensity of water repellency (molarity of an ethanol droplet test)
  - Chemical properties
    - Organic matter content (Walkley-Black)
    - pH
    - Organic nitrogen (N-Kjeldahl)
    - Available macroelements (atomic absorption spectrophotometry -Ca and Mg- and emission -Na and K-)
- Analytical pyrolysis (Py-GC/MS)

Statistical analysis

- Basic Statistics
- Normality test (normal distribution of data was rejected)
- Analysis of variance by ranks (Kruskal-Wallis test)
- Post-hoc test (Bonferroni test)

Figure 3. Brief description of the used methodology.

Study area

Soil samples were collected in the Doñana National Park (SW Spain; Figure 1). The type of climate is Mediterranean, with mean annual rainfall 830 mm (ranging between 1 mm in July and 110 mm in December) and mean monthly temperature 16.9 ºC (ranging between 9.5 ºC in January and 25.5 ºC in June and July). Soils are Arenosols developed from aeolian sandy sediments (Holocene), which form dunes stabilized by vegetation (mainly pine forest and shrubs).

Sample collection and analysis

Four soil samples were collected in a circular area (radius 5 m) under four representative vegetation types: *Quercus suber,* QS; *Pinus pinea,* PP; *Pteridium aquilinum,* PA; and *Halimium halimifolium,* HH (Figure 2).

In the laboratory, soil samples from each vegetation type were homogeneized and kept under lab conditions (25 ºC and approx. 50% relative humidity) during 1-week period. Dry soil samples were sieved (< 2 mm) to discard coarse elements and litter. Later, each combined sample was carefully divided in aggregate sieve fractions (1-2, 0.25-1, 0.05-0.25 and < 0.05 mm) by dry-sieving. Methodological processes are shown in Figure 3.

Results and Discussion

Table 1 shows the physicochemical characteristization of soil samples (< 2 mm) under the canopy of QS, PA, PP and HH. Soil acidity varied between pH 6.4 and 7.0. Soil water repellency ranged from slight (WDPT = 41 s, MED class = 5) and severe (WDPT = 619 s, MED class = 9). Soil samples can be ordered according to WDPT as follows: QS, PA, PP and HH. Organic matter content varied between 2.9 (PP) and 35.0 (QS). Soil texture in all samples is sandy. The content of macroelements is shown.

Table 1. Characterization of soil samples under different studied vegetation types.

Dominant species	Other species	WDPT	MED	pH	OM (%)	N (%)	Sand (%)	Silt (%)	Clay (%)	Ca (g/kg)	Mg (g/kg)	Na (g/kg)	K (g/kg)
Quercus suber	Calluna vulgaris Rubus ulmifolius Ulex sp.	619	9	6.4	35.0	1.0416	99.2	0	0.8	1.125	0.225	0.074	0.41
Pteridium aquilinum	Arbutus unedo Fraxinus angustifolia Populus alba	480	6	6.4	6.2	0.1904	99.14	0.02	0.84	0.225	0.055	0.068	0.056
Pinus pinea	Cistus salvifolius Halimium halimifolium Rosmarinus officinalis Ulex sp.	350	4	6.8	2.9	0.0406	99.16	0.02	0.82	0.15	0.01	0.05	0.02
Halimium halimifolium	Cistus salvifolius Rosmarinus officinalis Ulex sp.	41	5	7.0	3.4	0.0476	99.16	0	0.84	0.145	0.025	0.072	0.02

Table 2 shows the characterization of aggregate sieve fractions under the studied vegetation types (soil water repellency, WDPT; organic matter content, carbon preferency index of long-chained alkanes, CPI-L; average chain length, ACL; and number of long-chained ->10 C- and even –pair number of C- fatty acids, LC-FAP).

QS sieve fractions show the greater OM%. In all samples, the OM% is higher in the finer fraction (<0.05 mm), which also show the longer WDPT. Figure 4 shows the exponential relation between OM% and soil water repellency of aggregate sieve fractions.

Table 2. Characterization of aggregate sieve fractions under the studied vegetation types (QS, PA, PP and HH): soil water repellency (WDPT), organic matter content (%), carbon preferency index of long-chained alkanes (CPI-L), average chain length (ACL) and number of long-chained (>10 C) and even (pair number of C) fatty acids (LC-FAP).

Vegetation type	Sieve fraction (mm)	WDPT (s)	OM (%)	CPI-L	ACL	LC-FAP
QS	1-2	619	35.0	1.5	19.3	1
	0.25-1	1692	26.8	1.3	18.5	2
	0.05-0.25	1800	37.2	1.3	18.6	3
	<0.05	852	46.9	1.4	18.2	1
PA	1-2	480	6.2	1.6	17.3	3
	0.05-0.25	278	17.0	1.3	16.7	2
	<0.05	656	27.4	1.4	16.6	1
PP	1-2	350	2.9	2.0	16.5	5
	0.05-0.25	33	7.3	1.3	17.1	1
	<0.05	471	21.0	1.4	16.4	1
HH	1-2	41	3.4	1.4	19.0	2
	0.25-1	6	2.0	1.9	17.0	0
	0.05-0.25	0	3.7	1.1	18.1	0
	<0.05	278	25.0	1.2	18.0	0

Figure 6 shows the Total ion chromatogram (TIC) of the 1-2mm fraction of the soil sample under Pinus pinea, which is collecting all organic substances in the soil sample analyzed and chromatograms of each one of various types of organic compounds (in our case, alkanes / alkenes and fatty acids).

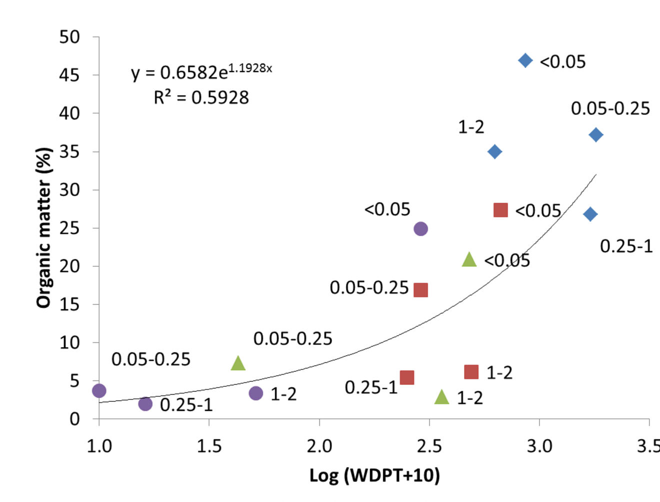

Figure 4. Exponential relation between organic matter (%) and soil water repellency (log WDPT+10) of aggregate sieve fractions.

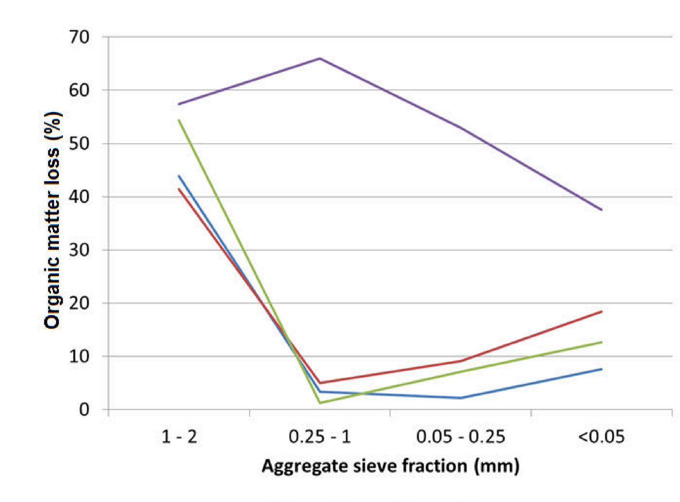

Figure 5. Relative soil organic matter loss (%) after pyrolysis for each aggregate sieve fraction under Halimium halimifolium (HH), *Pteridium aquilinum* (PA), *Pinus pinea* (PP) and *Quercus suber* (QS).

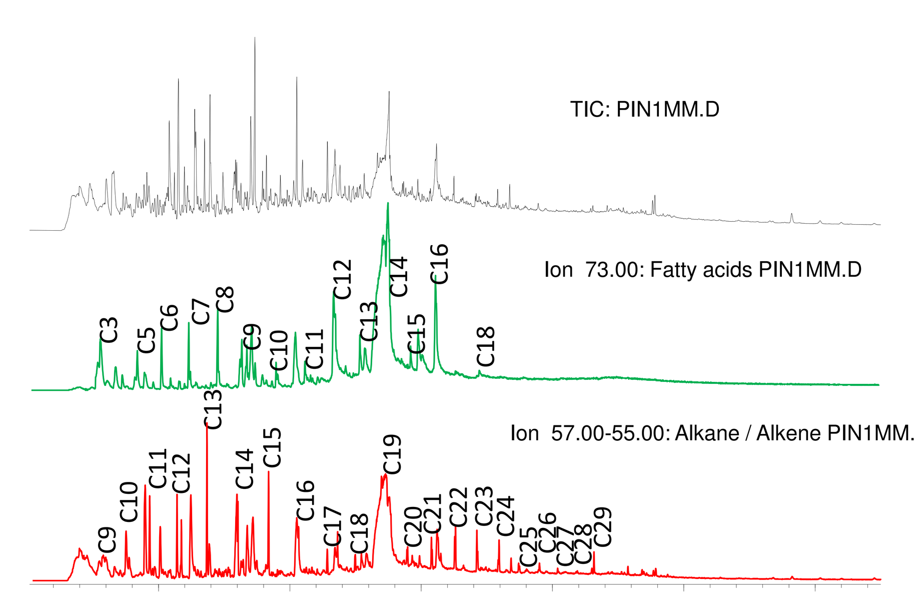

Figure 6. Total ion chromatogram (TIC) chromatogram of fatty acids (ion 73.00) and alkane/alkene (ion 57.00-55.00) of the 1-2 mm aggregate sieve fraction collected under *Pinus pinea*.

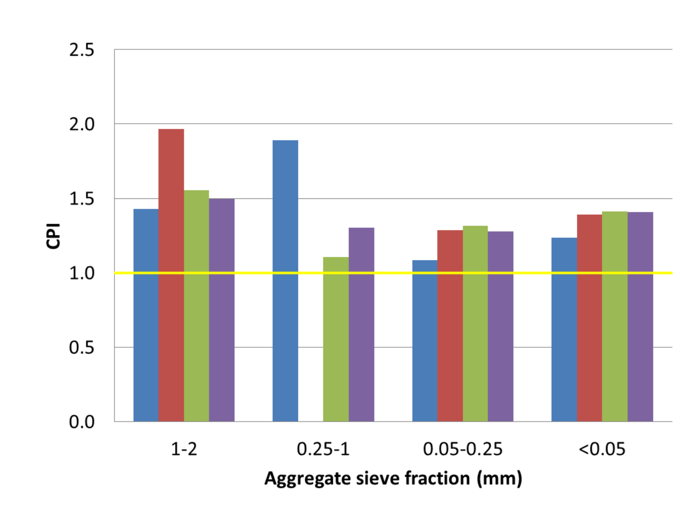

Figure 7. Carbon preferency index (CPI) for each aggregate sieve fraction under Halimium halimifolium (HH), *Pteridium aquilinum* (PA), *Pinus pinea* (PP) and *Quercus suber* (QS).

In general, that a relationship between the concentration of organic matter in soil and water repellency exists (Figure 4). The highest degree of water repellency was observed in QS sample, followed PA, PP and HH samples, which also has the least amount of organic material and the smaller amount of fatty acids. QS sample shows a relatively high concentration of organic matter (35%) compared to that of HH sample (3.4%). PA and PP samples also have a lower organic matter content number of fatty acids than QS (Table 2).

Figure 5 shows the relative soil organic matter loss after pyrolysis, with QS samples showing the highest organic matter loss.
Water repellency seems to be strongly related to the presence of fatty acids in the long-chain region (Table 2). Specifically, palmitic acid (C16) seems to be responsible for the high severity of water repellency in aggregate fractions of QS, PA and PP samples under (as shown in Figure 6 for PP sieve fractions). In the case of soils under HH, where strong repellency is found only in the finest fraction, palmitic acid was only detected in the 1-2 mm fraction. It is suggested that, in soils under HH, water repellency observed in the finest fraction may be controlled by other factors. With the data obtained in the chromatograms, it is possible to determine the source of organic matter present in each sample, obtaining the carbon preferency index of alkanes (CPI; Figure 7). The CPI of sieve fractions from all samples is greater than 1, whereby the source from which originate the organic matter present in soil is of vegetable origin (De la Rosa et al., 2012). The largest number of long-chained/even fatty acids from each fraction (Table 2) is observed in intermediate QS fractions (0.05-0.25 and 0.25-1 mm), and the coarser fraction (1-2 mm) of PA and PP and HH.

Differences in the degree of water repellency of the soil samples PA and PP are very mild, despite the difference in the organic matter content of the whole sample and the fractions of aggregates. However, similar in composition long chain fatty acids in the samples under both types of vegetation may arise from the presence of organic compounds in the soil inherited currently under PA or migrated from neighboring areas.

Conclusions

The research carried out in this work has focused on two factors: the influence of the amount and type of organic matter on soil water repellency, yielding the following conclusions:

- Soil water repellency under the different studied vegetation types was severe (QS), strong (PA and PP) and slight (HH). The intensity of the water repellency was extreme (QS), strong (PA), moderate (HH) and slight (PP).
- The persistence and intensity of soil water repellency increases with soil organic matter content.
- The presence of long-chain fatty acids and two fractions present in soil increases the persistence of water repellency in the soil.
- It has been observed the great importance of the finer aggregate fraction (<0.05 mm) in the development of water repellency. This relates to the evidence that the major proportion of organic material is associated with the finer aggregates.

The similarities observed between the composition of organic matter in samples collected under PA and PP, as the values of CPI-L suggest allow two working hypotheses:

- The existence of inherited organic compounds in the soils studied under PA, from ancient pine forests.
- The migration of organic compounds associated with fine aggregates from neighboring areas under PP, either by wind or by runoff.

Both hypotheses are supported by the fact that soils under PA are commonly found in the interface of wetlands with other vegetation types (PP being the most common).

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