BIO-GEOCHEMICAL MARKERS SURROGATED TO FIRE-INDUCED HYDROPHOBICITY

Model system: Doñana National Park sandy soils

Dr. Nicasio T. Jiménez Morillo

Premio a la mejor Tesis Doctoral en ciencias del suelo
por la Sociedad Española de Ciencias del Suelo (SECS) en 2018

MOSS IRNAS CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS UNIVERSIDAD DE SEVILLA SECS SOCIEDAD ESPAÑOLA DE LA CIENCIA DEL SUELO FuegoRED

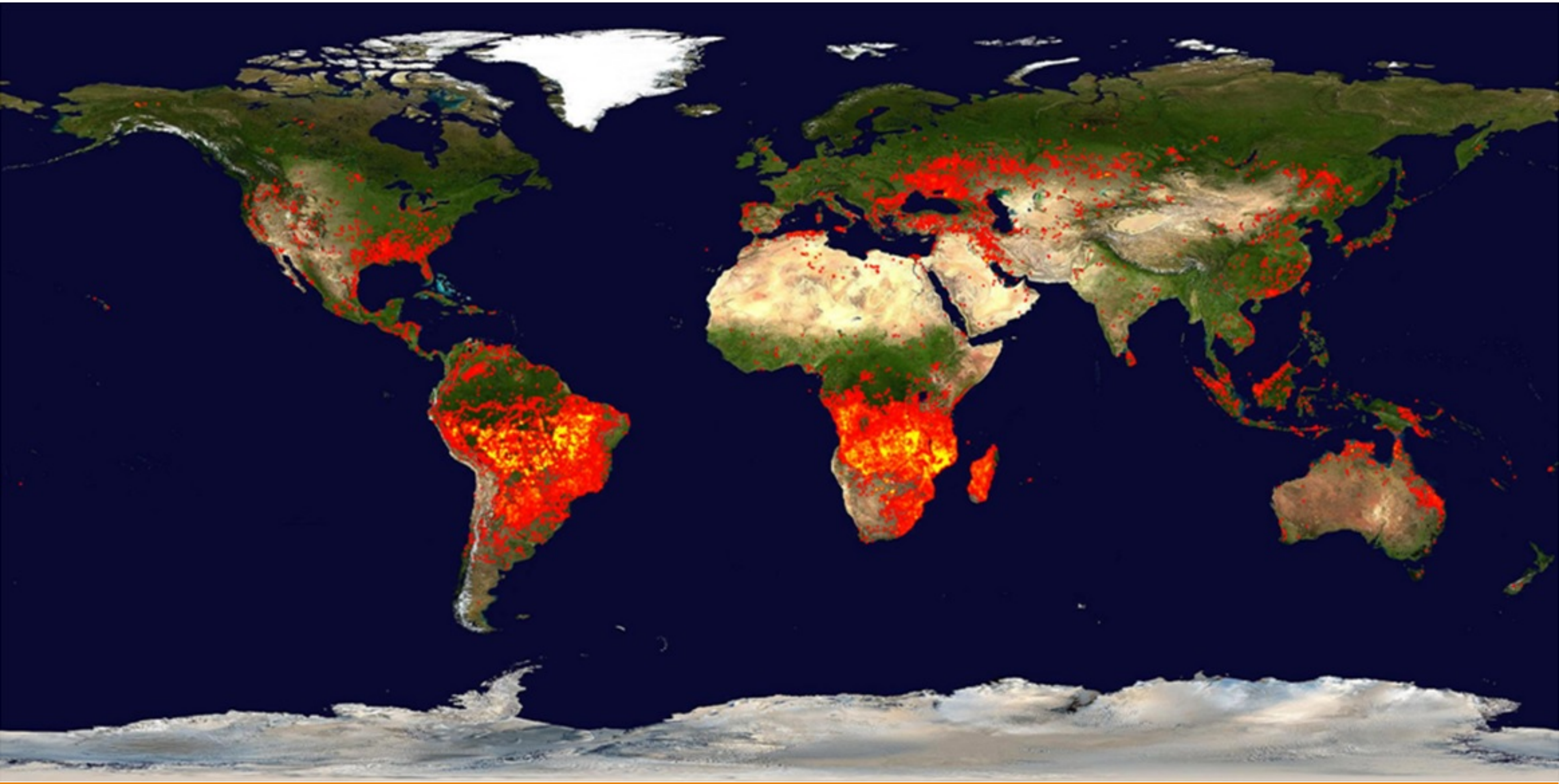
INDEX

Black and white ash after a fire. El Viso del Alcor, Sevilla, August 2015

INTRODUCTION

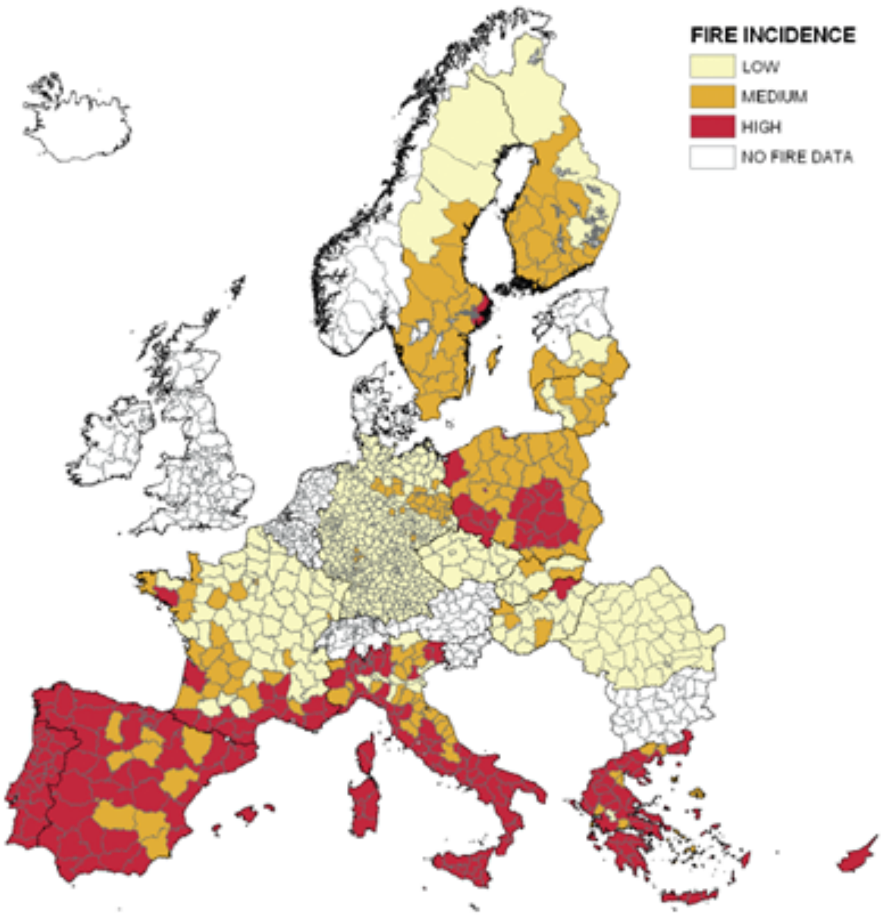
INTRODUCTION

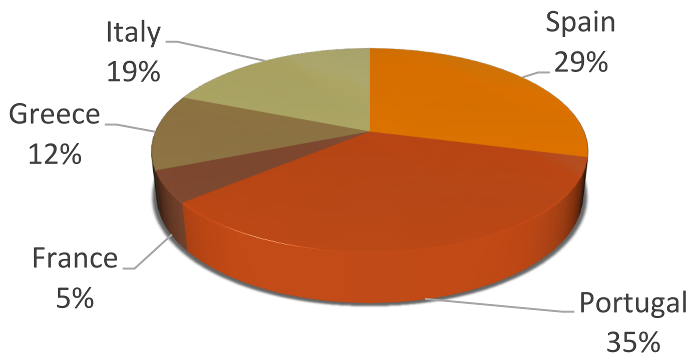
WILDFIRES IN THE EARTH SYSTEM



INTRODUCTION

WILDFIRES IN EUROPE



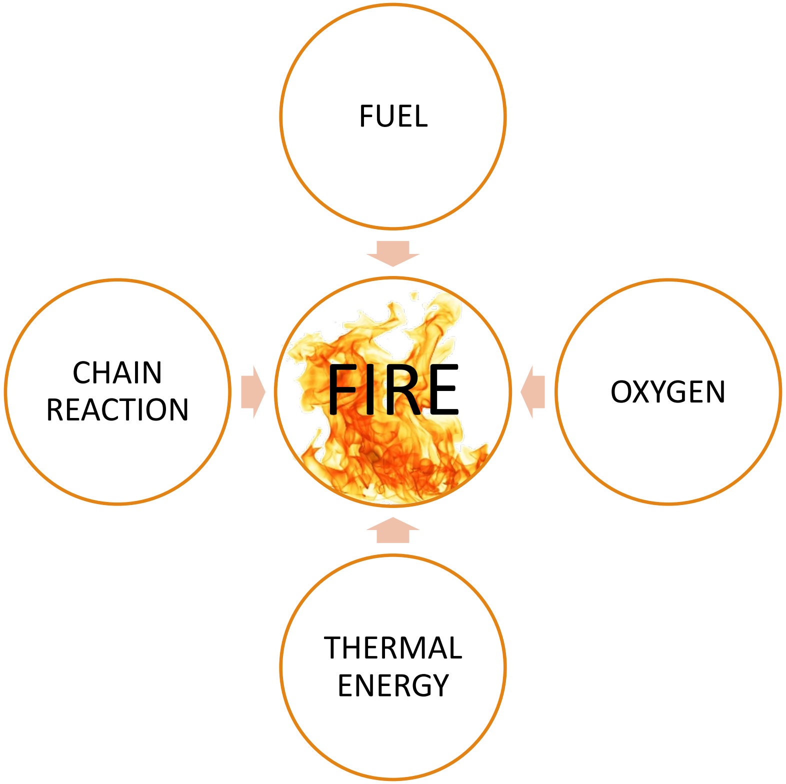


In average 90 to 95 % of forest fires at the EU occured in Mediterranean countries. Of these, c. 30 % corresponds to Spain and c. 65 % to the Iberian Peninsula.

Characteristics (Almendros & González-Vila, 2012):

- Dry and warm summers
- Noticeable water deficiency in soil
- Fire-adapted vegetation
- Socioeconomic factors:
    - Abandonment of rural areas
    - Intentionality of forest fire (provoked)

INTRODUCTION



Fire is the visual manifestation of the physical-chemical process known as combustion.

- Intensity
  It describes the thermal energy released by combustion of organic matter (Keeley, 2009).
- Severity
  Degree to which a site has been altered or disrupted by fire (NWCG, 2006).

INTRODUCTION. EFFECTS OF FOREST FIRES ON SOILS

Direct effects

Physical properties	Chemical properties	Biological properties
Water repellency	Quantity of organic matter	Microbial biomass
Structure stability	Quality of organic matter	Microbial community
Bulk density	Availability of nutrients	Biomass productivity
Particle-size distribution	Exchangeable capacity	
Mineralogical assemblage	Base saturation	
Colour	Acidity	
Temperature regime		

Indirect effects

Loss pf plant cover

Deposition of ash and charred litter

Hydrological consequences

Increased erosion risk

INTRODUCTION

WHAT IS SOIL WATER REPELLENCY?

WATER-REPELLENT SAND

WETTABLE SAND

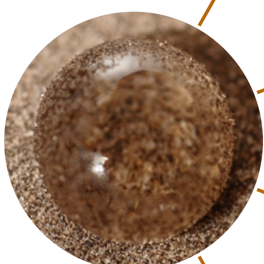
Water-repellent soils do not wet readily when in contact with water.

Thus, a water-repellent soil layer may offer strong resistance to the infiltration of water accumulated on the soil surface or in the upper wettable soil layer during periods of time that may range from a few seconds to hours, days or weeks.

INTRODUCTION

CONSEQUENCES OF SOIL WATER REPELLENCY AND ITS FACTORS

CONSEQUENCES OF SWR



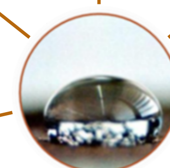
HYDROLOGY
- Decreased infiltration rate
- Preferential flow paths

GEOMOR-PHOLOGY
- Increased erosion risk

PLANT NUTRITION
- Leaching of nutrients
- Competition strategies

OTHER CONSE-QUENCES
- Increased aggregate stability
- Increased carbon sequestration

SWR FACTORS



- FIRE
- QUANTITY AND QUALITY OF SOIL ORGANIC MATTER
- SEASONAL VARIATIONS IN TEMPERATURE AND MOISTURE CONTENT
- ACTIVITY OF FUNGI AND MICROOR-GANISMS
- CLAY MINERALOGY
- VEGETATION TYPE
- SOIL PHYSICAL CHARACTER-ISTICS

INTRODUCTION

SOIL ORGANIC MATTER

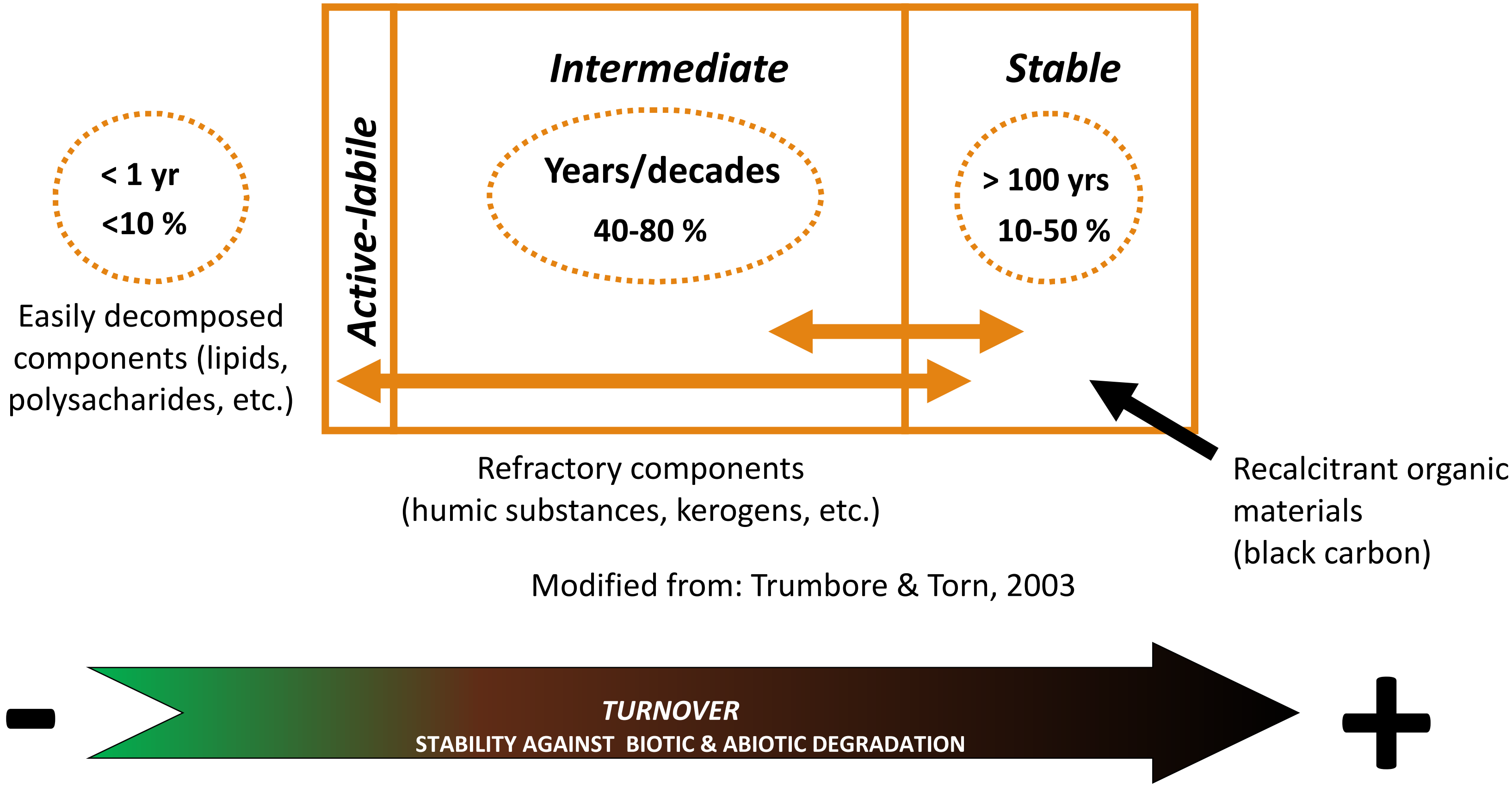
Soil organic matter is the main determinant of **soil health**.

Soil health refers to the biological, chemical, and physical features of soil that are essential to long-term, sustainable agricultural productivity with minimal environmental impact.

The SOM composition represents a molecular record of biogeochemical information which quantitatively reflects the effect of environmental factors.

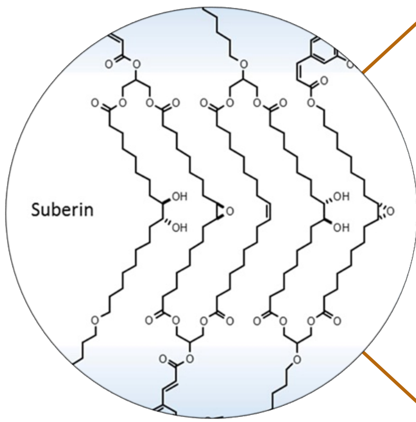
INTRODUCTION

POOLS AND FLUXES OF CARBON IN TERRESTRIAL ECOSYSTEMS



INTRODUCTION

SOIL LIPID FRACTION



Free Lipids

- < 10% of SOM
- Biomarkers of origin and/or state of SOM
- From simple structures (fatty acids, *n*-alkan-1-ols, etc.,) to complex structures (triterpenes or steroids)

Ester linkage Lipids

- Suberin and cutin biomarkers
- Highly resistant to microbial degradation

Non-hydrolysable Lipids

- Located in the non-removable fraction of soil
- Fundamental part of the soil C reserve

The lipid fraction is operationally described as a heterogeneous group of insoluble organic substances in water (hydrophobic) but extractable with organic solvent.

INTRODUCTION

FIRE EFFECTS ON ORGANIC MATTER

Quantity of SOM

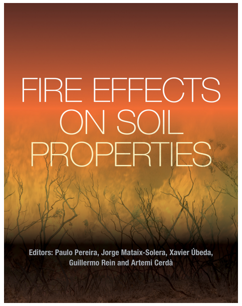
- Dramatic decrease (high-intensity combustion)
- Increase:
  - Mineral soil incorporation of litter or unaffected residue, therefore, are better protected form decomposition (Johnson & Curtis, 2001).
  - Fresh organic matter transformation in recalcitrant forms (Almendros et al., 1984).
  - Decrease in the rate of mineralization (Fernández et al., 1999).

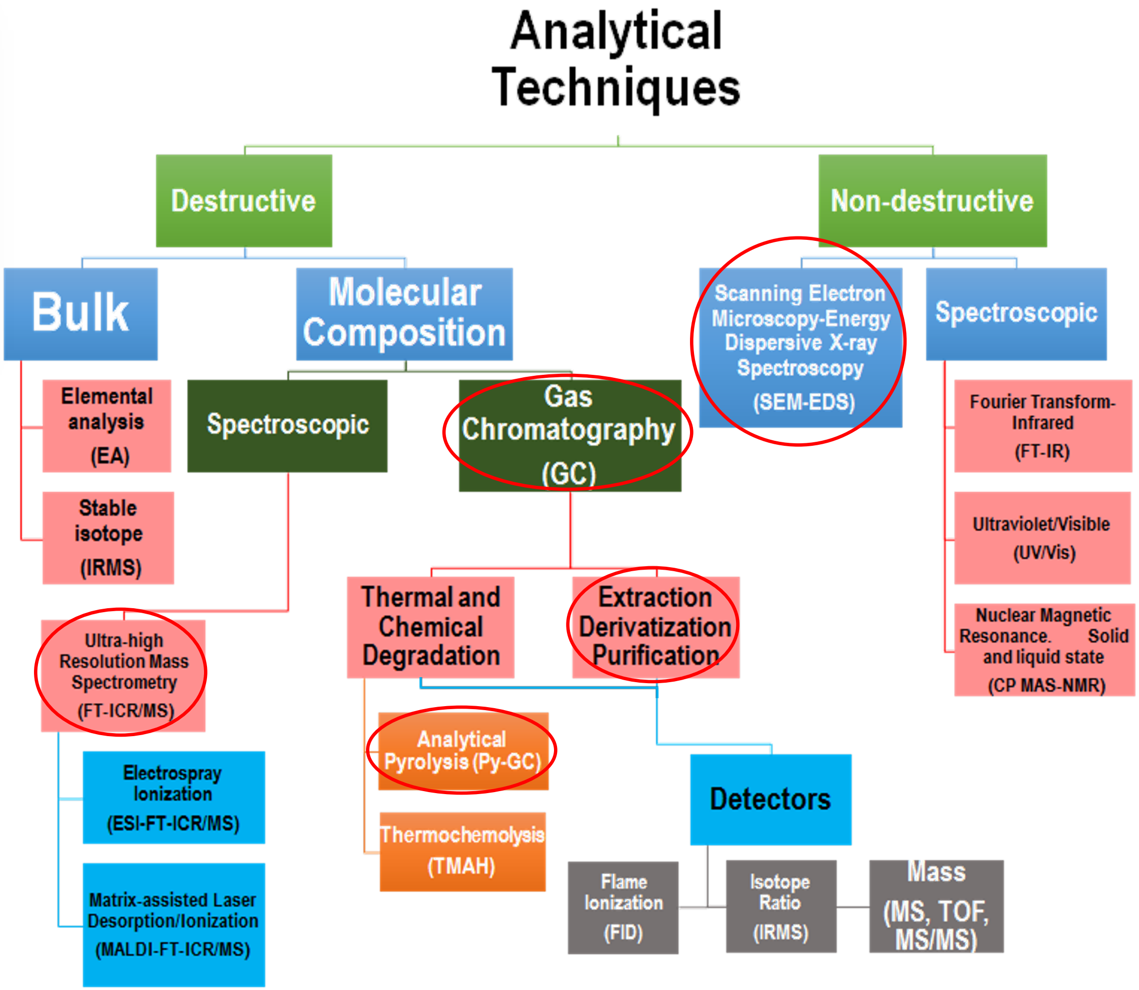
Quality of SOM

- Overall loss of external oxygen groups favoring the appearance of materials with a relatively low solubility.
- Reduction of chain length alkyl compounds, such as *n*-alkanes, fatty acids and alcohols.
- Flavoring carbohydrates and lipids.
- Formation of heterocyclic nitrogen compounds.
- Condensation of humic substances.
- Production of an almost unchanged component, black carbon, which originates at temperaturas between 250 and 500 oC as a result of incomplete combustion of the waste.

INTRODUCTION

ANALYTICAL METHODS TO ASSESS FIRE EFFECTS ON SOIL ORGANIC MATTER





Unburnt cork oak. Doñana National Park, Huelva, October 2015

OBJECTIVES

OBJECTIVES

GENERAL OBJECTIVES

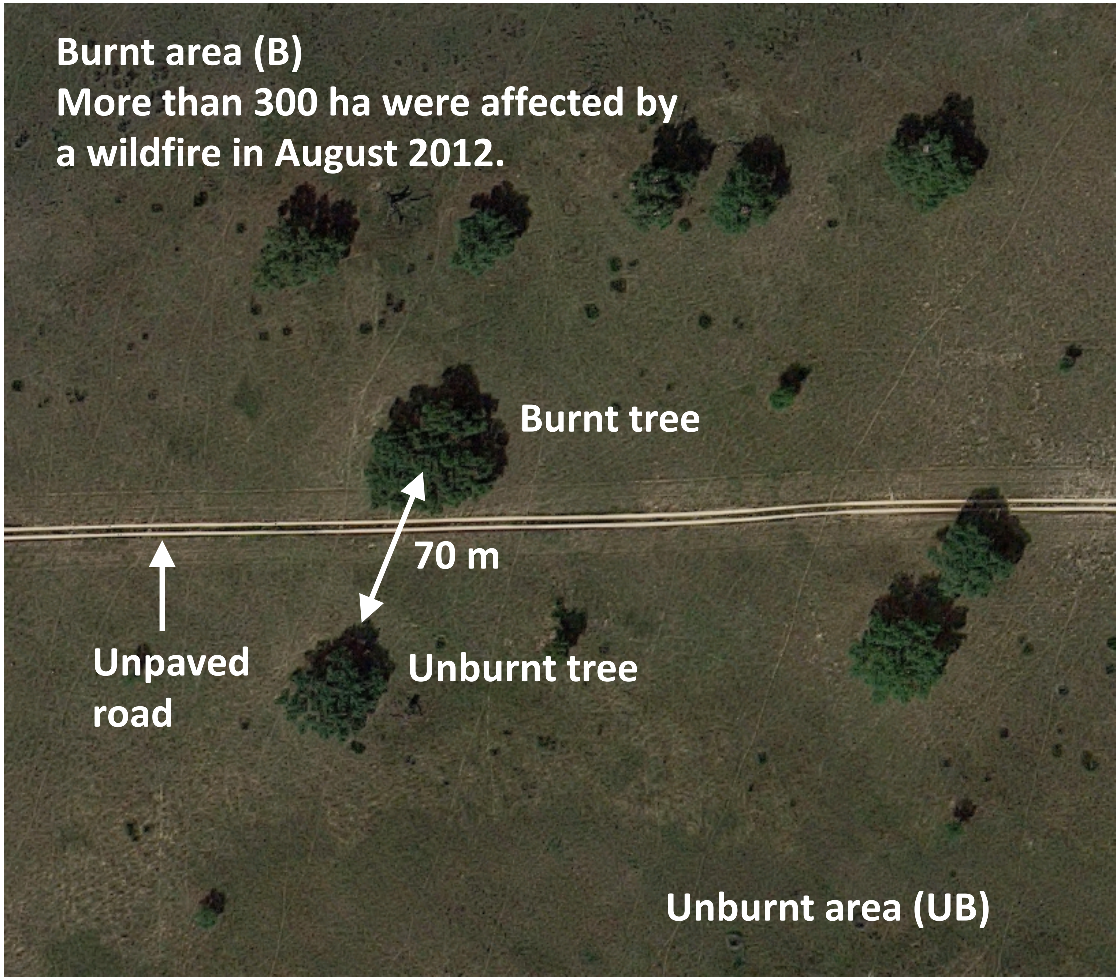
The main goal of this Doctoral Thesis, has been the characterization, by analytical techniques, of organic compounds responsible of the water repellency in fire-affected soils, into Doñana National Park.

The objective of this work was to shed light on some poorly studied aspects, in part due to, the enormous complexity of the soil systems, as well as the lack of new analytical techniques, with a sufficient resolution and sensibility.

STUDY AREA

CHAPTERS 1, 2 and 3

STUDY AREA AND SAMPLING SCHEME



Localization:
"Matasgordas", Doñana National Park (Southern Spain)

Type of Soil:
Typic Xeropsamment/Haplic Arenosol

Dominant vegetation:
Cork oak (*Quercus suber "QS"*) and shrubs

Sampling:
November 2014
Topsoil (0–3 cm)
Composite sample (5 sampling points)

Fractionation (mm):
1–2, 0.5–1, 0.25–0.5, 0.1–0.25, 0.05–0.1 and <0.05

Partially charred cork cover with formation of black carbon, Doñana National Park, Huelva, November 2015

FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOIL ORGANIC MATTER FRACTIONS UNDER CORK OAK COVER

Chapter 1

Jiménez-Morillo et al., 2016. Catena. 145, 266—273

FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOM

AIMS

This work is focused on the information provided by direct analytical pyrolysis of bulk and two particle size fractions (coarse and fine) with the aim of shedding light on the alterations in the SOM after a fire episode.

Objectives:

- To assess the chemical composition of organic matter in bulk soil and two different particle size fractions before and after a wildfire.
- To assess the thermal alteration processes in each of the fractions impacted by fire.

FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOIL ORGANIC MATTER

MATERIAL AND METHODS

Elemental Analyzer (EA)

Experimental conditions

- **Equipment:** Flash 2000 HT (Elemental microanalyzer)
- **Reactors:** Combustion (C and N)
- **Temperature:** 1020 ºC
- **Flow rate:** 80 mL min^{-1}
- **Oven temperature:** 40 ºC
- **Detector:** Thermal Conductivity Detector (TCD)
- **Mode:** Positive
- **Calibration:** Standard Materials (nicotinamide, aspartic acid and acetanilide)
- **Sample-weight:** 1– 1.5 mg
- **Capsule material:** Tin

Analytical Pyrolysis (Py-GC/MS)

Experimental conditions

- **Py:** Frontier Lab 2020i
- **Temperature:** 500 ºC – 1 min
- **Sample-weight:** 1 – 2 mg
- **Column:** DB-5 (low-polarity)
- **Range:** 50 – 300 ºC
- **Flow:** He, 1 mL min^{-1}
- **Detector:** Quadrupole mass spectrometer (5973 MSD, 70 eV ionization energy)

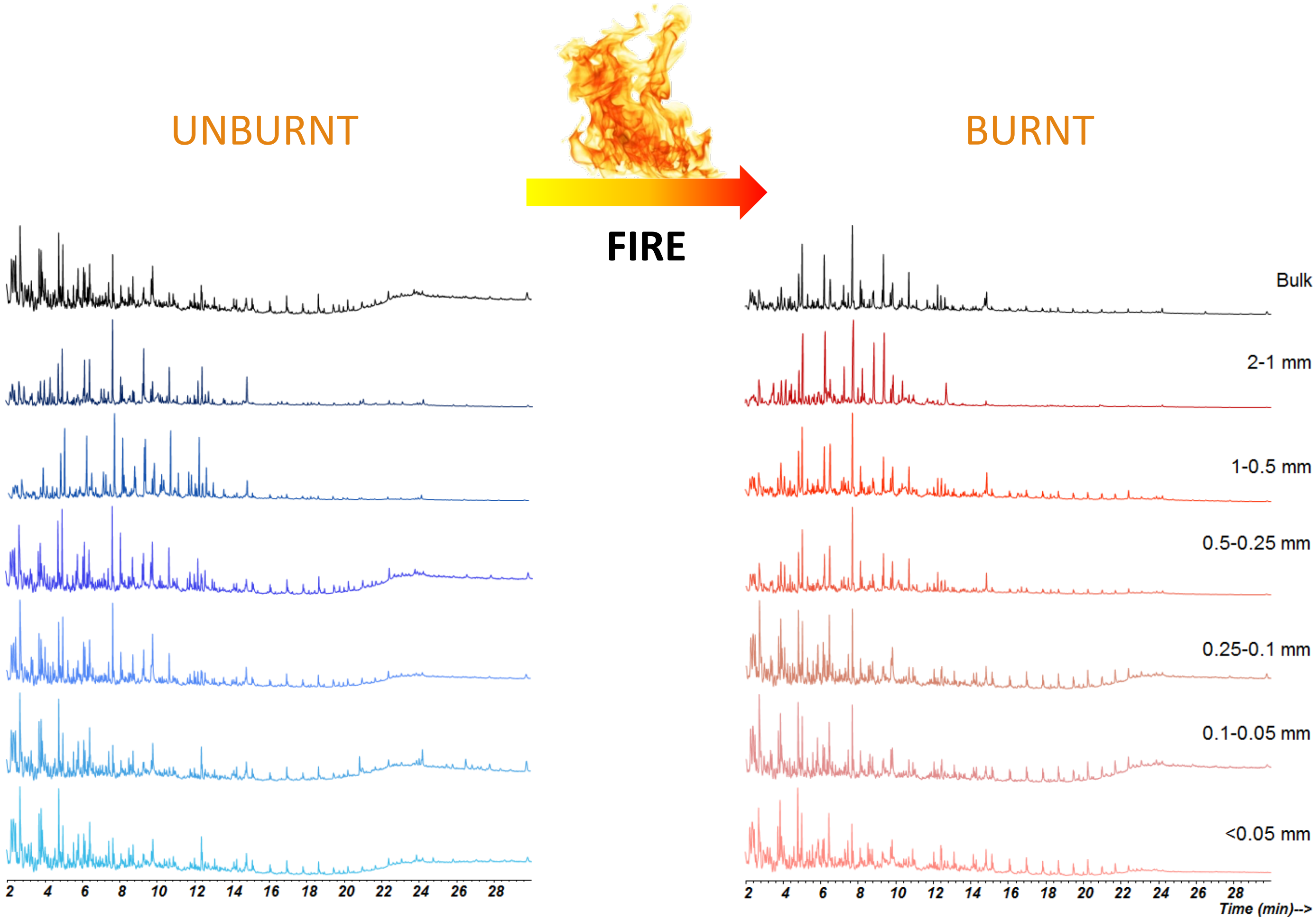
FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOM

ELEMENTAL C AND N CONTENT, AND C/N RATIOS FOR UNBURNT AND BURNT SOIL SAMPLES

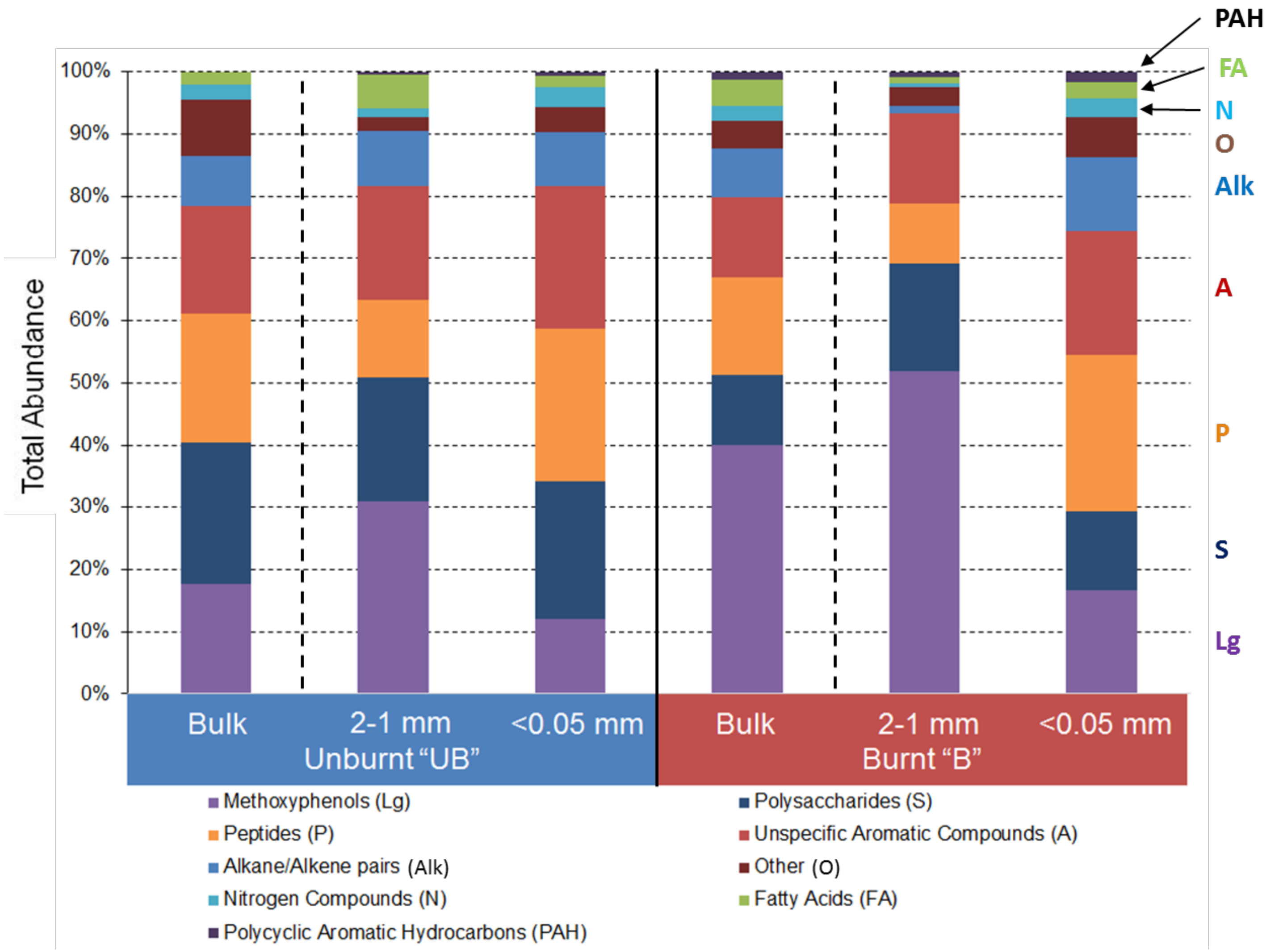
Soil samples	Sieve fraction (mm)	% C	% N	C/N
Unburnt	Bulk	6.7 ± 1.3	1.0 ± 0.1	6.8
	1–2	15.7 ± 2.7	1.5 ± 0.2	10.3
	0.5–1	14.0 ± 2.0	1.4 ± 0.1	10.3
	0.25–0.5	6.5 ± 0.3	1.0 ± 0.0	6.8
	0.1–0.25	5.8 ± 0.1	0.9 ± 0.0	6.3
	0.05–0.1	6.3 ± 0.4	1.0 ± 0.0	6.5
	<0.05	7.3 ± 0.0	1.1 ± 0.0	6.9
Burnt	Bulk	10.8 ± 1.1	1.3 ± 0.1	8.3
	1–2	27.9 ± 0.9	2.3 ± 0.0	12.1
	0.5–1	9.6 ± 0.1	1.2 ± 0.0	8.2
	0.25–0.5	7.7 ± 1.0	1.1 ± 0.1	7.2
	0.1–0.25	7.4 ± 0.1	1.1 ± 0.0	6.9
	0.05–0.1	7.5 ± 1.1	1.1 ± 0.1	6.9
	<0.05	9.6 ± 0.3	1.3 ± 0.0	7.4

FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOM

ANALYTICAL PYROLYSIS

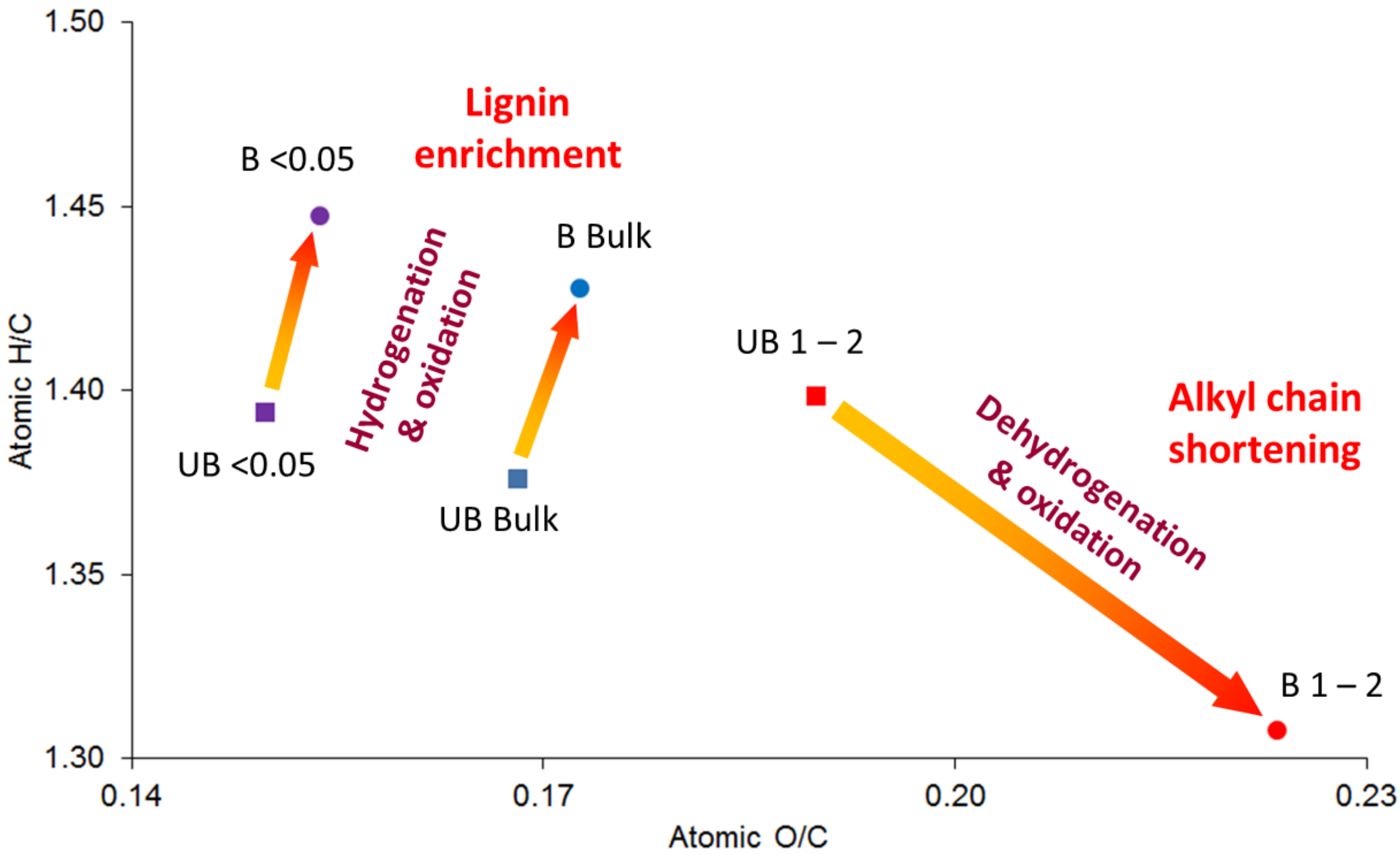


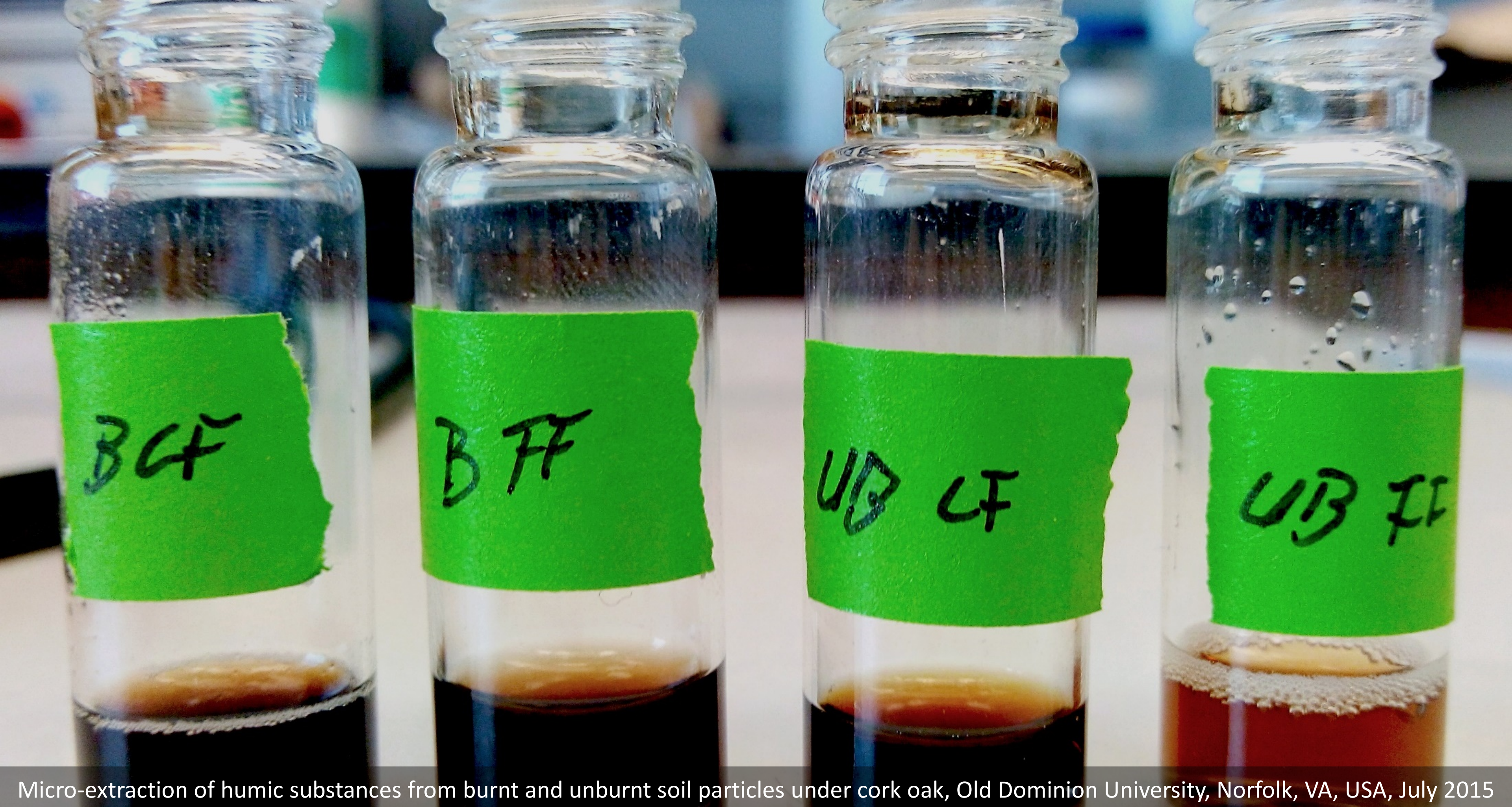
FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOM



FIRE EFFECT IN THE MOLECULAR STRUCTURE OF SOM

CHEMICAL ALTERATION PRODUCED BY FIRE ON SOIL ORGANIC MATTER





Micro-extraction of humic substances from burnt and unburnt soil particles under cork oak, Old Dominion University, Norfolk, VA, USA, July 2015

ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS) STUDY OF PHYSICAL SPECIATION PATTERNS OF ORGANIC MATTER

Chapter 2

Jiménez-Morillo et al., 2018. Journal of Environmental Management. 225, 139—147

ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

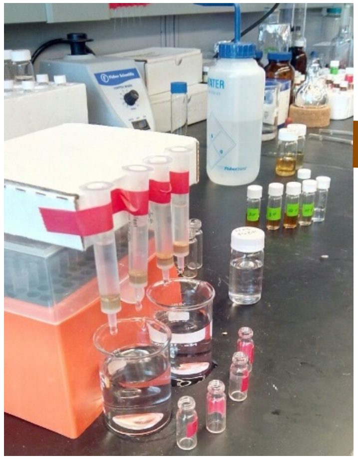
Aims

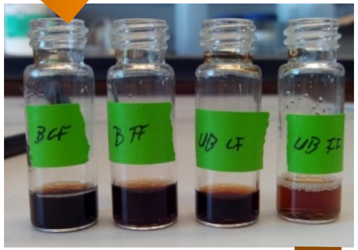
- A detailed characterization of the chemical composition of SOM in fire-affected and unaffected soils is carried out in two different particle size fractions (coarse and fine) in a sandy soil from Doñana National Park (SW Spain) using ultra-high resolution mass spectrometry

ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

MATERIAL AND METHODS

1. Weigh of the sample (100 mg)
2. Extraction of organic compounds using 1 *M* NaOH (1 mL)
3. Shake for 24 h in a temperature-controlled chamber
4. Filtration and purification using a cation exchange resin
5. Dilution in MeOH and MilliQ water
6. Analysis in (ESI)-FT-ICR-MS instrument





Ultra-High Resolution Mass Spectrometry (FT-ICR-MS)

1. Sample Introduction: Apollo II Electrospray Ionization (ESI)
2. Working Mode: Negative
3. Flow rate: 120 µL h^{-1}, with a nebulizer gas of 20 psi.
4. Detector: Mass Spectrometer (Bruker Daltonics 12 Tesla Apex Qe FT-ICR-MS)
5. Scans: 300 in a range of 200–1200 amu
6. Calibration: Polyethyleneglycol and fatty acid series

Experimental conditions

ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

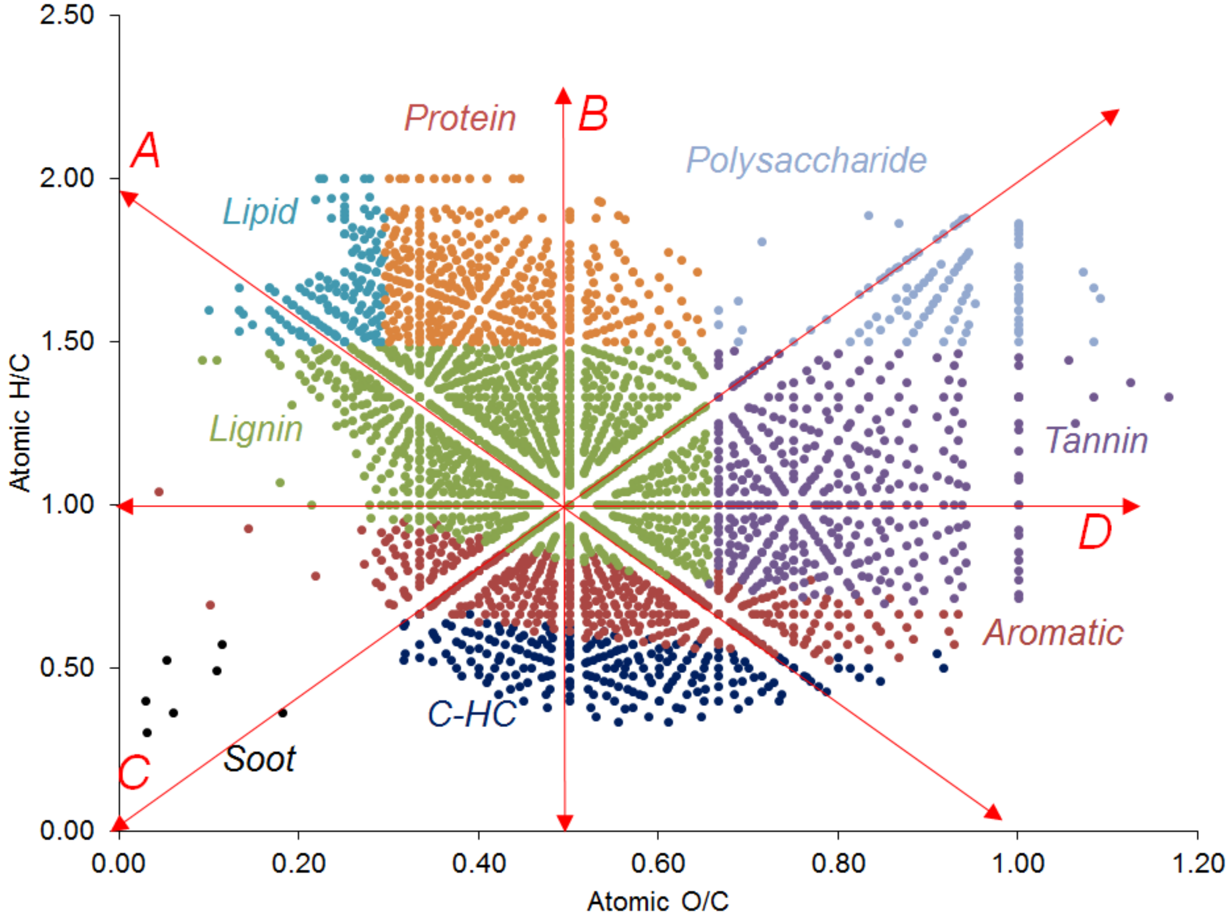
NUMBER OF TOTAL CHEMICAL FORMULAS FOUND IN PARTICLE SIZE FRACTIONS BY FT-ICR/MS

		UNBURNT		BURNT	
	Fractions	Coarse (UBCF)	Fine (UBFF)	Coarse (BCF)	Fine (BFF)
Elements	Number of compounds	7466	6244	3571	6457
C, H, O	Total*	2701	2080	2462	2352
	Common	1717	1717	1717	1717
	Unique	414	135	193	74
C, H, O, N	Total	804	624	673	1155
C, H, O, P	Total	40	141	24	71
C, H, O, S	Total	130	221	75	151

*Note that the sum of common and unique compounds is not equal to total CHO compounds. This is because in the common compounds group only compounds in common to all samples were considered, excluding CHO compounds only present in two or three samples.

ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

VAN KREVELEN DIAGRAM



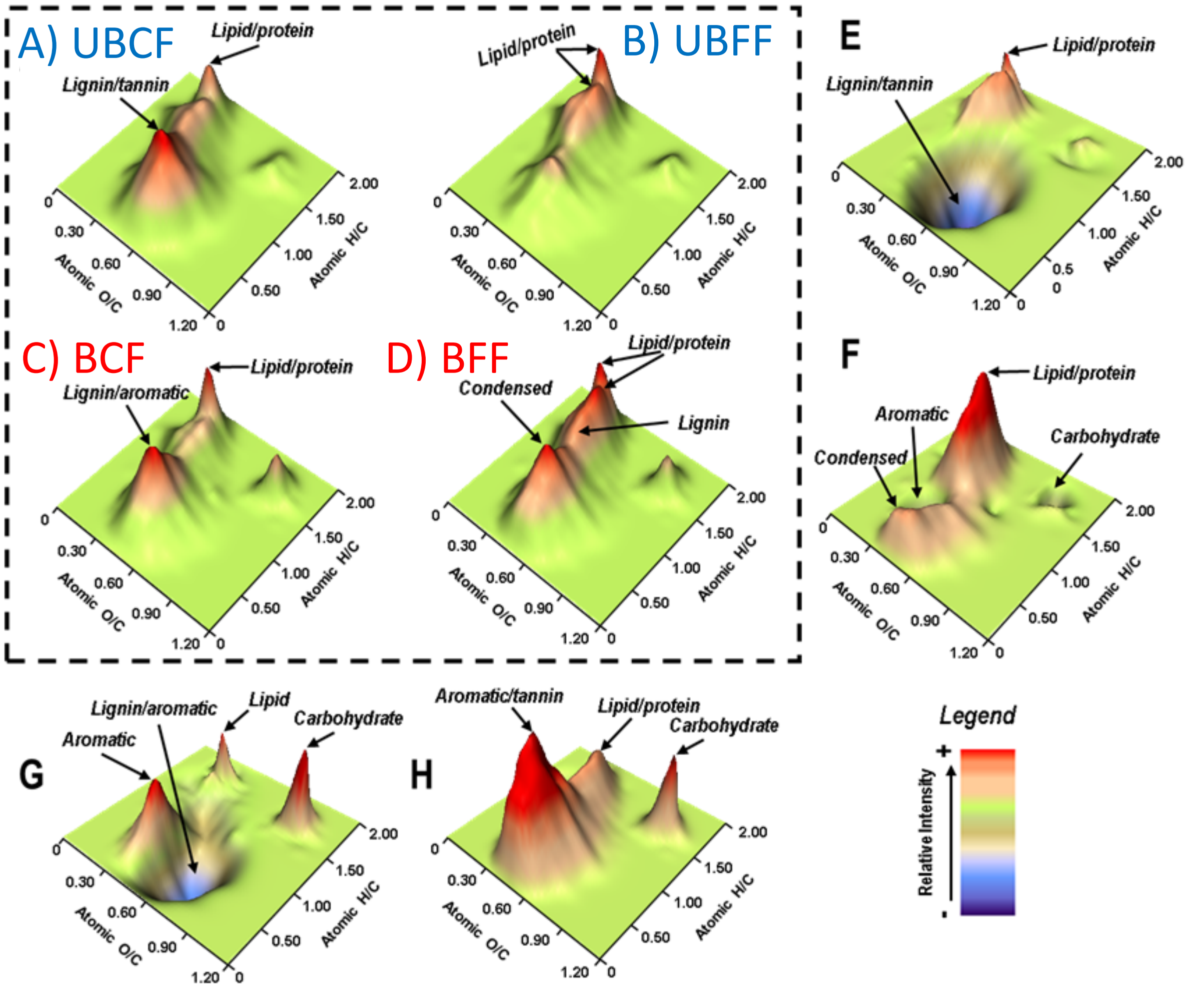
Trend lines represent reaction pathways that results in the formation of the families of compounds.

Line A: methylation/demethylation/increasing (alkyl) chain length; Line B: hydrogenation/ dehydrogenation;
Line C: hydration/condensation; Line D: oxidation/reduction

(Kim et al., 2003; Koch et al., 2005).

ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

3-D VAN KREVELEN DIAGRAMS OF COMMON *CHO* COMPOUNDS



Legend:

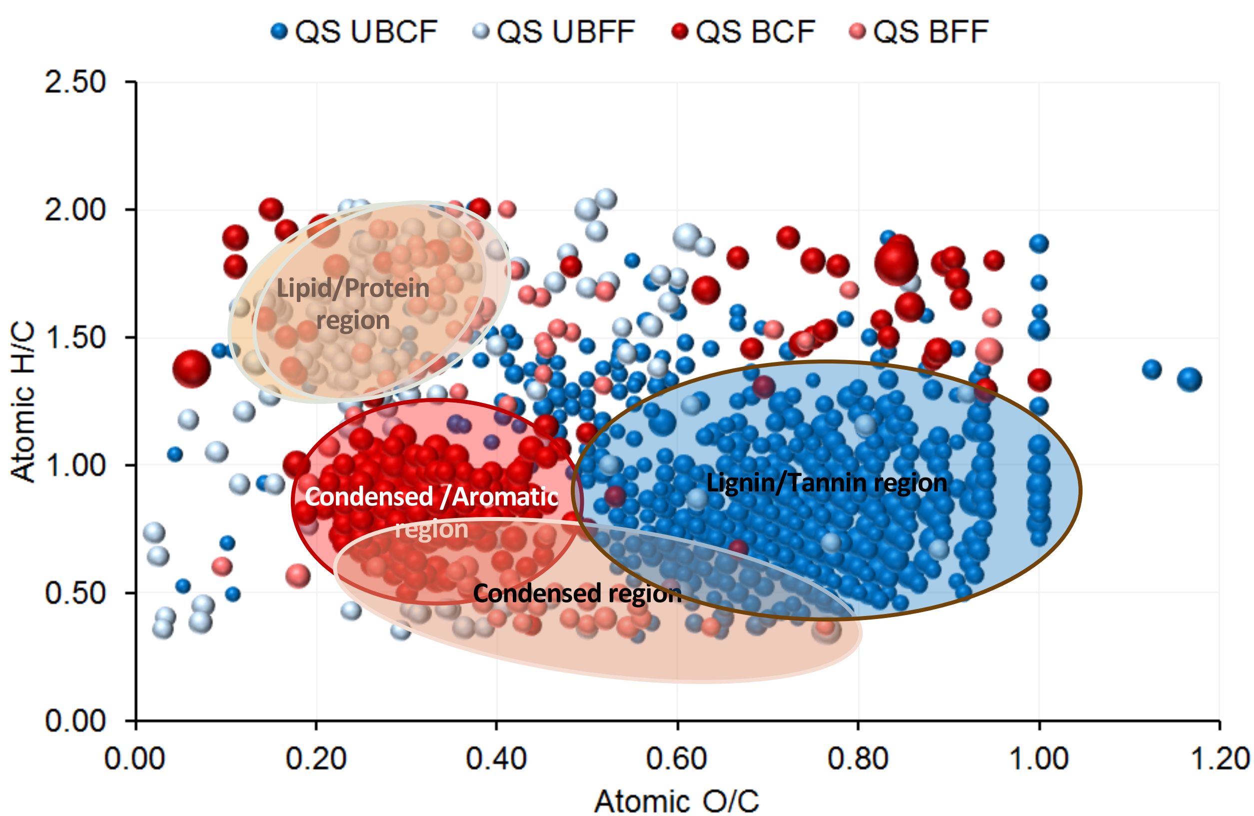
- **A. UB Coarse fraction (UBCF)**
- **B. UB Fine fraction (UBFF)**
- **C. B Coarse fraction (BCF)**
- **D. B Fine fraction (BFF)**

Subtract:

- **E. UBFF-UBCF**
- **F. BFF-BCF**
- **G. BCF-UBCF**
- **H. BFF-UBFF**

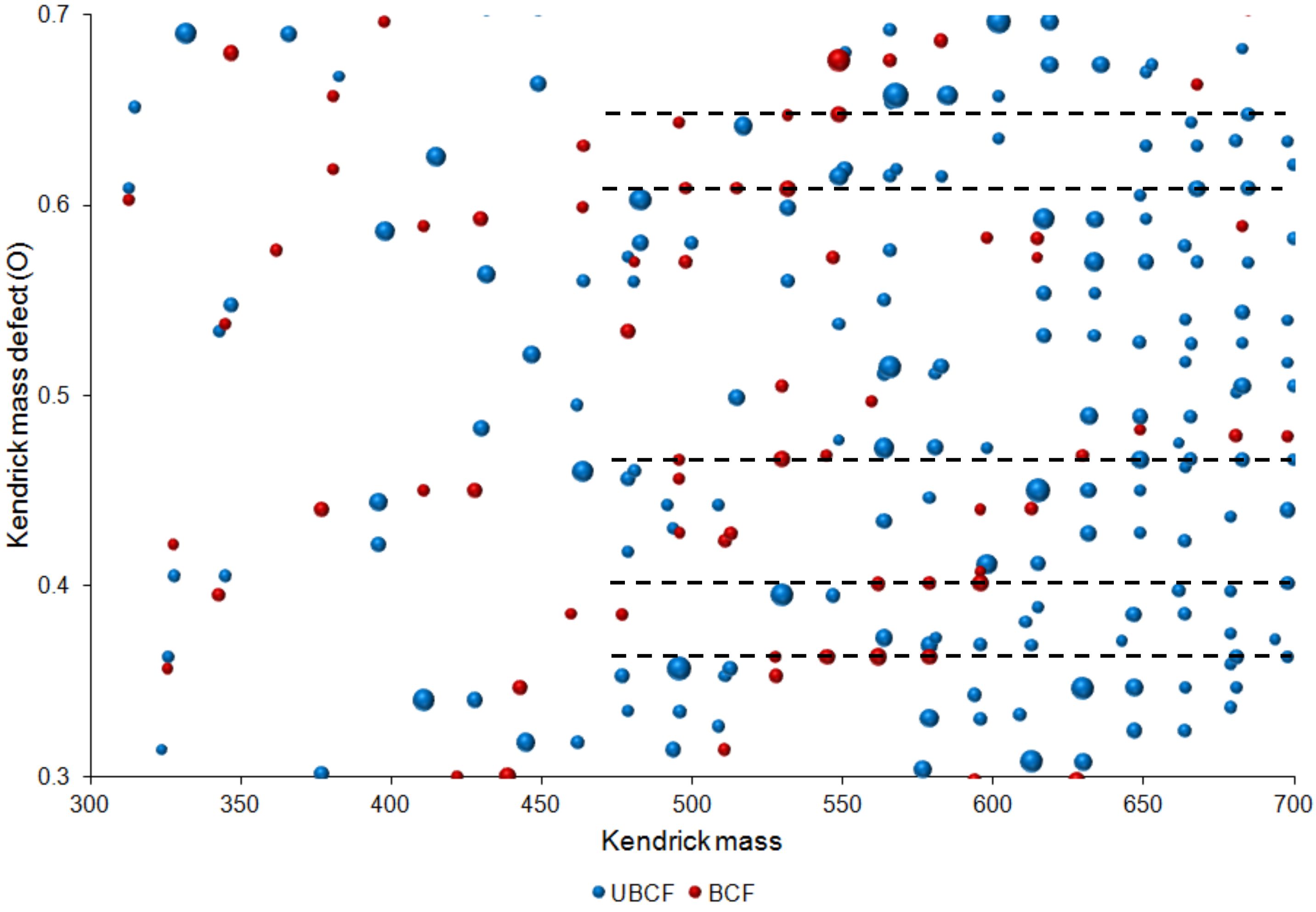
ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

2-D VAN KREVELEN DIAGRAM OF UNIQUE *CHO* COMPOUNDS



ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

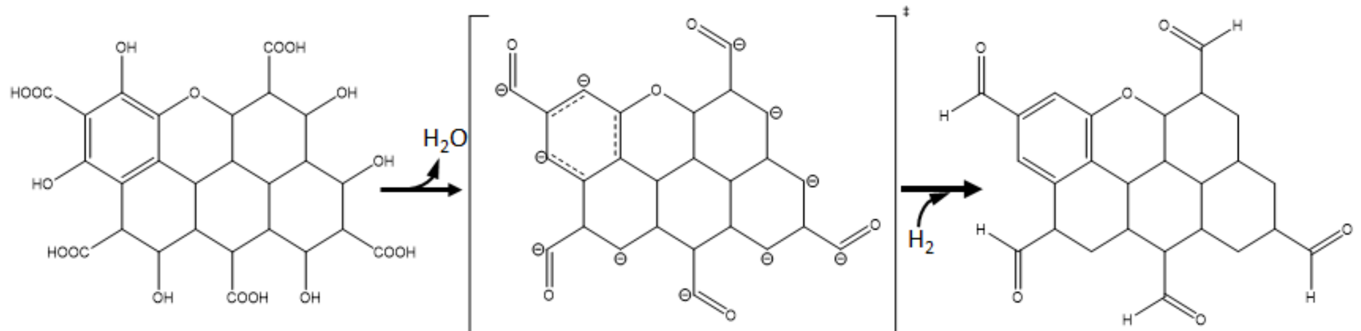
KENDRICK MASS DEFECT OF OXYGEN



ULTRA-HIGH RESOLUTION BROADBAND MASS SPECTROMETRY (FT-ICR/MS)

THEORETICAL MODEL REACTIONS

A

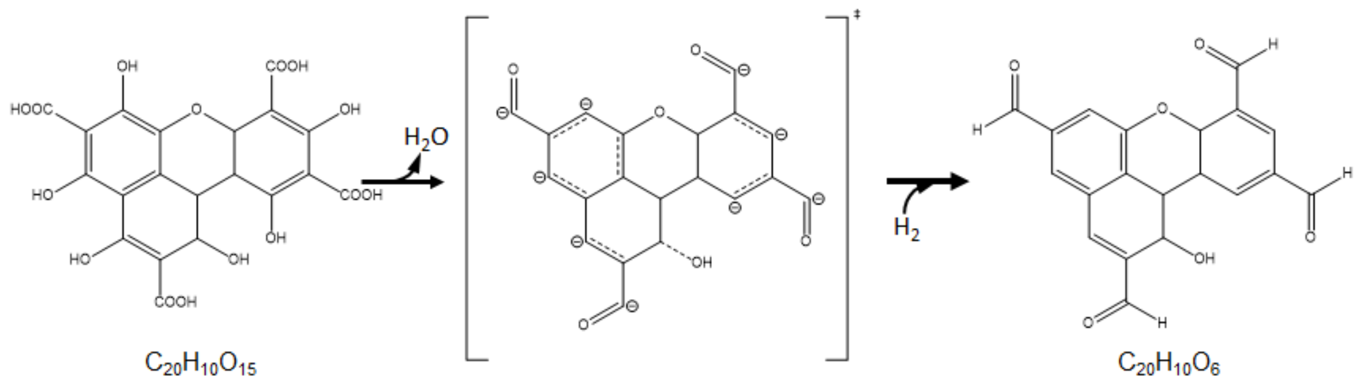


$C_{26}H_{26}O_{17}$
DBE = 14
H/C = 1.00
O/C = 0.65

Non-condensed-tannin compound

$C_{26}H_{26}O_{6}$
DBE = 14
H/C = 1.00
O/C = 0.23

B



$C_{20}H_{10}O_{15}$
DBE = 16
H/C = 0.50
O/C = 0.75

Condensed-tannin compound

$C_{20}H_{10}O_{6}$
DBE = 16
H/C = 0.50
O/C = 0.30

Cork oak affected by a forest fire during the summer of 2012, Doñana National Park, Huelva, November 2015

HYDROPHOBICITY OF BULK SOILS AND PARTICLE-SIZE FRACTIONS

Chapter 3

Jiménez-Morillo et al., 2017.
Environmental Research. 159, 394—405

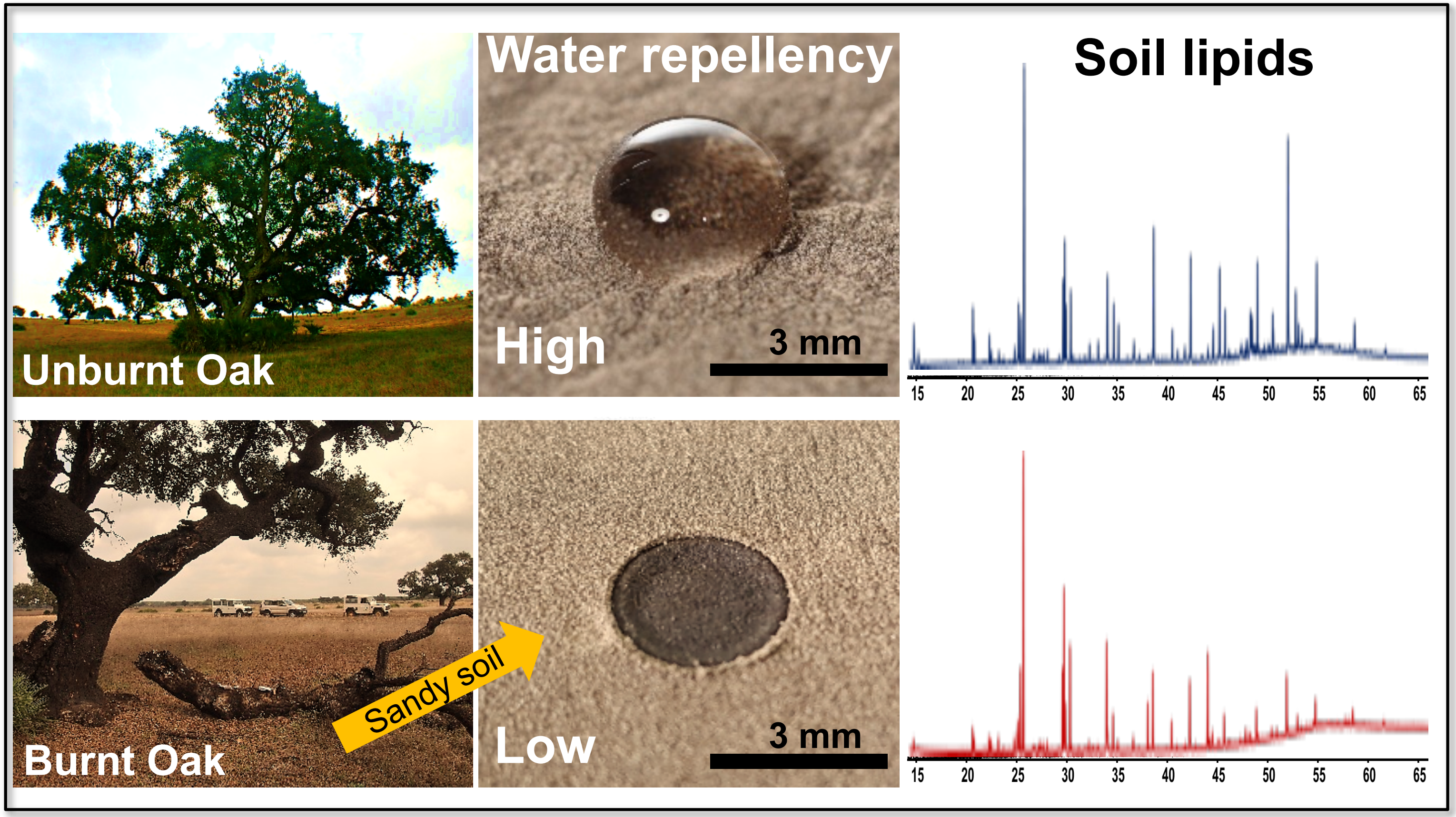
WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

AIMS

This study aims to unravel the chemical factors controlling the hydrophobicity in both burnt and unburnt sandy soils and particle size fractions.

WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

MATERIAL AND METHODS



WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

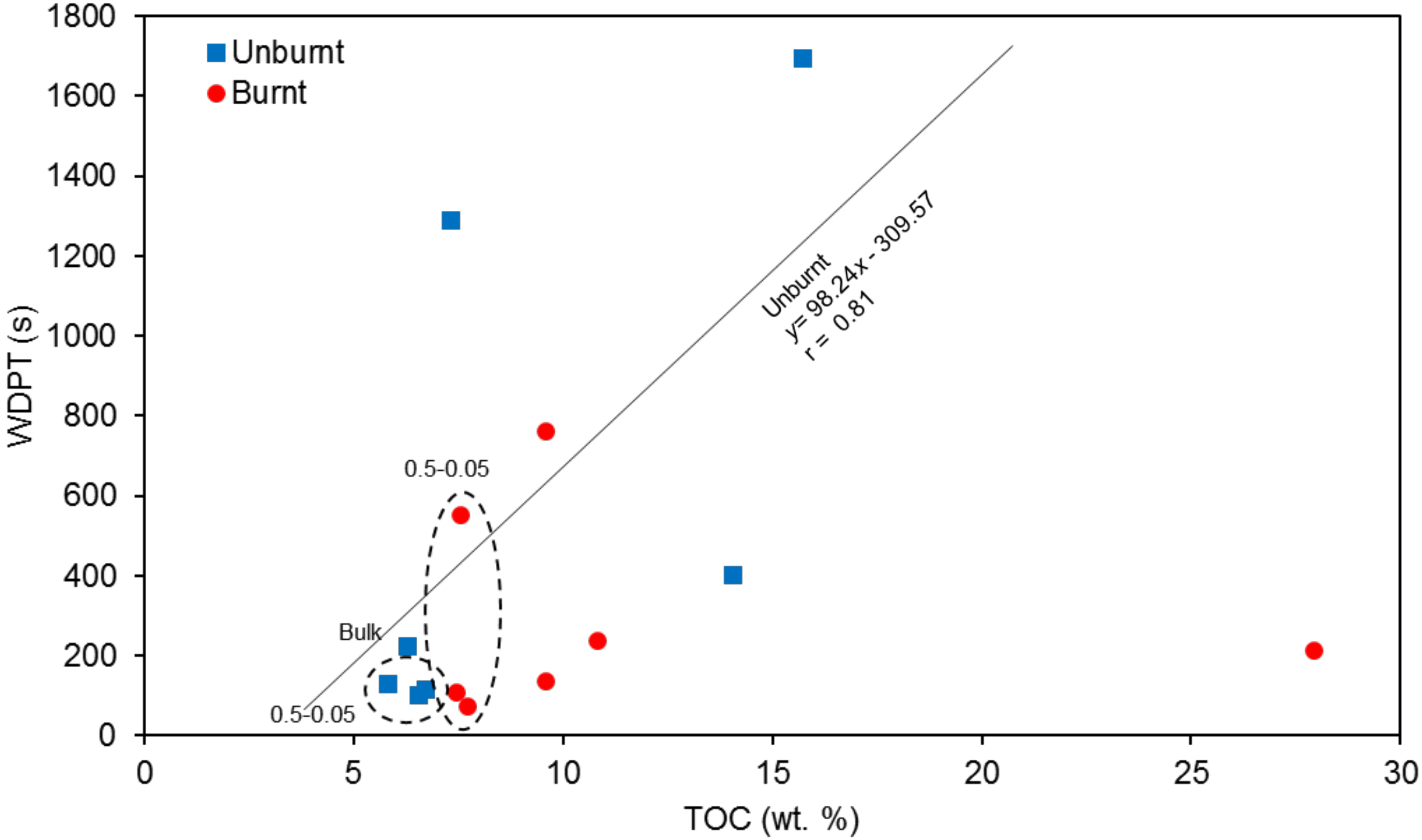
WATER DROP PENETRATION TIME OF BULK SOIL AND PARTICLE SIZE FRACTIONS

	Unburnt		Burnt	
Sample	Median	Range	Median	Range
Bulk	116	28	236	96
1–2 mm	1766	2257	247	252
0.5–1 mm	432	792	144	105
0.25–0.5 mm	104	66	65	48
0.1–0.25 mm	134	53	117	34
0.05–0.1 mm	233	57	549	118
<0.05	1366	364	783	396

N = 5

WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

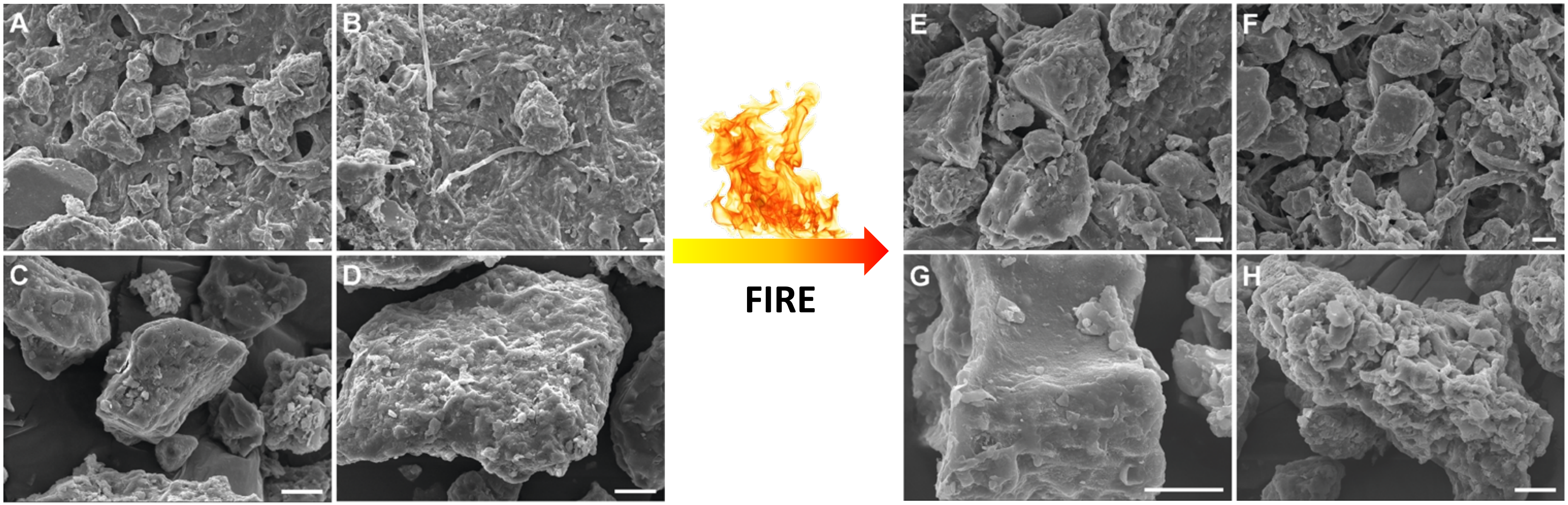
RELATION BETWEEN TOTAL ORGANIC CARBON (TOC) AND WATER REPELLENCY (WDPT)



WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

FESEM IMAGES OF UNBURNT (A–D) AND BURNT (E–H) SOIL SAMPLES

UNBURNT **BURNT**



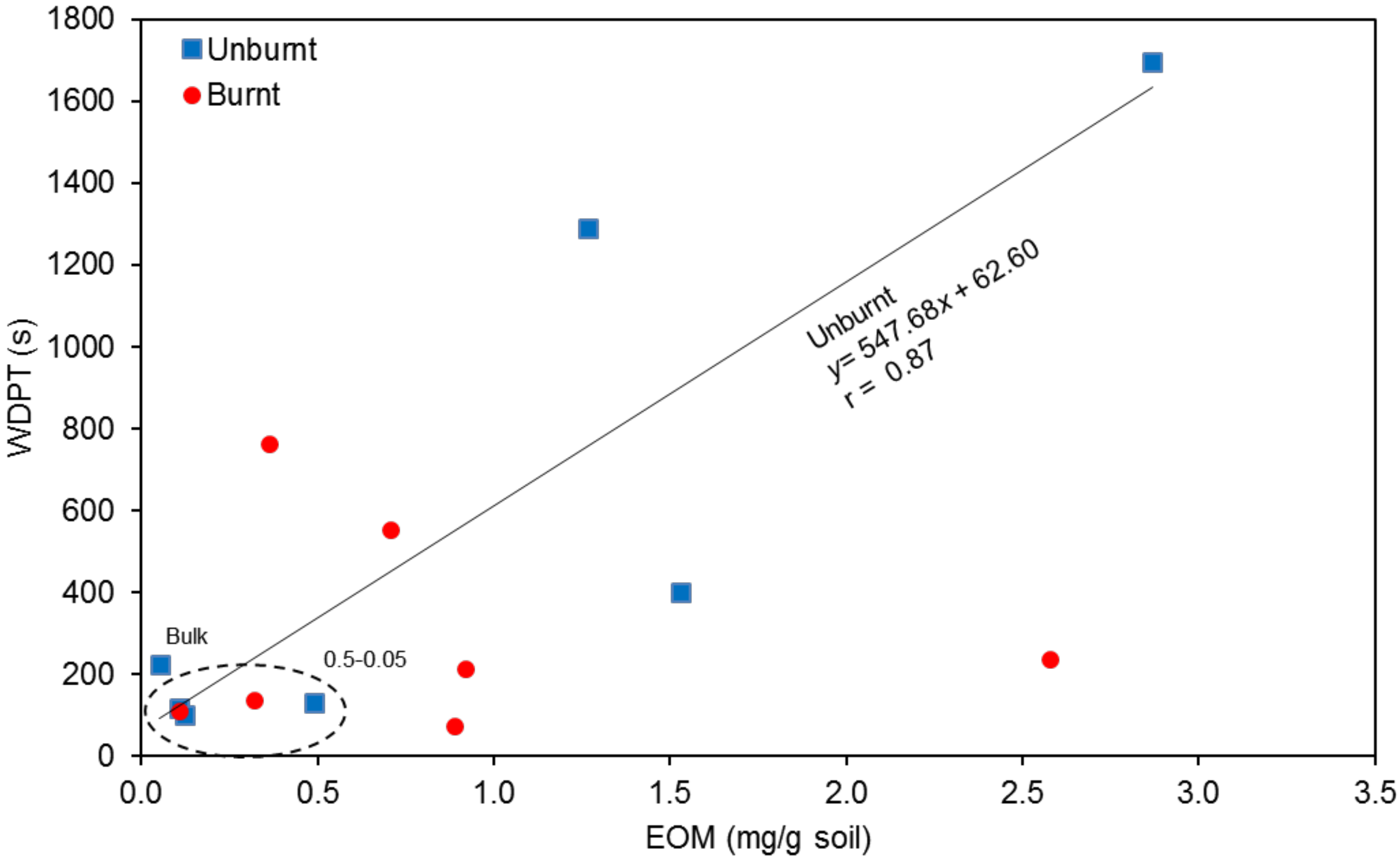
A-B → COARSE FRACTION
C-D → FINE FRACTION

E-F→ COARSE FRACTION
G-H → FINE FRACTION

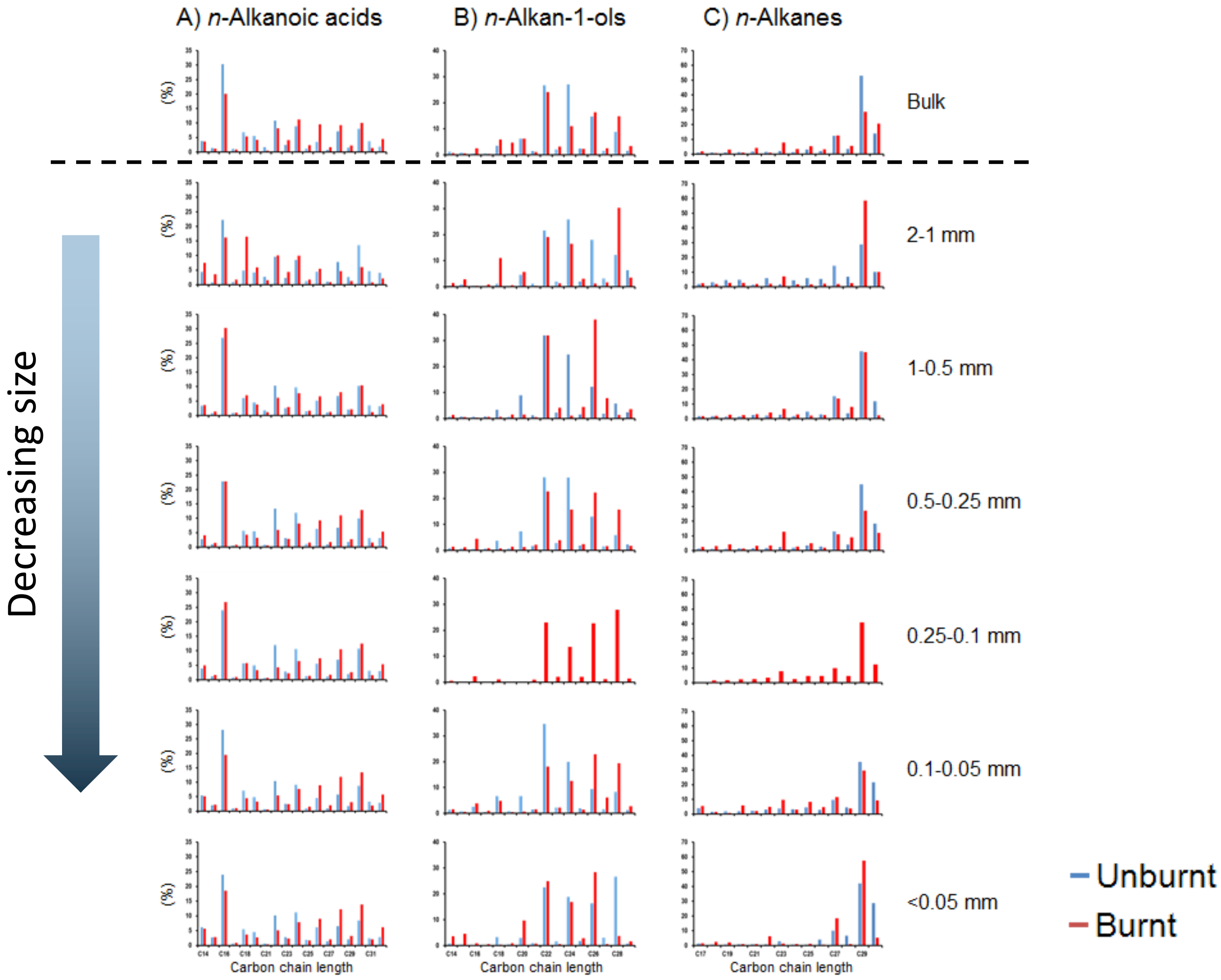
SCALE BARS ≈ 10 µm

WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

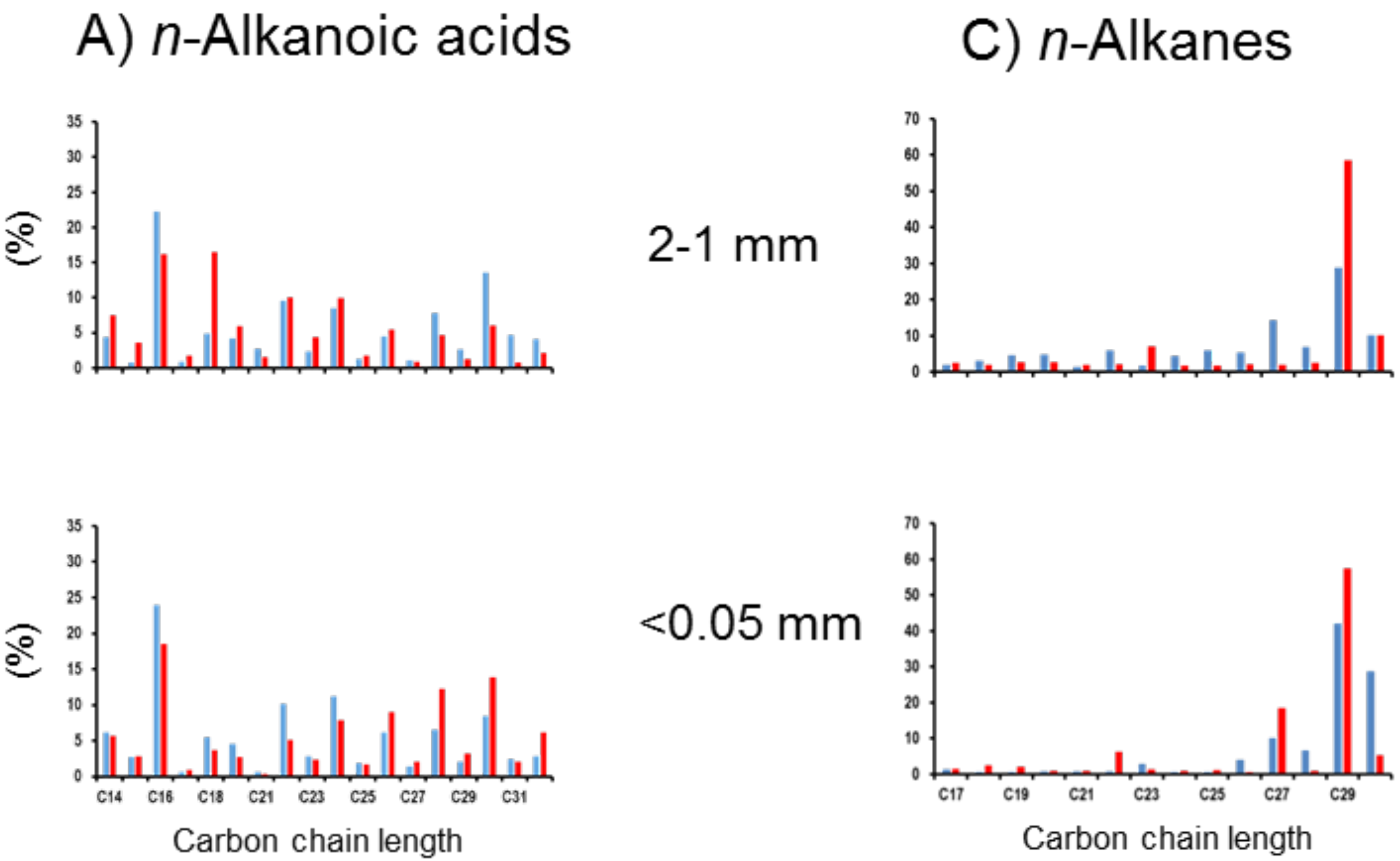
RELATIONSHIP BETWEEN EXTRACTABLE ORGANIC MATTER (EOM) AND WATER REPELLENCY (WDPT)



WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY



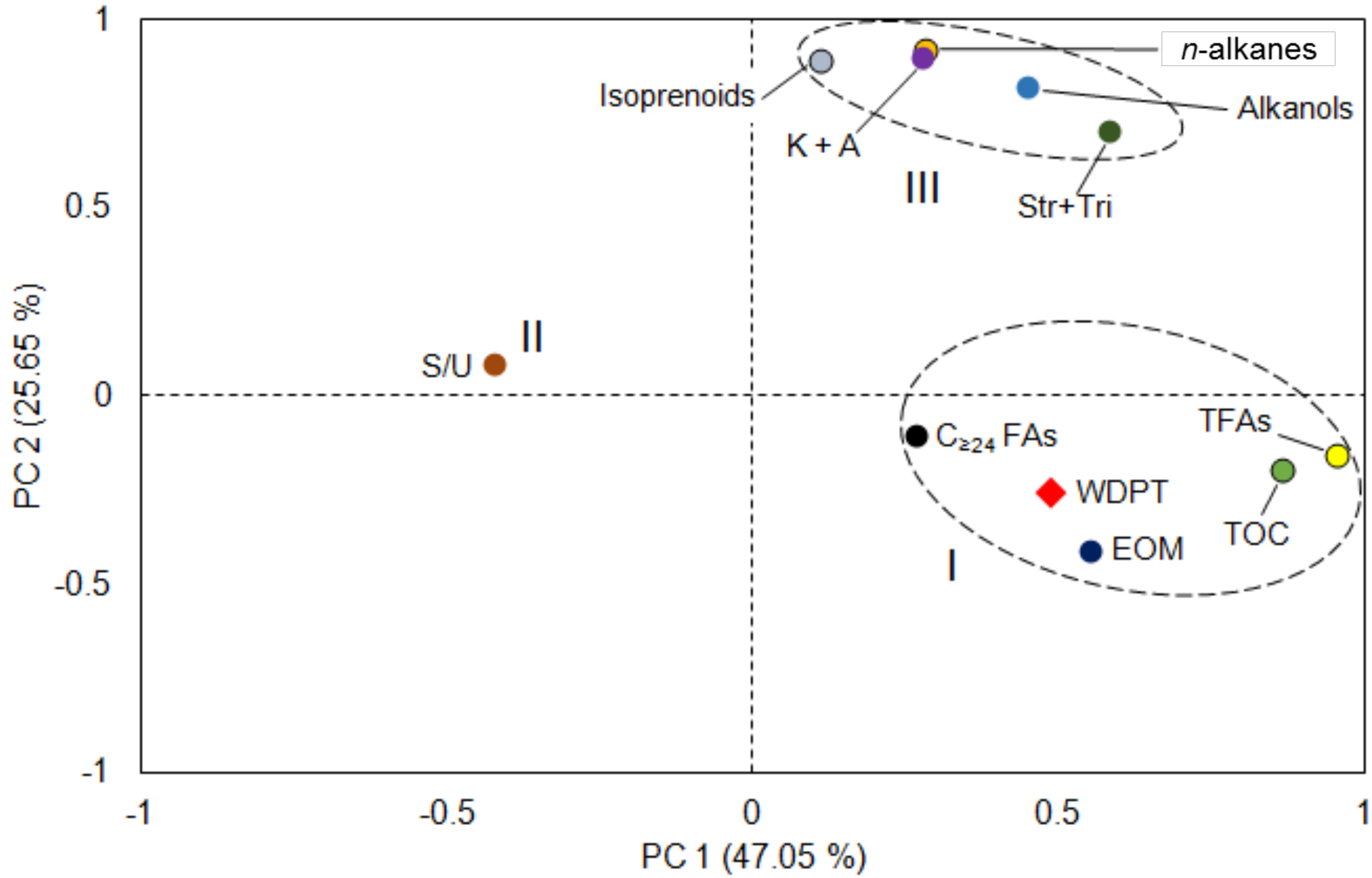
WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY



WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

PRINCIPAL COMPONENT ANALYSIS

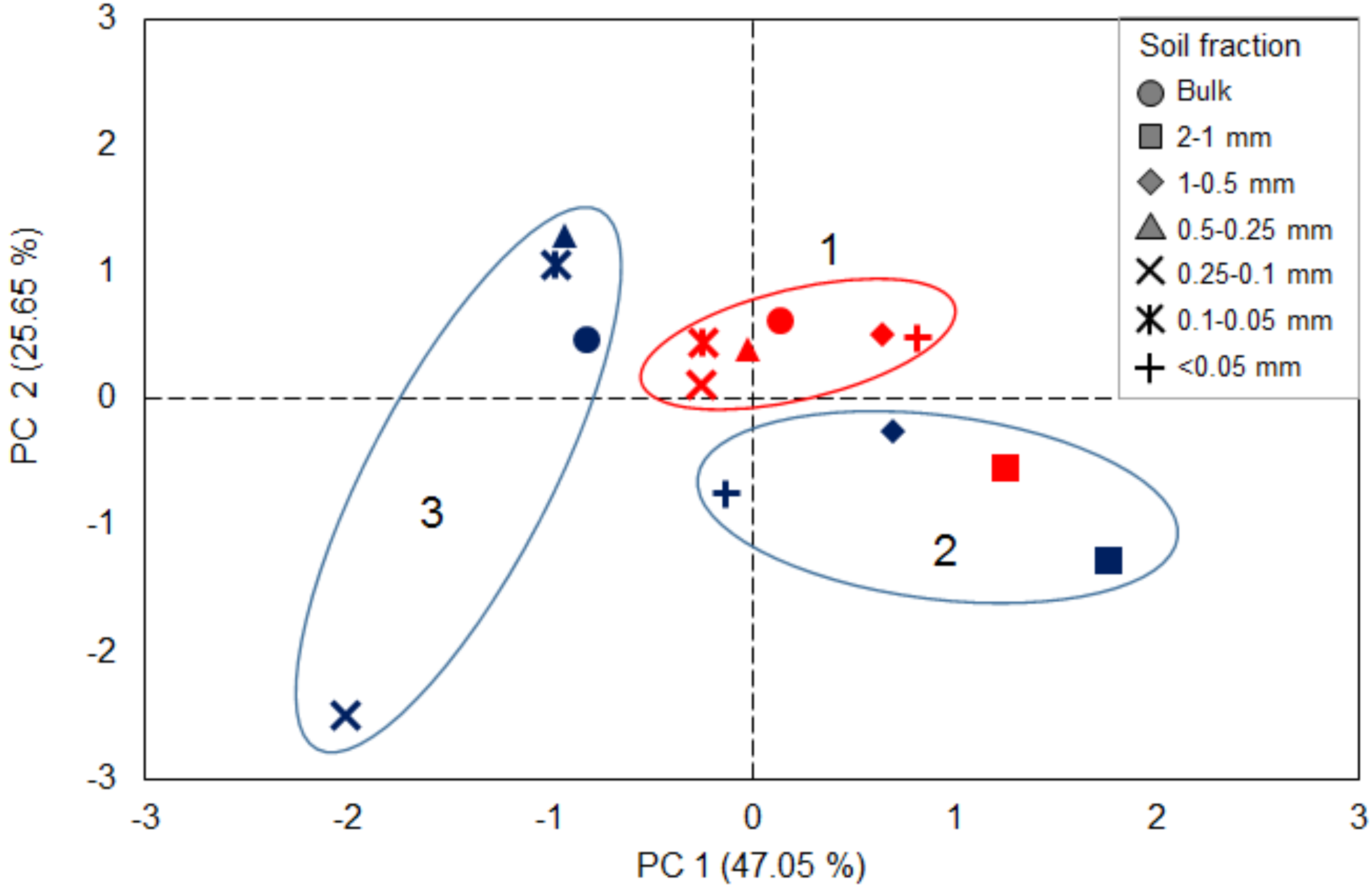
VARIABLE LOADINGS



WILDFIRE EFFECTS ON LIPID COMPOSITION AND HYDROPHOBICITY

PRINCIPAL COMPONENT ANALYSIS

SCORES OF SOIL SAMPLES AND SIZE FRACTIONS



SUMMARY OF ACHIEVEMENTS

SUMMARY OF ACHIEVEMENTS

- The assessment of soil organic matter status pointed out the existence of two well-differentiated organic carbon pools, dependent on size fractions:

  I. Coarse fractions showed an organic matter “fresh”, coming from standing vegetation.

  II. Fine fractions showed an organic matter highly evolved (humified), because of an apparently intense microbial activity (reworking)

- The existence of two pools conditioned the fire effects in soils, by the chemical alteration of own SOM and/or by an input of exogenous charred material.

- Soil water repellency depends upon standing vegetation, as well as, SOM quantity and quality. It is worth highlighting the fact that long-chain *n*-alkanoic acids may be considered as biomarkers surrogates to water repellency in sandy soils.

POST-FIRE EROSION RISK ASSESSMENT USING MOLECULAR MARKERS (EROFIRE)

EROFIRE

The main goals of the EROFIRE project are:

i) establishing a post-fire performance model based on the risk of soil and organic matter properties to assess the risk of soil loss.

ii) the development of a tool that allows monitoring the recovery of the soil.

To accomplish this, it will require:

- the identification and characterization of erodibility and the erosion mechanisms after fire.
- the identification of molecular markers subrogates to soil erodibility.
- the establishment of relations between fire behavior and soil parameters

Thanks for your attention


YO
SUELO