Manuscript Number: JEMA-D-18-02718

Title: Pyrogenic organic matter from palaeo-fires during the Holocene: A case study in a sequence of buried soils at the Central Ebro Basin (NE Spain)

Article Type: VSI:Fire in the Environment

Keywords: buried soils, fire record, charcoal, pyrogenic carbon, soil lipids, analytical pyrolysis

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Pyrogenic organic matter from paleo-fires during the Holocene: A case study in a sequence of buried soils at the Central Ebro Basin (NE Spain).

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Abstract

We studied the fire record and its environmental consequences during the Holocene in the Central Ebro Basin. This region is very sensitive to environmental changes due to its semiarid conditions, lithological features and a continuous human presence during the past 6000 years. The study area is a 6 m buried sequence of polycyclic soils developed approximately 9500 years ago that is exceptionally well preserved and encompasses four sedimentary units. The content and size distribution of macroscopic charcoal fragments were determined throughout the soil sequence and the analysis of the composition of charcoal, litter and sediments via analytical pyrolysis (Py-GC/MS). The high amount of charcoal fragments recovered in most horizons highlights the fire frequencies since the beginning of the Neolithic, most of which were probably of anthropogenic origin. In some soil horizons where charcoal was not found, we detected a distribution pattern of lipid compounds that could be related to biomass burning. On the other hand, the low number of pyrolysates in the charcoal could be attributed to high-intensity fires. No clear pattern was found in the composition of pyrolysates related to the age of sediments or vegetation type. The most ancient soil (Unit 1) was the richest in charcoal content and contains a higher proportion of larger fragments (> 4 mm), which is consistent with the burning of a relatively dense vegetation cover. This buried soil has been preserved *in situ*, probably due to the accumulation of sedimentary materials because of a high-intensity fire. In addition, the pyrogenic C in this soil has some plant markers that could indicate a low degree of transformation. In Units 2-4, both the amount of charcoals and the proportions of macrofragments > 4 mm are lower than those in Unit 1, which coincides with a more open forest and the presence of shrubs and herbs. The preservation of this site is important to continuing with studies that contribute to a better assessment of the consequences of future disturbances, such as landscape transformation and climate change.

Key words: buried soils, fire record, charcoal, pyrogenic carbon, soil lipids, analytical pyrolysis

Dear Editors:

Please find enclosed the article entitled “Pyrogenic organic matter from paleo-fires during the Holocene: A case study in a sequence of buried soils at the Central Ebro Basin (NE Spain)”, by C.M. Armas-Herrera et al. We would like it to be considered for publication in the Journal of Environmental Management. We certify that the submission is original work and is not under review at any other publication.

We carried out a work in an archaeological site located at La Poza Valley (Central Ebro Basin, NE Spain) where we studied a 6 m thick sequence of polycyclic soils, from the point of view of the fire record. This site has been recently subjected to an interdisciplinary study that included geomorphology and pedology, combined with an anthracological study, palynological studies and radiocarbon dating (Pérez-Lambán et al., 2018). This new paper provides new data on the paleoenvironmental history of La Poza valley, through the analysis of the composition of charcoal, litter and sediments via analytical pyrolysis (Py-GC/MS).

We hope that the editorial board and the reviewers will agree on the interest of our findings. Thank you for your time and consideration.

Sincerely,

Cecilia M. Armas-Herrera

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Highlights

PyC is studied in a sequence of buried soils covering most of the Holocene in the CEB

The abundance of charcoal fragments highlights the fire frequency, which are mostly human-induced

In some charcoal-free horizons, we found a pattern of lipids typical of burnt soils

The low number of pyrolysates of charcoal could be related to high-intensity fires

The presence of plant markers in the most ancient soils indicates PyC preservation

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1. Introduction

Fire-derived organic matter (also known as char, black carbon or pyrogenic carbon) is the result of the incomplete combustion of plant biomass and litter, from poorly thermally altered plant residues to highly condensed polycyclic aromatic materials (Hammes et al., 2007; Masiello, 2004; Poot et al., 2009). Pyrogenic C (PyC) generally has a longer mean residence time in the environment than its non-charred precursors, and is often considered a C sink that can favour long-term C sequestration at a centennial-millennial scale (Forbes et al., 2006; Santin et al., 2016). However, PyC is not an inert fraction because it can be decomposed in soil depending on its chemical composition and the existence of favourable conditions for microorganisms in the soil environment (Bird et al., 2015; Knicker, 2011).

Charcoal is a major component of PyC and is defined as the solid combustion residue derived from vegetation fires that retains a recognizable structure of the source plant (Forbes et al., 2006; Knicker, 2011). Charcoal is abundant in ancient sediments, and its analysis can thus provide information about fire history at a geological scale. This can be also used as a palaeoenvironmental source of information (Conedera et al., 2009; Knicker, 2011), including for the reconstruction of past vegetation (Figueiral and Mosbrugger, 2000) as well as for radiocarbon dating (Bird and Ascough, 2012). The pattern of lipid distribution in soils has also been used to detect soils affected by fires in geological times, especially when fire does not produce large amounts of charcoal (Eckmeier and Wiesenberg, 2009), e.g., in the case of non-woody vegetation fires (Figueiral and Mosbrugger, 2000). Soil lipids, which derive mainly from plants and microorganisms, are progressively degraded once incorporated into the soil, being reduced to a recalcitrant fraction that tends to be preserved in sediments and soils (Kolattukudy et al., 1976). These compounds are thus useful markers of biomass burning and could also be used to reconstruct the fire history of an area (Eckmeier and Wiesenberg, 2009; González-Pérez et al., 2008).

There are many studies about changes in climate, vegetation and human activities during the Holocene, including those concerning the impacts of fire on soils and the landscape (Carcaillet et al., 2002; Conedera et al., 2009; Kaal et al., 2008b; Wang et al., 2005), and sediment dynamics (erosion and deposition) (Bellin et al., 2013; Constante et al., 2010; Fuchs, 2007; Gerlach et al., 2012). Buried soils, including palaeosols and sediments, constitute an important archive of information on past human activities, not only from an archaeological point of view but also about agriculture, deforestation, biomass burning and other activities related to land management (Pietsch and Kühn, 2017).

The Mediterranean area is considered one of the European regions most affected by land degradation processes, mainly due to its arid-semiarid climate (Thornes and Wainwright, 2003). However, there have been few studies on the palaeosols and polycyclic soils in the semiarid Mediterranean areas of Europe. This is mainly because these soils are usually marginally developed and because they are rarely preserved due to the scarce vegetation cover and high erosion rates (Badía-Villas et al., 2013). The Central Ebro Basin (CEB) is a 'hot spot' for environmental changes that encompasses large amounts of sedimentary deposits from climatic oscillations in the Quaternary (Sancho et al., 2011). Therefore, this region is of interest from the point of view of palaeoenvironmental studies, where desertification is an important current issue.

This study aims to broaden our current knowledge about the impacts of fires during the Holocene exerted on soils in the CEB. In this region, La Poza Valley houses a 6 m buried sequence of polycyclic soils with signs of having been affected by frequent fires during the Holocene. This slope deposit likely began to form before 9.5 ky cal BP. Given the lithological and climatic characteristics of the CEB, the preservation of this palaeosoil is considered exceptional. This site was recently subjected to an interdisciplinary study that included geomorphology and pedology analyses, which were combined with an anthracological and palynological studies and radiocarbon dating (Pérez-Lambán et al., 2018). The main goal of that work was to interpret the palaeoenvironmental evolution of La Poza Valley during the Holocene. Our present paper provides new data on the palaeoenvironmental history of La Poza Valley from the point of view of the fire record. To do that, we use analytical pyrolysis (Py-GC/MS) as a powerful and rapid method for characterising complex organic matrices, such as PyC (González-Pérez et al., 2014), to better understand the fire conditions at this site during the Holocene. To the best of our knowledge, such a combination of techniques has rarely been applied in palaeoenvironmental contexts in the Mediterranean area. The specific objectives of this study are to (i) study the palaeofire conditions in La Poza Valley through the analysis of the content, size distribution and pyrolysis-GC/MS of charcoal fragments; (ii) analyse the distribution pattern of soil lipids to detect soils affected by fire; and (iii) assess the information gathered by the Py-GC/MS of charcoal and sediments in terms of long-term C stabilization.

2. Materials and methods

2.1. Site description and sampling

The study area is located in La Poza Valley in the CEB (NE Spain; ETRS89 UTM zone 30: X: 665746; Y: 4591561). This site is an ephemeral stream that is 7.3 km long and is found in the basin of the Huerva River, one of the main tributaries of the Ebro River. The CEB is one of the driest inland regions in Europe, with a mean annual precipitation and potential evapotranspiration of 400 and 1200 mm, respectively. In the upper course of the valley, we described and analysed a 6 m thick profile consisting of four sedimentary units and a sequence of six polycyclic soils (Figure 1). This sedimentary infilling covers the first two Holocene infill levels (H1 and H2) described for the CEB by Peña-Monné et al. (2018) and dated from 9.5 to 0.4 ky cal BP. We recognised a total of 18 layers from top to bottom (E1-E18) according to their physical properties and pedogenic processes. A detailed field description of all layers and the main physico-chemical soil properties can be found in Pérez-Lambán et al. (2018).

Unit 1 is formed by a soil developed on gypsum and marls located at the base of the profile that includes layers E13 to E18, representing a period of ca. 2.5 ky (from 9.5 to 7 ky cal BP).

This soil is classified as a Calcic Gypsisol (A-ABkc-Bwk-By-BCy-Cy-R) (R = Gypsum rock) and is the best-developed soil of the sequence. This soil shows a high degree of weathering and pedogenesis with some colluvium contributions, which well fits the moister conditions prevalent at the time of soil formation (Early-Middle Holocene) and very little vegetation disturbance by human activities. The soil in Unit 1 was affected by a fire that burnt a large mass of wood fuel. Charcoal fragments found in deeper soil horizons are probably the result of vertical movements through soil cracks and macropores. Anthracological identification of charcoal revealed a vegetation dominated by *Juniperus* and, to a lesser extent, by *Pinus halepensis* and some herbs and shrubs (*Fabaceae* and *Rosaceae*/*Maloideae*), with a small contribution of an evergreen *Quercus*.

Unit 2 is a fluvial accumulation dated from 7 to 6.7 ky cal BP (E9–E12) that began after the fire event located at the top of Unit 1 and buried the burnt Calcic Gypsisol. At this time, an increase in aridity and anthropogenic pressure on the plant cover accelerated the sedimentary processes in this area. The soil is a Fluvisol with a poor A-horizon (E9) above three unstructured C-horizons (E10–E12). In E9, a fire episode burnt the vegetation growing in the area, an open forest of junipers with isolated pines and some shrubs according to the anthracological analysis. The fragments of charcoal found in E11 and E12 were probably transported from the surface of Unit 1.

Unit 3 is formed by two layers of sediments (E7–E8) that started to accumulate just after the fire in E9, which rapidly buried and preserved the burnt Fluvisol. The soil is classified as a Haplic Gypsisol, with only two horizons (Bwy–Cy) due to the loss of the A-horizon by erosion of its upper part. Both the ^{14}C dates (9.5 and 7.7 ky cal BP) and the anthracological identifications in the E7 and E8 samples (*Juniperus* sp., *Fabaceae* and *Cistus*) indicate a chronological inversion (*Fabaceae* and *Cistus* are only present here and in Unit 1), i.e., Unit 3 was mainly formed by materials inherited from the slope erosion of Unit 1.

Unit 4 (E1–E6 layers) consists of the superimposition of three soils that are classified as Calcaric Regosols. The first subunit (dated in 0.93 ky cal BP) is a soil with two A-horizons (E5–E6) with almost identical soil properties and affected by cumulisation, i.e., a continued input of sediments combined with soil structuration processes and with a herbaceous plant cover. The second subunit (E3–E4) is a better developed Calcaric Regosol, formed by the sequence A–Bw and dated to 0.53–0.39 ky cal BP. The anthracological analysis revealed a plant composition similar to the current one dominated by *Juniperus*, *Pinus*, *Rosmarinus officinalis* and *Rhamnus*/*Phillyrea*. Finally, the third subunit (E1–E2) represents the current soil (under cultivation) formed by two horizons (Ah–AC) that originated with a new sedimentary input.

Soil samples were selected along the profile to study their compositions by pyrolysis-GC/MS. Specifically, we analysed the plant litter (E0), some A-horizons due to their relatively high OM contents (E3, E5, E6, E9, E13) and some B and C-horizons (E7, E8, E11) as a control for soils with low OM contents. In addition, we analysed charcoal fragments from the E3–E4, E6, E9, E12 and E13 soils. The choice of these samples was based on their potential diagnostic characters in the profile and representation of key periods of land use and climate. Macroscopic charcoal fragments (1-2, 2-4, and > 4 mm) were recovered from each layer by wet sieving.

2.2. Pyrolysis-GC/MS analysis

The pyrolysis of litter, soil, and charcoal was performed using a Double-Shot Pyrolyser (Frontier Lab Ltd., Fukushima, Japan, model 2020iD) attached to a GC–MS system (Agilent 6890N). Samples were introduced into a pre-heated micro-oven and heated at a temperature of 500°C (soil and litter) or 600°C (charcoal) for 1 min. In all samples, the evolved gases were directly injected into the GC–MS system. The GC instrument was equipped with a capillary column DB1701 (30 m, 0.25 mm i.d., 0.25 µm film thickness). The oven temperature was programmed to increase from 50°C (1 min) to 100°C at 30°C min^{-1} and 100 °C to 300°C at 10°C min^{-1} and remain at 300°C for 10 min. The carrier gas was helium at a controlled flow of 1 ml min^{-1}. The detector was an Agilent 5973 mass selective detector, and the mass spectra were acquired with 70 eV of ionising energy. The pyrolysis compounds were identified by ion chromatography for different homologous series, low resolution mass spectrometry and comparison of the spectra with published and stored data (Wiley and NIST libraries). The estimated areas of the peaks of the different pyrolysis products were calculated as the relative abundances to the total chromatographic area, considering that the sum of all peak areas corresponded to 100% of the total area of the ion chromatogram (TIC).

3. Results and discussion

3.1. Charcoal accumulation in soil

The total content of charcoal and its size fractions (1-2, 2-4, and > 4 mm) in soil and sediments are shown in Figure 2. The highest charcoal content was found in E13 (723 mg/kg), and in general, the contents were very high in E11, E12, E14 and E15 (average 164 mg/kg), corresponding to sedimentary units 1 and 2. The charcoal content values were intermediate in E3 and E9 (96 and 92 mg/kg, respectively) and lower in the rest, especially in E6 and E17 (5 and 2 mg/kg, respectively). We did not find charcoal fragments in E1, E2, E5, E10 or E18. Regarding the charcoal size distribution, we found relatively homogenous sizes in the layers with the presence of charcoal from Units 1 and 2 (E12–E16), whereas in layers E1-E11 (Units 2, 3, and 4), the recovered charcoal fragments were generally smaller, with little presence of fragments > 4 mm. The charcoal abundance in the profile can be considered as an indicator of frequent fires in the area (Carrión et al., 2010). However, the accumulation of charcoal in itself does not necessarily imply a more intense fire, and in fact, a low charcoal accumulation has been attributed to very intense fires that have produced a more intense volatilization of plant material (Bodí et al., 2014; Knicker et al., 2006; Mastrolonardo et al., 2017). Thus, the greater or lesser the abundance of charcoal does not seem to be a good indicator of fire intensity, although it may give an idea of the amount of woody biomass that was burnt. In addition, the burning of non-woody vegetation does not usually survive the process of charcoal formation (Figueiral and Mosbrugger, 2000). In this way, it is most likely that the charcoal macrofragments recovered from the soil come from the remains of woody vegetation (Gerlach et al., 2012; Kaal et al., 2008a; Nocentini et al., 2010). Thus, the higher proportions of charcoal > 4 mm found in the oldest sediment layers (E12–E16) are in agreement with the abundant burnt plant biomass, mainly *Juniperus* and *Pinus*, as indicated by the anthracological and palynological analysis (Pérez-Lambán et al., 2018). On the other hand, the smaller sizes of the charcoal fragments (1-2 and 2-4 mm) could be related to a more open forest with a higher presence of shrubs and herbs in Units 2, 3, and 4.

3.2. Charcoal pyrolysis

The composition of charcoal in all samples was completely aromatic, producing pyrolisates dominated by benzenes and polyaromatic hydrocarbons (PAHs). Eight main compounds were identified: 1-ring homocyclic aromatics (benzene, toluene, and styrene), polyaromatic hydrocarbons (PAHs) (naphthalene, biphenyl and phenanthrene/anthracene), and O-substituted heterocyclic aromatics (benzofuran and dibenzofuran), all of which are considered products of charred biomass (González-Pérez et al., 2014; Kaal and Rumpel, 2009). Benzene and toluene are the principal products of pyrolysis present in PyC, particularly with both increasing charring intensity and pyrolysis temperatures (Braadbaart et al., 2004; Kaal and Rumpel, 2009). The PAHs can be used as markers to identify fire-affected soils, the combustion of organic matter being the main source of PAHs in the environment (Denis et al., 2012; González-Pérez et al., 2014). Phenanthrene/anthracene can be formed from both organic matter combustion and diagenetic processes (Jiang et al., 1998), probably from terpenoids (Wakeham et al., 1980), and naphthalene can also be produced from polysaccharide rearrangements at high temperatures (Kaal et al., 2009). Benzofurans are heterocyclic compounds originating from incompletely charred lignocellulosic materials (González-Pérez et al., 2014).

We did not identify compounds derived from lipids, carbohydrates, lignins or proteins, as described in the literature by many authors (Kaal et al., 2008a; Kaal and Rumpel, 2009). Because of its aromatic nature, the charcoal analysed here might be considered as highly recalcitrant, which indicates that the impact of fires documented in this study was probably high. It is well known that the degradability of charcoal is directly related to the charring temperature; therefore, it can show a large range of recalcitrance depending on the intensity and severity of the fire (González-Vila et al., 2004). In addition, the stability of PyC increases as pyrolysis temperatures rise and is related to a higher content of polycyclic aromatic C (Bird et al., 2015). The interpretation of any product of pyrolysis should be made with caution because of the possible loss of diagnostic chemical groups related to secondary rearrangements that could appear during the pyrolysis process. In this sense, a temperature of 600°C for charcoal samples is considered as optimal for obtaining a high-quality pyrogram (Kaal et al., 2009).

The composition was quite similar in all charcoal samples, showing only few differences in the intensity of some peaks between the different layers. The pattern in E4 and E12 was very similar, with the exception of the peak of naphthalene that shows a higher intensity in E4 than in E12; E6 and E9 also show a similar pattern in both composition and peak intensity. Finally, the charcoal analysed in E3 and E13 show different patterns compared to the other samples. E3 is the poorest in pyrolysates, where only benzene, toluene and naphthalene were detected, whereas E13 did not show the toluene peak. However, the anthracological analysis and ^{14}C dating show important differences between the charcoal samples regarding the age and plant composition (Figure 3). Thus, charcoal from E4 is much younger (0.53–0.39 ky cal BP) than charcoal recovered from E12 (7.0–6.7 ky cal BP), a C horizon from fluvic materials. In addition, the anthracological analysis in E4 reveals a vegetation dominated by *Juniperus*, *Phillyrea*/*Rhamnus* and *Rosmarinus officinalis*, very similar to the current vegetation in the area, whereas in E12, where charcoal fragments have been transported from Unit 1 (Pérez-Lambán et al., 2018), the vegetation is arboreal and dominated mainly by *Juniperus* with the presence of *Pinus halepensis*. E6 and E9 are also different regarding their age (ca. 0.93 and 6.7 ky cal BP, respectively) and vegetation type, which are dominated by shrubs/herbs in E6 and an open forest in E12. This seems to indicate that neither the age nor the type of vegetation affect the composition of charcoal under these fire conditions. These results coincide with those reported by Kaal et al. (2009), who found no difference in the composition of charcoal samples from different plant species. However, Kaal et al. (2009) reported a difference in the composition of charcoal with ageing and Kaal and Rumpel (2009) found that PyC is affected by degradation processes in the soil, particularly the less intensely charred biomass.

3.3. Soil pyrolysis

The total ion chromatograms (TIC) and alkane (m/z 57) traces obtained by the GC/MS analysis of the pyrolysates are presented in Figure 4. The m/z 57 traces represent the alkane series (C10–C33), which normally come from plant waxes. In the soil litter (E0), the pyrogram shows the presence of plant biomarker alkanes (C29, C31, C33) from the current vegetation, with a maximum peak in C29. The long-chain alkanes (> 25) with a predominance of odd carbon are typical of higher plants (Eglinton et al., 1962). Alkane series with a maximum at *n*-C29 have been related to both the incorporation of herbs and woody biomass (Van Bergen et al., 1997), while series with a maximum at the *n*-C31 alkane would indicate the incorporation of herbs or crops (Maffei, 1996). These results are in accord with the current vegetation of the area (E0, E1), dominated by herbs and barley. This vegetal sign also clearly appears in the current soil (E1), whereas it disappears in the underlying soil horizons. However, the reappearance of plant markers in the E13 horizon is remarkable. This is probably due to the preservation of this palaeosoil (Unit 1) and to a sudden change in the environmental conditions, such as the supply of sedimentary materials that accumulated by erosive processes shortly after the fire event recorded here. This accumulation of materials, which currently form the Unit 2 (E10–E12), could have produced an *in situ* preservation of organic matter in this palaeosoil. These results are in accord with those reported by (Marin-Spiotta et al., 2014), who also found a persistence of plant lipids in a buried soil (early Holocene) in Nebraska.

In contrast, short-chain compounds with a bimodal distribution were detected (C10, C12, C15), especially in the current E1 soil. Short-chain alkanes (< 21) are considered indicators of soil reworking and microbial activity, although they could also derive from the decay process of plant products and the breaking of longer-chain compounds (Dinel et al., 1990). These biomarkers are also found in the A horizons E3, E5 and E6, tend to disappear in E7 (Bwy horizon), and are not detected in E8 (Cy horizon), E9 (ash layer), or E11 (C horizon). Here again, the reappearance of microbial markers in the E13 horizon is noticeable, still showing a bimodal distribution, which supports the idea of the *in situ* preservation of this soil (Unit 1).

It is known that the thermal degradation of vegetation due to fire induces changes in the patterns of lipid distribution in the soil because high temperatures produce more intense and rapid transformations in organic compounds (Eckmeier and Wiesenberg, 2009; González-Vila et al., 2001). A typical pattern of lipid distribution in soils affected by fires is that of short-chain even carbon-numbered n-alkanes (Eckmeier and Wiesenberg, 2009; Gerlach et al., 2012; Tinoco et al., 2006; Wiesenberg et al., 2009), probably due to an incomplete combustion of non-woody biomass at temperatures ranging from 400 to 500°C. This pattern agrees with that observed in the horizons E3, E5, E6, and E7, although without the predominance of *n*-C16 or *n*-C18. These results are interesting, since we did not recover any charcoal fragments in E5 and they were almost absent in E6. Thus, it can be stated that this soil was also affected by fires, although no visible fragments of charcoal (> 1mm) were recovered.

3.4. Significance and implications of the study

In the late Holocene, the Central Ebro Valley was subjected to climatic fluctuations in combination with an intense human activity derived from the expansion of Neolithic societies.

This caused intense soil losses from the surrounding slopes, resulting in processes of accumulation and incision of the valleys (Constante et al., 2011). This was the case for La Poza Valley, due to the combination of an increase of human activity during the Neolithic and a climatic change towards conditions of increasing aridity, mainly in the formation of the sedimentary Unit 2 (Pérez-Lambán et al., 2018). This is consistent with the anthracological and palynological studies made in Central and Southern Europe that point to an intense deforestation of most of the continent around 6.0 ky cal BP by the Neolithic populations, probably due to slash-and-burn practices, which caused intense erosive processes and an accumulation of charcoal in soils and sediments (Knicker, 2011).

A series of human-induced fires could explain the large supply of materials that buried the soil of Unit 1. However, it is known that very little biomass burning occurred during the early and middle Holocene (11.0-3.0 ky cal BP) (Carcaillet et al., 2002). Thus, with the available data, we cannot confirm the fire origin in Unit 1, whereas the fires from Units 2, 3, and 4 are most likely human-induced. Soil organic matter subjected to a rapid burial process can be stabilized in the long term and contribute to the carbon sequestration at depth (Marin-Spiotta et al., 2014). Thus, it is generally considered that buried soils are oxygen-depleted environments, and therefore, the PyC transformations would be of little relevance (Knicker, 2011). However, ancient charcoal fragments can be altered by oxidation processes, especially under alkaline conditions, reducing the size of the charcoal fragments and even generating new compounds by ‘self-humification’ processes (Braadbaart et al., 2009; Cohen-Ofri et al., 2006). This could be the case for the site at La Poza, where the soil pH ranges from 7.9 to 8.3 (Pérez-Lambán et al., 2018). However, the presence of plant markers in the soil of Unit 1 seems to indicate that, at least in this case, the soil organic matter has remained relatively stable.

According to recent works on the subject, further investigations are needed to estimate the soil organic carbon stocks in buried soils, including PyC (Mastrolonardo et al., 2018). Currently, there is no estimation of the PyC pool in terrestrial sediments, and most of the studies on the stocks, fluxes, mean residence times and long-term fate of the PyC in the environment have focused on the PyC stored in the first 100 cm of soil but not that below this depth (Bird et al., 2015). In this sense, many reports indicate that the stability of soil organic matter depends not only on its chemical composition but also on the biological and environmental conditions (Knicker, 2011; Marin-Spiotta et al., 2014; Santin et al., 2016). Thus, if the processes that promoted this accumulation and protection are altered and the organic matter is again surface exposed, this C can be lost as soon as in a few decades (Chaopricha and Marín-Spiotta, 2014).

The site at La Poza Valley is considered of great importance in terms of a palaeoenvironmental source of information, which complements other studies carried out in nearby archaeological sites (Pérez-Lambán et al., 2018). To our best knowledge, this is the first work in the CEB that studied the fire record for such a lengthy period (old and recent Holocene phases). The preservation of this site is important for future studies that complement our knowledge about environmental processes in the semi-arid Mediterranean since the end of Mesolithic in relation to human activities and climate changes. This will undoubtedly contribute to better assessing the consequences of future disturbances.

4. Conclusions

The site at La Poza Valley, located in the semiarid Mediterranean region of the central Ebro Valley, is considered of great interest from a palaeoenvironmental point of view, since it houses a sequence of polycyclic soils that covers most of the Holocene, which is unique in the area. This site has been affected by frequent fires since the beginning of the Neolithic, as seems to be indicated by the large amount of charcoal macrofragments found throughout the soil sequence. In some horizons where no charcoal fragments were detected, the distribution pattern of lipid compounds could be related to the combustion of biomass. The available data do not allow confirmation of the type of fire in Unit 1, whereas the fires in Units 2-4 were most probably human-induced. The low number of pyrolysis products released in the analysis of charcoal could be attributed to high-intensity fires. The types of pyrolysates do not seem to follow any clear pattern, either related to the age of the sediments or the type of vegetation. The ancient buried soil of Unit 1 was preserved *in situ*, probably due to the input of materials because of a high-intensity fire that caused intense soil losses and the accumulation of sediments. The presence of plant markers seems to indicate that PyC has not undergone significant changes, so it could be considered as fossil PyC. The preservation of this site is important to continuing with studies that contribute to a better assessment of the consequences of future disturbances, such as landscape transformation and climate change.

Acknowledgements

This was supported by MINECO projects INTERCARBON (CGL2016-78937-R), FUEGONEO (CGL2016-76620-R), and Paisaje y Sociedad. El valle medio del Ebro entre el 6000 y el 500 cal ANE (HAR2015-65620-P).

Figure captions

Figure 1. General view of the polycyclic soil sequence of La Poza catchment

Figure 2. Charcoal content (mg kg^{-1}) and size distribution

Figure 3. Analysis of charcoal by analytical pyrolysis (Py-GC/MS)

Figure 4. Analysis of soil samples by analytical pyrolysis (Py-GC/MS)

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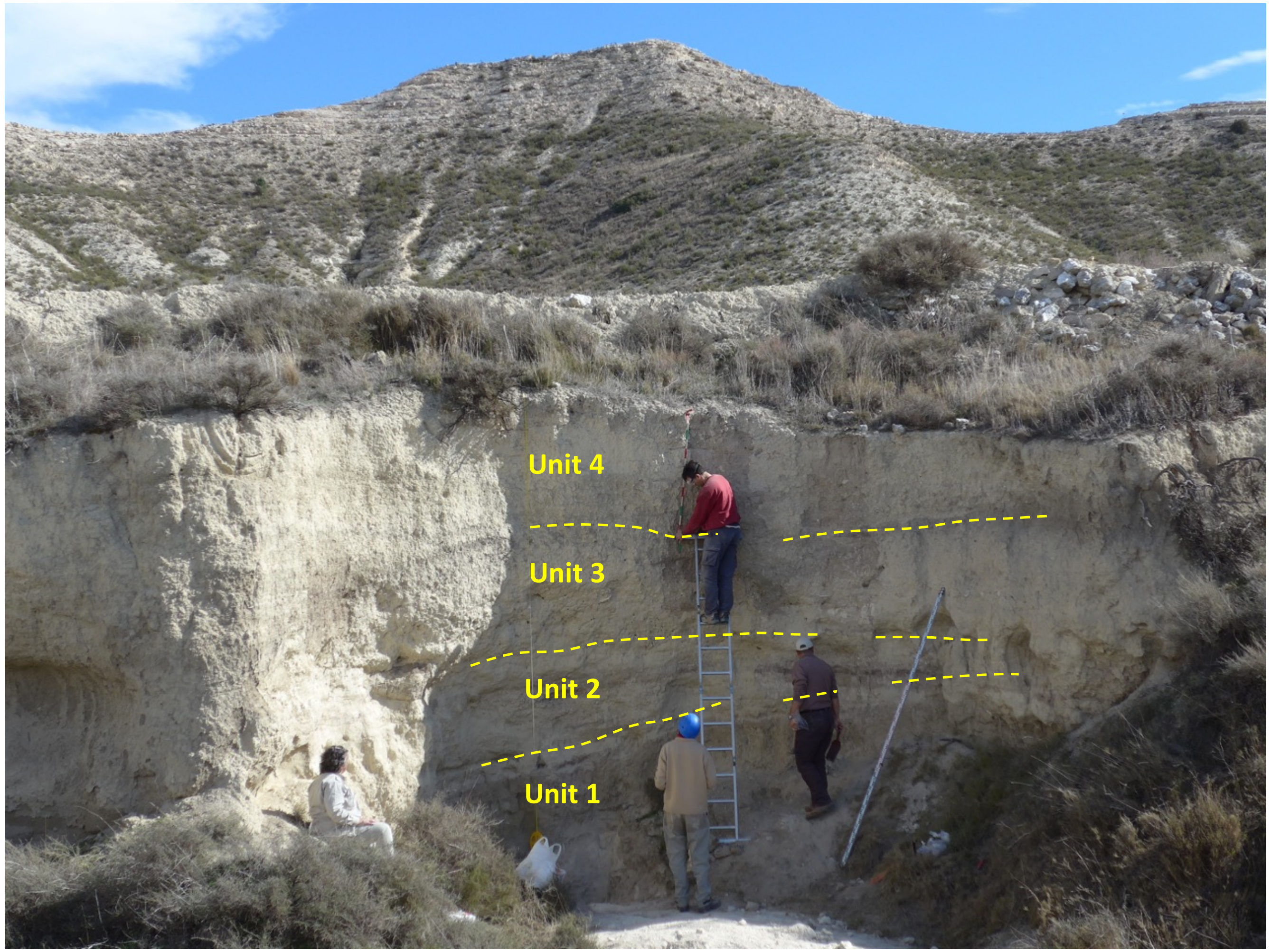
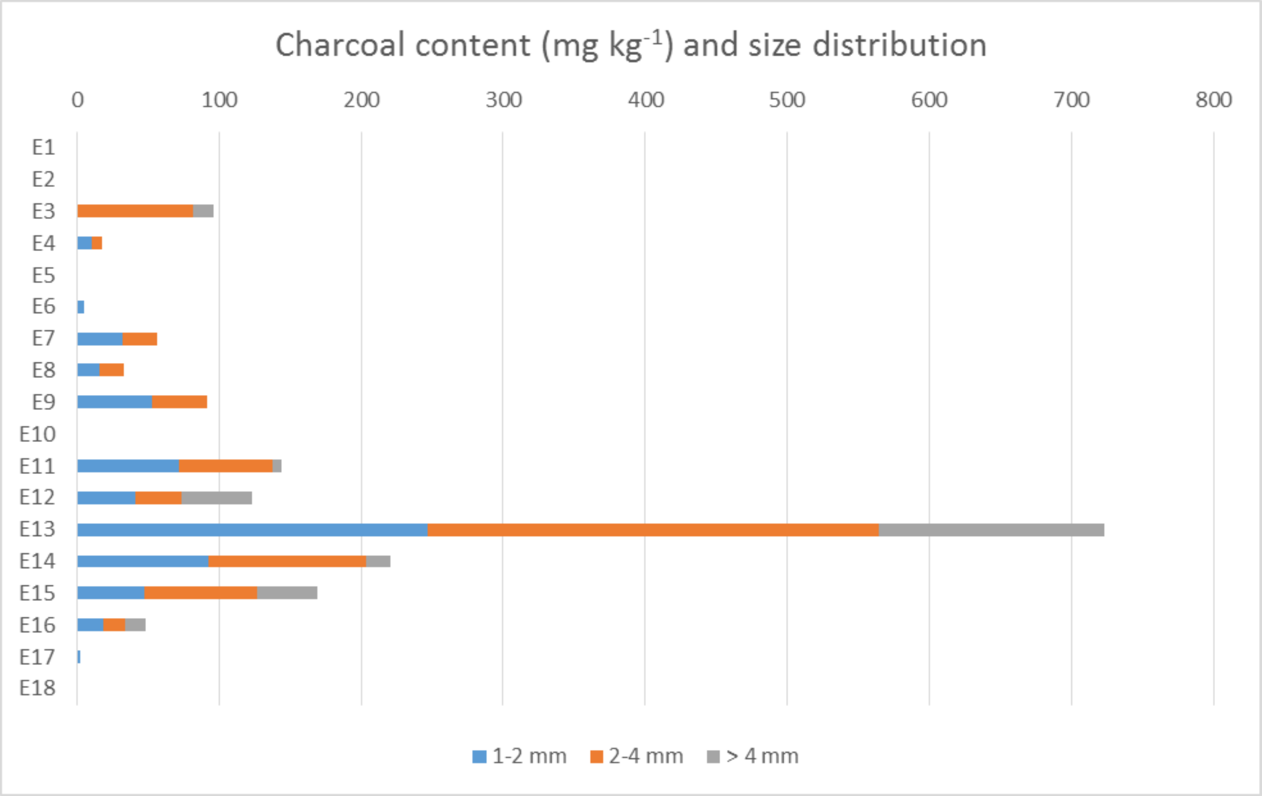


	Layer	Soil depth (cm)	Soil horizon	Soil classification (IUSS Working Group WRB, 2014)
Unit 4	E1	20	Ah	Calcaric Regosol
	E2	40	2A	
	E3	73	3A	Calcaric Regosol
	E4	109	3Bw	
	E5	160	4A1	Calcaric Regosol
	E6	185	4A2	
Unit 3	E7	217	5Bwy	Haplic Gypsisol
	E8	275	5Cy	
Unit 2	E9	285	6A	Fluvisol
	E10	309	7C	
	E11	337	8C	
	E12	367	9C	
Unit 1	E13	382	10A	Calcic Gypsisol
	E14	403	10ABkc	
	E15	432	10Bwk	
	E16	452	10By	
	E17	471	10BCy	
	E18	500	10Cy	


Charcoal content (mg kg^{-1}) and size distribution
0
100
200
300
400
500
600
700
800
E1
E2
E3
E4
E5
E6
E7
E8
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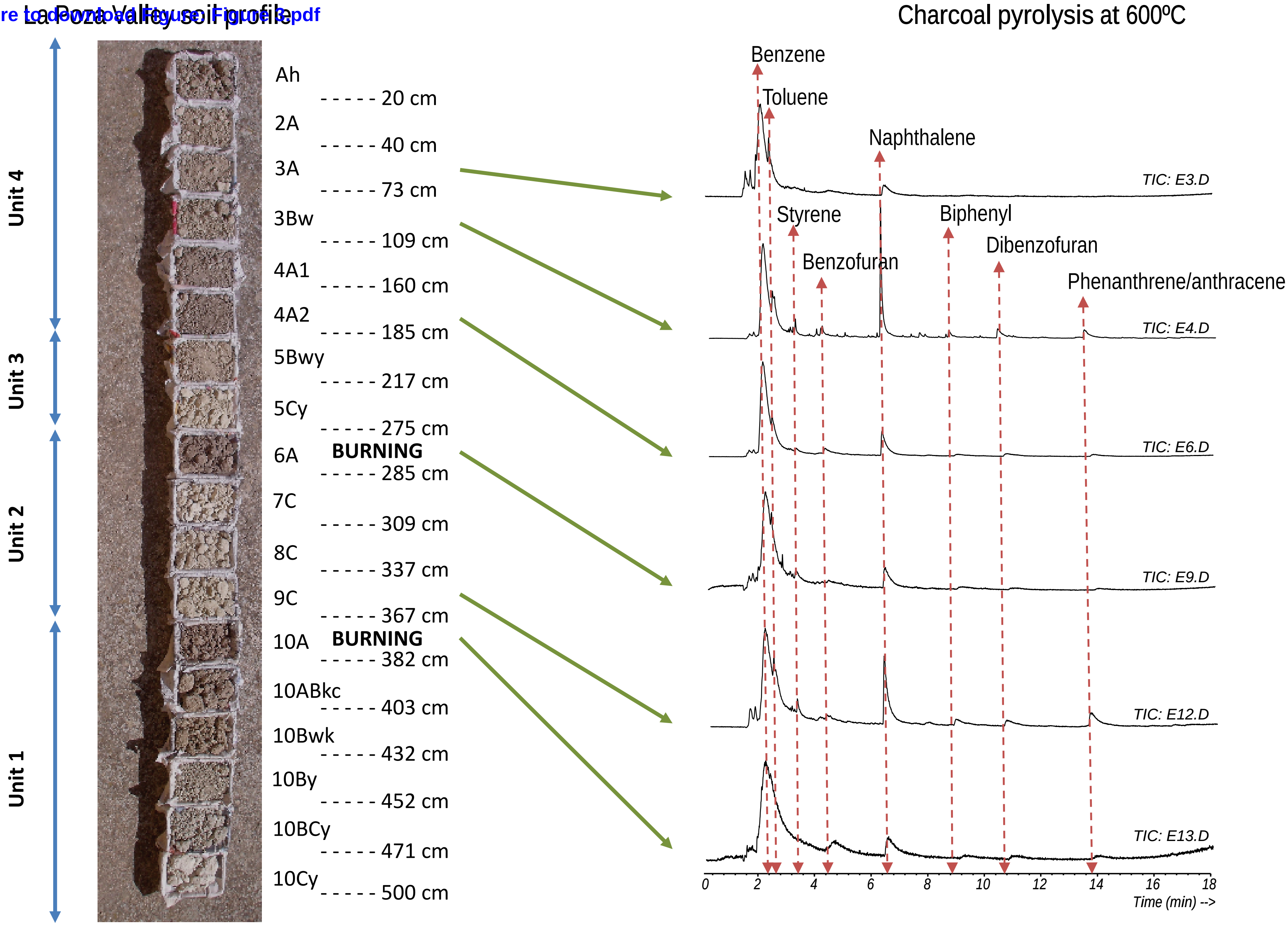
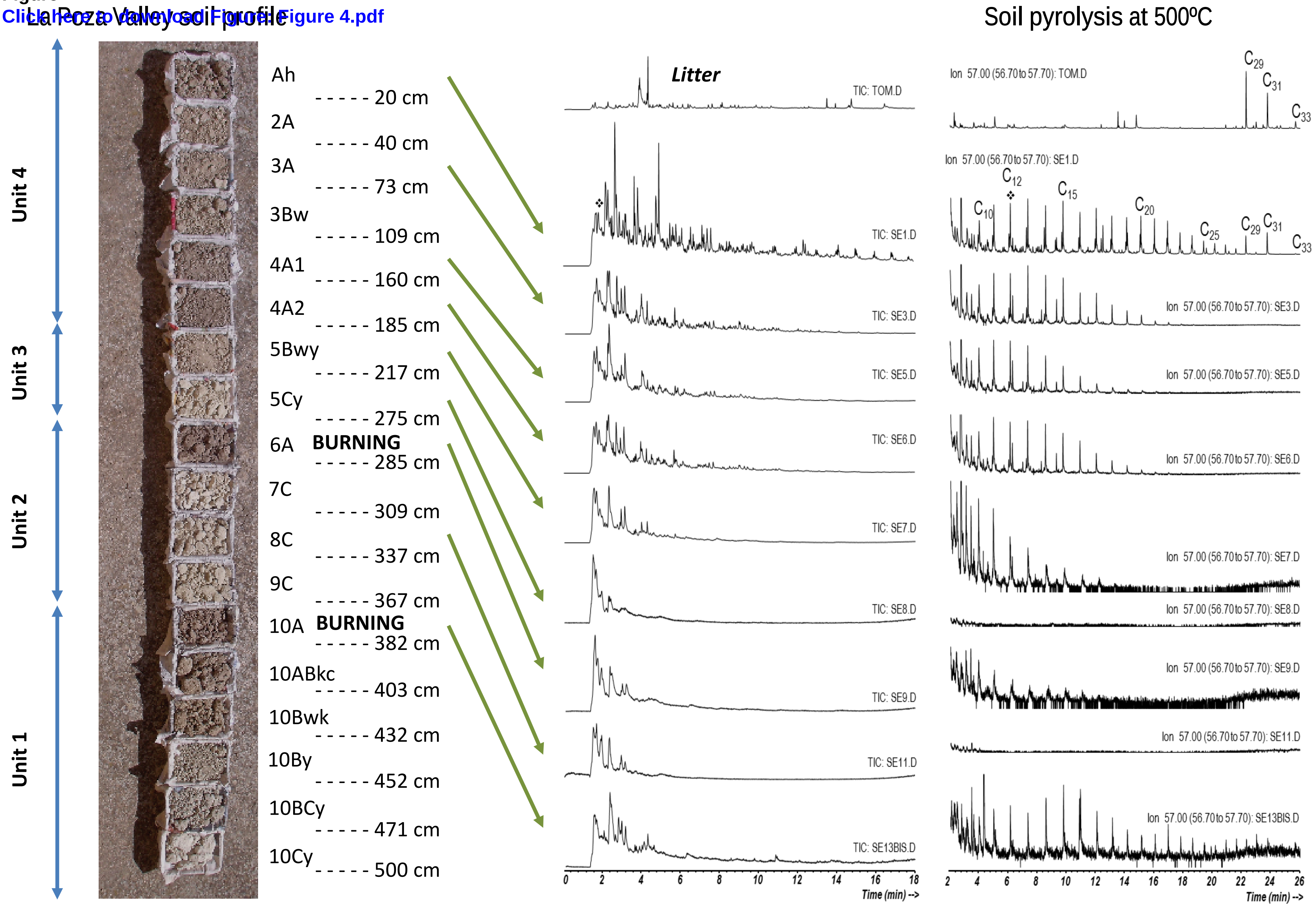
1-2 mm
2-4 mm
> 4 mm



La Poza Valley soil profile

Charcoal pyrolysis at 600ºC


La Poza Valley soil profile
Soil pyrolysis at 500ºC
Unit 4
Unit 3
Unit 2
Unit 1
Ah
- - - - - 20 cm
2A
- - - - - 40 cm
3A
- - - - - 73 cm
3Bw
- - - - - 109 cm
4A1
- - - - - 160 cm
4A2
- - - - - 185 cm
5Bwy
- - - - - 217 cm
5Cy
- - - - - 275 cm
6A BURNING
- - - - - 285 cm
7C
- - - - - 309 cm
8C
- - - - - 337 cm
9C
- - - - - 367 cm
10A BURNING
- - - - - 382 cm
10ABkc
- - - - - 403 cm
10Bwk
- - - - - 432 cm
10By
- - - - - 452 cm
10BCy
- - - - - 471 cm
10Cy
- - - - - 500 cm
Litter
TIC: TOM.D
TIC: SE1.D
TIC: SE3.D
TIC: SE5.D
TIC: SE6.D
TIC: SE7.D
TIC: SE8.D
TIC: SE9.D
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TIC: SE13BIS.D
0 2 4 6 8 10 12 14 16 18
Time (min) -->
Ion 57.00 (56.70 to 57.70): TOM.D
C_{29} C_{31} C_{33}
Ion 57.00 (56.70 to 57.70): SE1.D
C_{10} C_{12} C_{15} C_{20} C_{25} C_{29} C_{31} C_{33}
Ion 57.00 (56.70 to 57.70): SE3.D
Ion 57.00 (56.70 to 57.70): SE5.D
Ion 57.00 (56.70 to 57.70): SE6.D
Ion 57.00 (56.70 to 57.70): SE7.D
Ion 57.00 (56.70 to 57.70): SE8.D
Ion 57.00 (56.70 to 57.70): SE9.D
Ion 57.00 (56.70 to 57.70): SE11.D
Ion 57.00 (56.70 to 57.70): SE13BIS.D
2 4 6 8 10 12 14 16 18 20 22 24 26
Time (min) -->