1 **Molecular features of organic matter in anthropogenic earthen mounds, canals and lagoons**
2 **in the Pago Lindo archaeological complex (Tacuarembó, Uruguayan lowlands) are controlled**
3 **by pedogenetic processes and fire practices**

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5 **Joeri Kaal ***

6 ^a Instituto de Ciencias del Patrimonio (Incipit), Consejo Superior de Investigaciones Científicas
7 (CSIC), Santiago de Compostela, Spain. ^b Pyrolyscience, Santiago de Compostela, Spain

8
9 **Camila Gianotti**

10 Universidad de la República – Centro Universitario Regional del Este, Rocha, Uruguay

11
12 **Laura del Puerto**

13 Universidad de la República – Centro Universitario Regional del Este, Rocha, Uruguay

14
15 **Felipe Criado-Boado**

16 Instituto de Ciencias del Patrimonio (Incipit), Consejo Superior de Investigaciones Científicas
17 (CSIC), Santiago de Compostela, Spain

18
19 **Mercedes Rivas**

20 Universidad de la República – Facultad de Agronomía - Centro Universitario Regional del Este,
21 Rocha, Uruguay

22
23 * Corresponding autor (J. Kaal). Calle Vallehermoso 15, 28015 Madrid (Madrid), Spain. E-mail:
24 joeri@pyrolyscience.com

Abstract

The Pago Lindo site in the River Plate basin (Uruguay) is an important pre-hispanic mound settlement (ca. 3000–600 B.P.), of which the technologically and socially advanced nature have only recently been revealed. Different angles of pedogenetic and palaeo-ecological science are rapidly improving our understanding of the history of the site and the relationships between human activity and habitat alteration. Here we add to this progress by molecular characterization of soil organic matter (SOM) in anthropogenic earthen mounds, canals and lagoons from Pago Lindo, by pyrolysis-GC-MS. The results showed that the SOM in the earthen mound and the archaeological lagoon are composed of microbial (partially chitin), aliphatic (partially root-derived) and pyrogenic (from fireplaces or wildfires) materials, whereas the canal and younger lagoon contained SOM with larger proportions of relatively intact plant remains (lignin and polysaccharides from herbaceous species). In most systems, a clear degradation trend can be observed with increasing depth –either from intact plant remains to microbial tissues (canal, young lagoon), or from microbial tissues to recalcitrant aliphatic and pyrogenic sources (earthen mound, ancient lagoon)– which is indicative of a strong control of decay intensity on SOM composition. Multivariate statistics confirmed that most variability in pyrolysis fingerprints can be attributed to degradation/preservation dynamics, which probably erased most of the molecular information on habitat development under the influence of past societies, including nearby maize cultivation.

Keywords: South America; lowland archaeology; pyrolysis-GC-MS; earthen mounds; site formation processes: soil organic matter; degradation/preservation dynamics.

1. INTRODUCTION

The South American lowlands are among the most ancient regions of earthen mounds construction by hunter-gatherer-horticulturists (López-Mazz, 2001; Bracco, 2006; Iriarte, 2006a). The Uruguayan earthen mounds, known as *cerritos de indios*, are distributed along the southeast and northeast of Uruguay and southern Brazil (López-Mazz, 2001; Gianotti, 2005; Bracco, 2006; Cabrera, 2013; Milheira and Gianotti, 2018). They emerged around 5000 yrs BP and mark the early complexity of societies with mixed economies based on the utilization of wild resources (game, recollection, fishing) (López-Mazz, 2001; Iriarte 2007) and the cultivation of maize and beans since approximately 3500 cal BP (Iriarte, 2007; Gianotti et al., 2013; del Puerto, 2015; Milheira and Gianotti, 2018). Many of the mounds were used as a cemetery until the European conquest (Sans et al., 2012; Figueiro et al., 2017).

The category “cerritos” (Arechavaleta, 1892) or “Indian earthquakes” (Ferrés, 1927) was introduced to define a wide range of architectural forms including round mounds, long mounds, platforms, ring mounds and microreliefs, the functional diversity and chronology of which still require further studies (Milheira and Gianotti, 2018). The mounds, typically around 30-40 m in diameter and 1-5 m elevation, are composed mainly of an organic-rich sediment matrix from the direct surroundings (Capdemont et al., 2005; Suárez-Villagrán and Gianotti, 2013), forming an admixture with cultural remains such as food waste, lithic waste, tools, ceramics, ochre, charcoal and sometimes burnt anthill material (Bracco et al., 2000; López-Mazz, 2001; Iriarte, 2006a; Gianotti and Bonomo, 2013). Associated structures that are frequently found in mound sites include anthropogenic lagoons, canals and areas that were depleted of their soil resources (“soil mines”), e.g. for mound construction (Gianotti et al., 2009; Gianotti, 2015). The earthen mounds are located in the Pampa biome (Roesch et al., 2009), characterized by large areas of floodplains, subtropical temperate grasslands (pasturelands) and native forests along the margins of creeks and rivers. The widespread grasslands from Uruguay have been shown to form

a stable ecosystem since the mid-Holocene (Mourelle, 2015), especially after the increase in precipitation around 3000-4000 cal BP (Iriarte, 2006b; Bracco et al., 2005). The nucleus of mound creation was in the region of India Muerta in southeast Uruguay, around 5000 cal BP. The expansion to other areas of Uruguay and Brazil, mostly in the plains around lagoons and rivers along the Atlantic coast, is more recent (ca. 3000 cal BP) (Milheira and Gianotti, 2018). Many sites with earthen mounds, especially in the lowlands, were domestic villages with multiple occupation phases (Iriarte, 2006a; Gianotti, 2015), whereas on hilltop mounds mark ceremonial and territorial conformation functionalities (Gianotti, 2015; López-Mazz, 2001). The long history of the Uruguayan mounds is reflected by evidence of domestic functions (Bracco et al., 2000; López-Mazz, 2001; Gianotti and Bonomo, 2013) and abandonment (Cabrera and Marozzi, 2001; Gianotti, 2005; Iriarte, 2006a), funerary events (Femenías et al., 1990; Gianotti and López Mazz, 2009), crop cultivation (del Puerto, 2015; del Puerto et al., 2016; Gianotti et al., 2013) and episodes of reshaping and maintenance of the constructions (Gianotti, 2005, 2015; Suárez-Villagrán and Gianotti, 2013). In fact, the mounds are the synthesis of intentional practices and relicts of indirect effects of soil management, fire practices and garbage management very similar to the formation of dark earth (*terras pretas*) in the Amazonian region (Erickson, 2003; Miranda et al., 2002; Lehmann et al., 2003; Arroyo-Kalin, 2014; McMichael et al., 2014; Schmidt et al., 2014). Such dark earths are evidence of controlled fire and vegetation clearance (Leal, 2010; Iriarte et al., 2012; Rull et al., 2015) by slash-and-burn (or slash-and-char) practices, and possibly biochar production (Arroyo-Kalin, 2012).

The earthen mounds provided evidence of diverse indigenous practices of ecological management, such as (1) the conditioning of the area and construction and maintenance of mounds, generating a positive relief in the structures and a negative relief in the surroundings (areas where the raw material was sourced) (Gianotti and Bonomo, 2013; Castiñeira et al., 2016); (2) these modifications also affected the soil water regime and natural drainage patterns; (3) there are signs of modification of natural geofoms, such as small lagoons and channels, for

the purpose of water regulation (Gianotti, 2015; Gianotti and Bonomo, 2013, del Puerto et al., 2016a); (4) identification of various wild and domesticated plant and animal species, used for food, technology and combustion purposes (Iriarte et al., 2004; Inda and del Puerto, 2007; Gianotti et al., 2013; Moreno, 2014; del Puerto et al., 2016a, 2016b, 2016c; Suárez et al., 2016). Nevertheless, the long history of the Uruguayan mound settlements and the environmental changes in the surrounding anthropized landscapes are poorly understood in the context of global transformations of prehistoric landscapes (Balée, 2010; Walker, 2012; Clement, 2014; Piperno et al., 2015).

Analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS) is based on the application of thermal energy in the absence of reactants to break down natural polymers (macromolecules) into smaller fragments (pyrolysis products) and their subsequent separation (GC) and identification (MS) (Moldoveanu, 1998; Wampler, 2006; Voorhees, 2013). Pyrolysis-GC-MS allows for rapid screening of soil organic matter (SOM) composition (e.g. Schnitzer and Hoffman, 1964; Sáiz-Jiménez and de Leeuw, 1986; Derenne and Quénéa 2015; Kögel-Knabner and Rumpel, 2018), including SOM from deposits in archaeological settlements (Schellekens et al., 2013a,b). The pyrolysis fingerprint of SOM from archaeological contexts can provide information on pre-historical land use (Schellekens et al., 2013a,b; Kaal and Mailänder, 2018), even though it is often difficult to anticipate the kind of information that can be obtained when the degree of SOM preservation is unknown. Pyrolysis-GC-MS is considered a powerful tool for initiating research on SOM composition as it has the potential to identify and discriminate source materials (human artefacts, bone collagen, plants, animals, soil microorganisms, etc.) and the post-depositional degradation processes that have acted on it. Molecular characterization of SOM can be particularly informative in deposits that accumulated during the period of interest, either naturally (colluviation, sedimentation in aquatic bodies) or intentionally (continuous growth models of anthropogenic structures such as the earthen

mounds), when a reliable depth/age profile can be determined, allowing to identify *changes* in sources of organic remains and environmental conditions.

In this paper, we applied Py-GC-MS to the SOM in samples from anthropogenic earthen mounds, lagoons and a canal from Pago Lindo mound site (Tacuarembó, Uruguay). The main objective is to identify the sources of the SOM in these deposits and relate them to anthropogenic activities and soil formation processes at Pago Lindo site. Considering that this is the first time analytical pyrolysis is used in the contexts of Uruguayan mound settlements, another objective was to identify the potential of Py-GC-MS and the suitability of the samples from the various kinds of deposits for unravelling the site's environmental history.

2. METHODS AND MATERIALS

2.1 Pago Lindo mound village

The Pago Lindo mound site is located in the floodplains of the Caraguatá stream in Tacuarembó (Uruguay) (Figure 1), which is part of the lowlands of the Río Negro catchment. During the last 15 years almost 1000 mounds were found in the floodplains of the Yaguarí and Caraguatá streams (Gianotti and Bonomo, 2013). Research in three important earthen mound sites (Lemos, Cañada de Caponcitos and Pago Lindo) gave rise to a chronological model of mound construction and site occupation spanning the period between 3250 and 500 cal BP (Gianotti, 2015). During this period these sites were well-organized villages with domestic, funerary and agricultural practices, located at places with abundant hydrological and other resources (del Puerto et al., 2016; Gianotti, 2005, 2015; Gianotti and Bonomo, 2013).

From Pago Lindo, 37 earthen mounds and micro-reliefs of different typologies (round mounds, oval mounds, long mounds, ring mounds, platforms, earthworks, raised fields), with 0.5 to 4.0 m height and a diameter of 30-50 m (circular mounds) or 30x300 m (long mounds), have been identified, in an area of 0.5 km². Areas of soil depletion, anthropogenic circular

150 lagoons (one active and one buried) and a canal connecting the lagoons have also been
151 identified (Figure 1). Between 2006 and 2011, multiple excavation zones were distributed
152 among the mounds, lagoons and canals of Pago Lindo (Gianotti et al., 2009; Gianotti and
153 Bonomo, 2013).

154 For the present study, several soil profiles were obtained from a complex earthen
155 mound (Em-1, Em-2 and Em-3), infillings of an archaeological lagoon (La-1), an active lagoon
156 sediment (La-2) and the infillings of an anthropogenic canal (Ca) that discharged into La-1 (Figure
157 2; Table 1). More specifically, we studied samples ($n=27$) from columns taken from the three
158 excavation profiles of earthen mound PU061110Q23-Q25 (Gianotti, 2015) (Table 2). The
159 complexity of the earthen mound is reflected by the presence of submounds that became
160 integrated and unified as the system evolved, eventually obtaining the shape of a horseshoe. A
161 total of 18 stratigraphic units and seven phases of occupation between 3000 and 600 cal BP
162 were identified (Gianotti, 2015; Gianotti and Bonomo, 2013; Table 1). Excavation of the complex
163 mound showed evidence of a domestic hut, occupation floor, cultivated plant consumption,
164 ceramic fabrication and lithic materials from tool production (Gianotti, 2015; Suárez Villagrán
165 and Gianotti, 2013; del Puerto et al., 2016). From this mound sector, a soil profile in the middle
166 of the mound (Em-1) and a smaller profile in the SW border of the mound (Em-2) were taken.

167 The stratigraphy of the deposit of the anthropogenic (rectilinear) canal and previous
168 analyses showed that the canal was active and in connection with the lagoon (La-1) during the
169 later occupation phases of Pago Lindo (Gianotti, 2015; Suárez Villagrán and Gianotti, 2013; del
170 Puerto et al., 2016). Eight samples were obtained from the border of the excavation trench.

171 The profile from the center of the archaeological lagoon infilling (La-1) provided a record
172 of biogenic silica (phytoliths, diatoms), which pointed towards the existence of an expanding
173 lacustrine system between ca. 3000 cal BP until its recent eutrophication and progressive
174 infilling (del Puerto et al., 2016). The lagoon was in use as a reservoir within the settlement,
175 during the occupational phases of the excavated mounds (Gianotti 2015; del Puerto et al., 2016).

The canal possibly served to drain the water from the fluvial plain during peak discharge. Finally, a deposit from the active lagoon La-2, situated at 8 m from the excavated mound, was examined. Contrary to La-1, this lagoon is still a permanently open water environment. In total, nine samples were selected from the two lagoon structures.

2.2 Pyrolysis-GC-MS and sample pretreatment

Preliminary Py-GC-MS analyses of untreated bulk samples gave unsatisfactory results (low signal-to-noise, low diversity of compounds). Therefore, samples were subjected to hydrofluoric acid treatment to remove reactive minerals that catalyse pyrolysis reactions. After three phases of overnight 2% HF treatment and subsequent centrifugation/decantation, samples were rinsed with water until the elution was colourless and of neutral pH (cf. Zegouagh et al., 2004). The residue was dried at 35 °C.

Pyrolysis-GC-MS was performed with a platinum filament coil probe Pyroprobe 5000 (Chemical Data Systems, Oxford, USA) coupled to a 6890 GC and 5975 MS system from Agilent Technologies (Palo Alto, USA). Residues after HF treatment (ca. 1.0 mg) were embedded in glass wool-containing fire-polished quartz tubes, and pyrolyzed at 650 °C for 5 seconds (heating rate 10 °C/ms). The interface and GC inlet were set at 325 °C. The GC inlet was set in splitless mode. The oven of the GC was heated from 50 to 320 °C at 20 °C/min and held isothermal for 5 min. The GC-MS transfer line was at 325 °C, the ion source (electron impact mode, 70 eV) at 230 °C and the quadrupole detector at 150 °C, measuring fragments in the m/z 45-500 range. The GC was equipped with a (non-polar) HP-5MS column (length 30 m; internal diameter 0.25 mm; film thickness 0.25 µm). Helium was used as the carrier gas (constant gas flow, 1 ml/min). Compounds were identified using the NIST '05 library and Py-GC-MS literature. The relative proportions of pyrolysis products, expressed as % of total quantified peak area (TQPA) was calculated from the peak areas of targeted m/z fragments of each compound. This allows for a

more detailed interpretation of pyrolysis chromatograms than visual inspection alone, and enables statistical data evaluation. The relative proportions data was evaluated by means of Principal Component Analysis (PCA) to identify the mechanisms that control the variation in the pyrolysis fingerprints of the SOM, using Tanagra software, which automatically normalizes the percentage data to Z-scores. No rotations were applied.

3. RESULTS AND DISCUSSION

3.1 Pyrolysis-GC-MS: sources and significance of pyrolysis products

The 102 pyrolysis products (Table 3) were categorized according to chemical structure and likely source: methylene chain compounds (MCC; *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, prist-1-ene), monocyclic aromatic hydrocarbons (MAHs), polycyclic aromatic hydrocarbons (PAHs), carbohydrate products (acetic acid, furans, furaldehydes, pyrans, anhydrosugars), nitrogen-containing compounds (pyrroles, pyridines, acetamide, benzonitriles, diketopiperazines), phenols (phenol, alkylphenols), methoxyphenols (guaiacols, syringols) and other compounds. Example chromatograms are provided in Figure 3.

The abundance of N-compounds in general, i.e. 12.3 % (average) $\pm$ 3.5 % (standard deviation) of TQPA (Supplementary Material), illustrates significant SOM reworking (Schulten and Schnitzer, 1998; Nierop et al., 2005; Buurman and Roscoe, 2011; Yassir and Buurman, 2012). In particular, acetamide, 3-acetamidopyrone and 3-acetamido-6-methylpyrone are strong indicators of biologically remediated SOM as they can be sourced to chitin, i.e. a nitrogen-containing polysaccharide based on *N*-acetylglucosamine (Stankiewicz et al., 1996, 1998; Nierop et al., 2005; Gupta and Cody, 2011), present in arthropod exoskeleta and fungal cell walls. The presence of these compounds suggests that the more abundant but less specific N-containing

products (pyrroles and pyridines) originate from microbial SOM as well, and that the indole and diketopiperazines correspond predominantly to chitin-entangled protein (Stankiewicz et al., 1998). Among the N-containing products, benzonitriles are not related to chitin or other microbial components, but to pyrogenic SOM (PySOM) (Kaal et al., 2008). The presence of PySOM implies that unknown proportions of pyridine and methylpyridine, and to a lesser extent also pyrrole, may correspond in part to charred and not microbial tissues, but this contribution is expected to be minor.

The abundance of microbial SOM is in agreement with the polysaccharide pyrolysis fingerprints observed. Whereas the carbohydrate products are the most abundant group of pyrolysis products (36.4 ± 10.5 % of TQPA), the main products of intact plant-derived polysaccharides, namely 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one, dianhydrorhamnose, 1,4:3,6-dianhydro- α -D-glucopyranose and levoglucosan, are relatively scarce (4.6 ± 6.7 %) (Pouwels et al., 1987, 1989). In addition, these products from intact polysaccharides are more abundant in the younger lagoon La-2 and the surface of the canal deposit (12.8 ± 9.5 %) than in the earthen mound (Em-1–Em-3) and archaeological lagoon infillings (La-1) (2.0 ± 1.6 %). Hence, microbial polysaccharides prevail in the samples studied, with the unsurprising exceptions of the canal and younger lagoon infillings.

The methoxyphenols (1.9 ± 3.1 % of TQPA), which includes the *p*-coumaric acid product 4-vinylphenol, originate from lignin in vascular plants (hence, not reassimilated by the soil microbial community) (Hedges and Mann, 1979). 4-Vinylguaiacol and 4-vinylphenol are the dominant lignin products, which suggests that the lignin originates from herbaceous rather than woody sources (van der Hage et al., 1993). The sum of these compounds is relatively high in the younger lagoon infilling La-2, and the surfaces of the archaeological lagoon infilling (La-1) and canal deposit suggesting that relatively intact plant-derived SOM is concentrated in these deposits/layers. This in agreement with the observations made for the polysaccharides

fingerprint. Guaiacyl dominates over syringyl moieties, but considering the evidence of SOM degradation further source identification is not sustained (Dorado et al., 2003).

Phenol and methylphenols (cresols) account for 4.4 ± 3.4 % of TQPA. These compounds can be produced upon pyrolysis of many sources, including plant polyphenols and microbial proteins (Tsuge and Matsubara, 1985; van Heemst et al., 1999; Leenheer and Croué, 2003). Their dominant sources vary among the different deposits studied. Similarly, the MAHs (18.2 ± 3.9 %) can originate from different materials including PySOM, microbial SOM and polyphenols (González-Vila et al. 2001; Kaal et al. 2008). In general terms, benzene is more associated with PySOM whereas microbial SOM is a prolific of toluene overshadowing its possible PySOM precursor in pyrolysis fingerprints of SOM admixtures with higher microbial than pyrogenic contents.

The PAHs are more specific products of PySOM (González-Vila et al., 2001; Ross et al., 2005; Rumpel et al., 2007; González-Pérez et al., 2014). The PAHs account for 1.6 ± 0.5 % of TQPA. In particular naphthalene, biphenyl and phenanthrene/anthracene are useful markers of PySOM, but potential formation through secondary reactions during pyrolysis (i.e. artificial production), from resins and from trace concentrations of PAHs in uncharred plant materials demand caution in the interpretation of these compounds (Sáiz-Jiménez, 1994). Their co-occurrence with the benzonitriles is a good indication of a predominantly PySOM source and is corroborated by observation of charcoal fragments during the excavations and micromorphological assessments (Gianotti, 2015; Suárez-Villagrán and Gianotti, 2013).

The compounds based on methylene chain structures (MCC) are abundant in most samples (23.6 ± 10.3 %). They are dominated by homologous series of C_{11} - C_{33} alkanes and C_9 - C_{33} alkenes, but include several other compounds such as C_{16} - and C_{18} -fatty acids and prist-1-ene. They originate from plant waxes, free fatty acids and aliphatic biopolyesters such as cutin and suberin or non-hydrolyzable analogues cutan and suberan (Nierop, 1998; Kolattukudy, 2001).

278 Finally, products that could not be identified account for $1.5 \pm 0.9\%$ (other compounds).

279 These compounds include a tentatively identified C₂₀-alkylcyclohexane compound that is
280 frequently associated with intact plant remains, a polar product with dominant *m/z* 95 (possibly
281 N-containing) and a compound with *m/z* 110 in the tail of 5-methyl-2-furaldehyde.

283 3.2 Principal Component Analysis: variability in SOM fingerprints

285 An initial PCA showed that the basal clay sample in earthen mound Em-1, which has an
286 extraordinary high proportion of MCC (67.4 %), was very distinct from the other samples
287 showing by far the strongest scores on both PC1 and PC2. To avoid biased results, the PCA was
288 repeated omitting this outlier. The first three principal components (PC1—PC3) combined
289 account for 58.4 % of total variance in the dataset (Supplementary Material).

290 The long-chain (C₂₇–C₃₃) *n*-alkanes and *n*-alkenes, 2-methylfuran, benzonitrile and
291 benzene have the highest (>0.5) positive loadings on PC1 (29 %), whereas high negative loadings
292 (<-0.5) are found for most lignin products, several carbohydrate products, phenols, N-containing
293 compounds (C₀–C₁-pyrrole, indole, C₁-benzonitrile, diketodipyrrole, diketopiperazine, 3-
294 acetamidopyrone), short/intermediate *n*-alkanes (C₁₁–C₂₃) and *n*-alkenes (C₁₇–C₂₃), and several
295 MAHs and PAHs (those that bear alkyl groups) (Figure 4; Supplementary Material). The negative
296 loadings are indicative of a mixture of microbial SOM (N-containing polysaccharides, proteins
297 and probably MCC) and plant-derived lignin and polysaccharides (Buurman and Roscoe, 2011;
298 Suárez et al., 2011; Kaal et al., 2009), whereas positive loadings correspond to an aliphatic
299 fraction composed of plant waxes and perhaps biopolyesters (Nierop, 1998) and PySOM. It is
300 noted that the distribution of alkyl-PAHs with negative loadings and unsubstituted PAHs,
301 benzene and benzonitrile with positive loadings, may suggest a differentiation of relatively labile
302 weakly condensed PySOM (negative loadings) and recalcitrant strongly condensed PySOM
303 (positive loadings), similar to interpretations of PySOM composition by Fabbri et al. (2011), Justi

et al. (2017) or Suárez-Abelenda et al. (2017). It is thought that in this case the alkyl-PAHs may well originate not only from weakly condensed PySOM but also from resin and native free PAHs in plants. Therefore, in the following discussion, when the presence of PySOM is inferred, we refer to the signal from benzene, benzonitrile and unsubstituted PAHs, of which a PySOM precursor is less ambiguous.

The lignin products and predominantly plant-derived polysaccharides (levoglucosan, dianhydrorhamnose, 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one) have the highest positive loadings on PC2 (16 %), accompanied by phenols and pristine. High negative loadings on PC2 correspond to C₀-C₁-pyridines, short-chain alkanes (C₁₂-C₁₆) and alkenes (C₉-C₁₂) and fatty acids (C₁₆, C₁₈) (Figure 4). These combinations imply that samples with relatively large proportions of pyrolysis products from intact and plant-derived lignocellulose have positive PC2 scores, whereas negative scores would indicate the absence of such intact materials and relative abundance of microbial and residual aliphatic material. Apart from this separation in PC2 loadings on the negative side of PC1, a second separation on PC2 (for compounds with positive loadings on PC1) can be observed for the long-chain MCC (positive) and PySOM products (negative loadings) (Figure 4).

Positive loadings >0.5 for PC3 (13 %) were found only for naphthalene, biphenyl and phenanthrene/anthracene (not shown; Supplementary Material), i.e. the unsubstituted PAHs which are the most likely products of a PySOM fraction. Negative loadings <-0.5 correspond to the C₂₃-C₂₇ alkanes and C₁₂-C₂₆ alkenes. Hence, positive PC3 scores correspond to samples in which the “stable” SOM is enriched in PySOM whereas negative scores correspond to samples where the stable SOM is the result of accumulation of recalcitrant aliphatic moieties.

The PC1, PC2 and PC3 scores of the different deposits are shown in Figure 5. Firstly, PC2 had been identified to represent early degradation, eliminating intact plant materials and forcing the accumulation of degraded microbial and aliphatic SOM. In general terms, the young lagoon (La-2) and surface samples of the canal infillings have the highest positive scores,

indicating that the SOM **in** these samples is relatively well-preserved. These samples are probably natural infillings after abandonment of the site. The predominance of non-woody (herbs, sedges, ferns etc.) vegetation in these (semi-)aquatic environments, as suggested by the lignin composition, is not surprising and confirms phytoliths (Gianotti 2015; del Puerto et al., 2016) and pollen data (Mourelle, 2015). In the earthen mound, lignin and plant-polysaccharides remains are much scarcer, but could be identified in all samples and confirmed the overall dominance of non-woody sources to the SOM as well.

The controlling factor of PC1 is a **more profound** degradation **effect**, i.e. from microbial tissue and lignin (negative scores) to recalcitrant aliphatic SOM and PySOM (positive scores). Negative scores are observed for La-2 and canal infillings, but also the surface levels of other profiles (Figure 5). Furthermore, in earthen mounds Em-1 and Em-3 and the archaeological lagoon La-1, a significant depth trend in PC1 scores can be observed. In Em-2, the situation is more complex, as the depth trend is interrupted by a local minimum at intermediate depth around 50-55 cm. The occurrence of coatings on soil particles in this layer of Em-2, observed by micromorphological examinations (Suárez-Villagrán and Gianotti, 2013), suggests that this feature of Em-2 might be related to incipient podsolization. In well-drained soils from (sub)tropical environments, podsolization is driven by selective preservation mechanisms, where E horizons are enriched in microbial SOM and the underlying B horizons show relative accumulation of aliphatic biopolymers (Nierop and Buurman, 1999; Buurman et al., 2013). This is in good agreement with the interpretation of the PC1 loadings distributions of the pyrolysis products. There is no local maximum in relative proportions of the “typical” constituents of dissolved organic matter (DOM) (phenols, furans, MAHs, etc.) (Leenheer and Croué 2003), suggesting that the coatings correspond to predominantly **clay illuviation. On the other hand**, the fluctuations in PC1 and PC2 scores in the deeper levels of Em-2 may also represent different construction episodes, in the sense that differences in age, exposure time at the surface, or parent material composition, can account for differences in degradation/preservation state of

the layers at 40-50 cm, 50-60 cm and 60-70 cm. For this section of the mound only one radiocarbon date is available (780-670 cal BP at 40 cm).

PySOM, represented by positive scores on PC3, tends to increase with depth in all records (Figure 5). This depth trend can be explained by selective preservation of PySOM, the polycondensed aromatic domains of which have a recalcitrant character. Here it is noted that the basal samples of Em-1 and Em-3 break this overall trend, which is probably the consequence of a lack of human imprint on SOM chemistry (clay basal levels, i.e. non-anthropogenic sediment underneath the barrows).

In summary, the results of the present study show that the majority of the variation in pyrolysis fingerprints can be ascribed to differences in the degradation/preservation state of the SOM. PC1 is associated with the degradation of mainly microbial SOM and relative accumulation of long-chain MCC compounds and, to a lesser extent, PySOM. This process can be recognized in most soil profiles as a clear trend with depth. PC2 reflects an earlier degradation process causing depletion of polysaccharides and plant polyphenols, and relative accumulation of mainly microbial SOM but also MCC-based compounds. In earthen mound profile Em-2, both PC1- and PC2-type degradation seem to respond also to a podsolization mechanism typical of well-drained soils in (sub)tropical areas, i.e. the accumulation of microbial SOM in incipient E horizon and relative accumulation of aliphatic biopolymers, probably from roots, in the B horizon (Nierop and Buurman, 1999), and/or different mound construction episodes. Podzols are abundant in-and-under barrows in N-Europe (e.g. Runia and Buurman, 1987; Bourgeois and Fontijn, 2012). From micromorphological analysis of thin sections, clay coatings and evidence of organic amendments, which could have stimulated the podsolization, were only observed in the corner of the mound where Em-2 was taken. PC3 is related to the relative proportion of recalcitrant MCC and PySOM. Even though it cannot be discarded that PC3 is influenced by degradation, it seems more likely that the PC3 scores represent differences in the input of plant-derived MCC and PySOM, and is therefore indicative of the input of fire for vegetation clearance

or charcoal from domestic fireplaces. If we combine this argument with the indications of predominantly herbaceous lignin and overall scarcity in macroscopic charcoal fragments, the burning probably corresponds to elimination of weeds.

3.3 Linking depth variations and site history

The bottom sample of earthen mound profile Em-1 (55-60 cm depth) corresponds to the basal clay deposit. The SOM is composed predominantly of MCC (67 %), which is considerably higher than 21.6 ± 2.7 % for the SOM from the layers on top, which indicates the strong contrast in SOM composition between the anthropogenic mound and the underlying soil/sediment. This sample corresponds to natural soil development, which is in agreement with the lack of archaeological remains. The predominance of MCC and lack of PySOM products indicate that the SOM was formed upon selective accumulation of plant-derived aliphatic material, and the virtual absence of PySOM markers suggests that artificial cyclization during pyrolysis is not a major source of PAHs in any of the samples (thus, we are confident that Py-GC-MS provides a reliable signal of fire residues). During excavation, the sample at 50 cm was labelled as a transition between the basal clay and the first anthropogenic layers of the earthen mound. According to its SOM composition, it corresponds completely to the anthropic deposit. There is a decrease in PySOM proportion from 50 cm depth towards the surface, which might be indicative of decreasing inputs of PySOM, but an influence of degradation processes cannot be discarded. In comparison with SU003 (50-20 cm), SU002 (0-20 cm) has lower PySOM content and higher proportions of recognizable chitin, intact polysaccharides and lignin, but the similar PC1-PC3 scores (Fig. 3) show that there is no strong contrast in SOM chemistry between these different layers of the anthropogenic deposit, which are thought to represent two different construction phases radiocarbon dated at ca. 990 and 690 BP (Gianotti, 2015). The SOM pool that is associated with biological activity may point towards the importance of bioturbation in

the deposits (Suárez-Villagrán and Gianotti, 2013; Gianotti 2015), which could have homogenized the SOM in the mounds. In general, the SOM of Em-1 has a large content of microbial SOM, which is in agreement with the abundance of excremental fabric in thin sections (Suárez-Villagrán and Gianotti, 2013). In nearby areas of Em-1, SU002 and SU003 were prolific of maize-derived phytoliths, but the SOM fingerprints are not useful for stressing this issue as we have no unequivocal tracers of maize detritus (see below).

Earthen mound profile Em-2, shows a more complex variation in SOM fingerprints. Here, the basal clay deposit (100-115 cm) has not been selected for analysis. The deepest sample, at 80 cm, corresponds to the first occupation of this mound zone (SU029) and is thought to be a mixed anthropogenic/natural deposit. The SOM contains relatively large proportions of plant-derived polyphenols, microbial N-compounds and PySOM. The sample from completely anthropogenic deposit SU022 (60 cm), and the transition sample at 70 cm, have similar SOM fingerprints. Thin section analysis of the sample at 70 cm showed conspicuous dusty clay coatings, possibly from human trampling as this layer corresponds to a construction platform for domestic occupation (Suárez-Villagrán and Gianotti, 2013). From SOM fingerprints, stratigraphic unit SU004-SU006 (55-30 cm) can be subdivided into three sections, i.e. a) 55-50 cm (abundant microbial SOM and PySOM, few MCC), b) 45-40 cm (abundant MCC, few microbial SOM and PySOM), and c) 35-30 cm (abundant microbial SOM, moderate PySOM, few MCC). The level with abundant MCC may correspond to the incipient B horizon, whereas the more superficial layers are enriched in microbial SOM (pseudo-E horizon). During the excavation of these stratigraphic units, numerous small charcoal fragments were observed throughout the anthropogenic deposit. The surface layers (SU002 at 20 cm, and the actual A horizon at 10 cm) were enriched in intact polyphenols.

In terms of molecular fingerprint, profiles Em-1 and Em-3 have similar SOM composition and depth trends. The sample at 60 cm depth (basal clay deposit) from profile Em-3 has a high MCC content and very little PySOM, which is similar to the basal clay sample of Em-1. There is a

clear difference in SOM fingerprints of the basal clay deposit, which is a buried soil formed through natural pedogenetic processes and possibly post-burial effects (Gerasimov, 1971), and the mound materials. This suggests that the natural sediments from or surrounding the Pago Lindo site did not contain PySOM, and therefore that the PySOM in the anthropogenic deposits is strictly related to human activities, rather than a background natural fire regime. The PySOM in the barrows originates from either periodical vegetation clearance and/or from domestic activities. The fact that only small amounts of morphologically recognizable wood charcoal were observed during the excavation and thin section analysis, may point towards the first source, as that would correspond to elimination of herbaceous vegetation. Analogous to observations in Em-1, the overlaying earliest anthropogenic deposit (50 cm depth) has an elevated PySOM content. The proportion of PySOM decreases towards the surface (SU019, SU016), whereas that of recalcitrant aliphatic SOM increases. Intact plant-derived SOM is more abundant in the surface material (SU001).

The SOM composition of the oldest materials of the anthropogenic lagoon infillings (La-1; 50-60 cm) are enriched in carbohydrates and N-compounds from degraded microbial matter, and PySOM. The abundance of PySOM may suggest that the early infillings (dark sandy-silt) are derived from local burning or erosion after vegetation clearance of the surrounding anthropogenic sediments, including the earthen mounds (transported into the lagoon through the anthropogenic canal which is linked to La-1). The more recent sediments (dark grey silty sand) have higher proportions of phenols and methoxyphenols from relatively intact plant debris and chitin markers from recent microbial sources, and contain little PySOM. It is hypothesized that these materials are less strictly associated with the charcoal-rich anthropogenic soils from human activities in the site, and may correspond to influx of sediments from canal discharge well after the Pago Lindo site was abandoned. Indeed, there is a large discrepancy between the earliest ^{14}C age from the profile (3160-2925 cal BP, base of profile,

corresponding to first occupation of the site) and the top of the profile at 600-560 cal BP when the lagoon was already filled with sediment (Gianotti 2015; del Puerto et al, 2016).

The three samples from the recent lagoon La-2 clearly contain the youngest, or best-preserved, SOM of all samples. The lignin content is high and clearly shows the herbaceous nature of the terrestrial plant debris. Aquatic sources may be reflected by the C₁₆ and C₁₈ alkylnitriles (not quantified) and extraordinary high proportions of prist-1-ene (Peulvé et al., 1996). PySOM and especially microbial SOM are relatively scarce in these samples.

Finally, the SOM fingerprints of the superficial samples (10-15 cm) of the canal infillings resemble those of active lagoon La-2, i.e. composed predominantly of intact plant debris. The sample at 20 cm (level 3-4 transition, dated 790-685 cal BP) until the base of the profile (45 cm) have similar SOM fingerprints, characteristic of abundant microbial SOM and PySOM, and few recognizable plant remains. Micromorphological and phytoliths analysis showed abundant charcoal spicules in this section of the profile as well (Gianotti, 2015). It seems likely that anthropogenic materials, for example from the mounds, had eroded from the surroundings and were deposited in the canal.

The importance of fire practices in conditioning and maintaining domestic and agricultural areas has been widely documented, also for the pre-hispanic communities in South America lowlands. Fire was used for forest clearance, creation and maintenance of pastureland (hunting), agroforestry practises (shifting agriculture), domestic waste elimination for pest control and other strategies such as snake deterring (Leal et al., 2016; Rull et al., 2015; Behling et al., 2004, Iriarte and Behling, 2007; Holz et al., 2016; Huertas et al., 2019). It is well-known that fire played a critical role in the formation and maintenance of the temperate grasslands of Uruguay (Gautreau, 2010; Bernardi et al., 2016), an ecosystem with great biodiversity (Modernel et al., 2016) that is nowadays under considerable threat (Henwood, 2010), but it remains unclear when the use of fire became a relevant agent in vegetation community dynamics due to the lack of palaeoenvironmental records in close proximity of archaeological settlements from the

Pampa biome. From the results of the present study a good control on fire management can be inferred even from the earliest phases of mound construction, here at ca. 3000 cal BP, and it would not be surprising if fire was also involved in the maize cultivation system (weed control, fertilization by ash and char, etc.).

One of the main characteristics of the Pago Lindo site is the evidence of maize (*Zea mays*) cultivation, as identified from phytoliths in the earthen mound and the surroundings of the canal (not studied) and archaeological lagoon infillings (del Puerto et al 2016). We analyzed samples of maize straw to identify possible biomarkers, but none of the less abundant (and less ubiquitous among the Poaceae) products was witnessed from the pyrolyzates of the SOM from Pago Lindo. A possible exception to this rule is the unidentified compound with m/z 110 (base and molecular ion) and smaller ion fragments m/z 68 and 82, possible from a carbohydrate structure in maize straw, but we have insufficient data to support this statement. The profound biological alteration of the SOM, in combination with the poor preservation of maize detritus in mineral soils (Gleixner et al., 2002) and perhaps waste management (including fire clearance), may be responsible for this. The phenolic products could be traced back to predominantly herbaceous sources such as maize, but the level of structural detail is insufficient to confirm or discard a maize source to the SOM in any of the samples studied.

4. CONCLUSIONS

In the deposits studied here, the SOM is composed of mixtures of plant-derived, microbial, pyrogenic and recalcitrant aliphatic SOM. Statistical evaluation of the data show that most variability in molecular composition of SOM is associated with degradation/preservation dynamics. It seems likely that microbial decay processes would have eliminated most of the features of anthropogenic nature (residues of domestic activities). A notable exception to this rule is the variation related to the proportion of PySOM, which is related directly to human activities, in particular, clearance of herbaceous vegetation (e.g. cleaning the mounds of weeds).

This pyrogenic SOM is more abundant in the deeper layers of the anthropogenic mounds, corresponding to the initial construction phases, and virtually absent in the underlying natural soil/sediment. These results, which are consistent with the archaeobotanical record (e.g. few macroscopic charcoal in the mound and abundant microscopic char particles in the canal infilling), represent a new line of evidence in the unravelling of the archaeology of the South American lowland mound environments. The abundance of PySOM from herbaceous vegetation in all anthropogenic layers of the earthen mounds can be considered evidence of frequent practicing of fire clearance, which is consistent with prolonged and continuous human occupation and therefore the process of sedentarization of the pre-hispanic populations in the region. Even though the main activity that can be identified by molecular characterization using conventional Py-GC-MS is the recurrent use of fire clearance, future studies using GC-MS of lipid extracts and “derivatization-Py-GC-MS” (THM-GC-MS) may well provide molecular evidence of additional activities.

These are the first results of the application of Py-GC-MS to earthen mound contexts in Uruguay. Cross-comparison of the molecular information with evidence from other techniques (soil micromorphology, sedimentology, palaeobotany, among others) allowed to elaborate detailed reconstructions of site history and the nature and cause of pedological processes and are an example of complementarity of different tools in complex archaeological environments where single observations can usually be explained by multiple processes or events.

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Figure captions

Figure 1: Geographical information of the Pago Lindo study area. The deposits that were studied are indicated in the contour map and aerial photograph (taken from a XXX balloon at X m height): the mounds were sampled from the Sector 1 (Em-1 and Em-2) and 5 (Em-3) excavation areas; the lagoons deposits are indicated as La-1 and La-2, and the canal associated with La-1 as Canal.

Figure 2: Schematic representation of the excavated deposits from the Pago Lindo site. The extracted columns (grey-coloured rectangles) from earthen mounds (Em-1, Em-2 and Em-3) and canal deposit were sliced at regular intervals of 5 cm. Each sampling point in the deposits of the lagoon deposits are indicated by individual grey rectangles. The stratigraphic units identified (Table) are indicated by SU followed by a two-digit numerical value. The SU allow to relate radiocarbon datings (red circles) of materials that are not part of the sampled deposits. The red asterisks in the canal deposits indicate archaeological ceramic and lithic remain.

Figure 3: Examples of pyrolysis chromatograms (plotting retention time against total ion current abundance) of organic matter (after HF treatment) from earthen mound and lagoon deposits, indicating a series of peaks. Methylene chain compounds (*n*-alkane and *n*-alkene doublets) are indicated with the carbon number (C_n), LG=levoglucosan.

Figure 4: Loadings plot from Principal Component Analysis of the pyrolysis-GC-MS data (PC1-PC2). MCC= methylene chain compounds, MAH/PAH= monocyclic and polycyclic aromatic hydrocarbons. Labels are explained in the pyrolysis products list (Table 3).

Figure 5. Scores from principal components PC1, PC2 and PC3, obtained by Principal Component Analysis (PCA) of the pyrolysis-GC-MS dataset. The scores are plotted against depth of the profiles of the earthen mound (Em-1, Em-2, Em-3), lagoons (La-1, La-2) and canal (Can).

849 Table 1 – Main stratigraphic units (SU) documented in sector 1 mound excavation.

Sector	SU	SU characterization	Anthropic activities	Radiocarbon dates (cal yrs BP)
1	SU 02	Very dark brown sandy loam with archaeological material (lithic, ceramic, red ochre and charcoal)	Restructuring and construction episode associated with domestic area	684 – 637 yrs BP (Ua 36275)
	SU 03	Greyish brown sandy loam with archaeological material (lithic, ceramic, red ochre and charcoal)	Restructuring and construction episode associated with domestic area	962 – 896 yrs BP (Ua 36274)
	SU 04	Very dark brown sandy loam with archaeological material (lithic, ceramic, red ochre and charcoal)	Eastern mound construction episode	781-673 yrs BP (Ua 36276)
	SU 06	Very dark brown sandy loam with archaeological material (lithic, ceramic, red ochre and charcoal)	Eastern mound construction episode	-
	SU 05	Greyish brown sandy loam with archaeological material (lithic, red ochre, charcoal and postholes)	Habitation floor	1608-1415 yrs BP (Ua 38297)
	SU 17	Dark grey sandy clay loam with few iron oxide nodules. Lithic artefacts	Natural soil underneath habitation platform at SU22 and SU05 interpreted as possible first human occupation in the area	3341-3140 yrs BP (Ua 38300)
	SU 22	Brown sandy loam, with archaeological material (lithic, red ochre and charcoal)	Possible habitation floor. Very similar to SU05	-
	SU 29	Very dark grey sandy clay loam with few lithic artefacts	Natural soil beneath the habitation platform at SU 22 interpreted as possible first human occupation	-
5	SU 16	Dark brown sandy loam with many archaeological materials (stone tools, pottery, red ochre and charcoal)	Construction episode associated with domestic occupation	-
	SU 19	Dark brown sandy loam with stone artefacts	Construction episode associated with domestic occupation	1191-1057 yrs BP (Ua 38299)
	SU 32	Grey brown sandy loam with stone artefacts	Accretional deposit related with first anthropic occupation in the area	-

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852 Table 2: Deposit and sample list of the materials from Pago Lindo. Each indicated depth marks a
853 sample that was analysed (n=44) by pyrolysis-GC-MS. SU=Stratigraphic unit. Tr.=transition.

Type	Stratigraphic unit	Depth (cm)
Earthen Mound		
Em-1	SU002: anthropic deposit	10
Sector 1	SU002: anthropic deposit	15
Profile: south	Tr. SU003-SU002: anthropic deposit	20
Corner: southeast	SU003: anthropic deposit	25
Mu090227Q01	SU003: anthropic deposit	30
	SU003: anthropic deposit	35
	SU003: anthropic deposit	40
	SU003: anthropic deposit	45
	Tr. Basal clay-SU003	50
	Basal clay	55
Earthen Mound		
Em-2	Tr. SU002/endorganic horizon	10
Sector 1	SU002	20
Profile: north	SU004-006	30
Corner: northwest	SU004-006	35
Mu090226Q08	SU004-006	40
	SU004-006	45
	SU004-006	50
	Tr. SU029/SU004-006	55
	SU022: anthropogenic deposit	60
	Tr. SU029/SU022	70
	SU029: mixed natural/anthropogenic	80
Earthen Mound		
Em-3	Tr. SU001/endorganic horizon	10
Sector 5	SU016: anthropogenic deposit	20
Profile: north	SU016: anthropogenic deposit	30
Corner: west	SU019: anthropogenic deposit	40
Mu091208Q02	Tr. SU032: natural/anthropogenic	50
	Tr. Basal clay/SU032	60
Lagoon		
La-1	Silty sand	10
Sector 6	Dark grey silty sand	20
Mu090221Q02	Dark grey silty sand	30
Profile: southern border	Dark sandy-silt	40
	Dark sandy-silt	50
	Bottom sample	60
Active lagoon		
La-2	Top sample	S1
Sector 11	Middle sample	S2

Canal	Profile: center Mu090214Q05	Sandy base of deposit	S3
	Canal	Level 1 (endorganic layer)	10
	Sector 3	Level 3	15
	Profile: east	Tr. Level 4/3	20
	Mu090220Q02	Level 4	25
		Level 4	30
		Tr. Basal clay/Level 4	35
		Basal clay	40
		Basal clay	45

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Table 3: List of pyrolysis products obtained after Py-GC-MS of the soil profiles from Pago Lindo, with product codes (used in Figure 4), retention times (RT), ion fragments (m/z) used for the semi-quantification (in parenthesis characteristic fragments not used for quantification) and the group label of each compound: CARB=carbohydrate; LIG=lignin; MAH=monocyclic aromatic hydrocarbon; MCC=methylene chain compound; NCOMP=N-containing compound; PAH=polycyclic aromatic hydrocarbon; PHEN=phenol.

#	Label	pyrolysis product	RT (min)	m/z	group
1	2mf	2-methylfuran	1,756	82+53	CARB
2	benzene	benzene	2,021	78	MAH
3	25dmf	2,5-dimethylfuran	2,223	95+96	CARB
4	acac	acetic acid	2,399	60	CARB
5	pyrrole	pyrrole	2,706	67	NCOMP
6	pyridine	pyridine	2,711	79+52	NCOMP
7	toluene	toluene	2,716	91+92	MAH
8	C1-pyridine	C1-pyridine	3,344	93+66	NCOMP
9	3/2f	3/2-furaldehyde	3,458	95+96	CARB
10	C1-pyrrole	C1-pyrrole	3,555	80+81	NCOMP
11	C2b	C2-benzene	3,645	91+106	MAH
12	e9	C9:1 alkene	3,899	55+69	MCC
13	C2b	C2-benzene	4,018	91+106	MAH
14	chitin1	acetamide	4,195	59	NCOMP
15	4af	4-acetylfuran	4,511	95+110	CARB
16	e10	C10:1 alkene	5,134	55+69	MCC
17	5m2f	5-methyl-2-furaldehyde	5,227	110+109	CARB
18	uni1	unidentified compound	5,442	110	OTHER
19	pyran	4-hydroxy-5,6-dihydro-(2H)-pyran-2-one	5,663	114+58	CARB
20	phenol	phenol	5,757	94+66	PHEN
21	bnit	benzonitrile	5,882	103+76	NCOMP
22	indene	indene	5,969	115+116	PAH
23	rhamnose	dianhydrorhamnose	6,229	113+128	CARB
24	e11	C11:1 alkene	6,405	55+69	MCC
25	a11	C11:0 alkane	6,499	57+71	MCC
26	g	guaiacol	6,701	109+124	LIG
27	C1-phenol	C1-phenol	6,893	107+108	PHEN
28	lnone	levoglucosenone	7,054	68+98	CARB
29	C1-bnit	C1-benzonitrile	7,355	117+90	NCOMP
30	e12	C12:1 alkene	7,645	55+69	MCC
31	a12	C12:0 alkane	7,733	57+71	MCC
32	naph	naphthalene	7,790	128	PAH
33	pyranose	1,4:3,6-dianhydro- α -D-glucopyranose	8,548	57+69	CARB
34	uni2	unidentified compound	8,612	95	OTHER
35	4vp	4-vinylphenol	8,718	120	LIG

36	e13	C13:1 alkene	8,823	55+69	MCC
37	a13	C13:0 alkane	8,916	57+71	MCC
38	4eg	4-ethylguaiaicol	8,979	137+152	LIG
39	C1-naph	C1-naphthalene	9,124	142+115	PAH
40	C1-naph	C1-naphthalene	9,326	142+115	PAH
41	indole	indole	9,399	117+90	NCOMP
42	4vg	4-vinylguaiaicol	9,415	135+150	LIG
43	s	syringol	9,515	154	LIG
44	e14	C14:1 alkene	9,944	55+69	MCC
45	a14	C14:0 alkane	10,016	57+71	MCC
46	biph	biphenyl	10,048	154+153	PAH
47	chitin2	3-acetamidopyrone	10,084	111+82(153)	NCOMP
48	C2-naph	C2-naphthalene	10,566	156+141	PAH
49	4ms	4-methylsyringol	10,919	168+153	LIG
50	C3g	C3:1-guaiaicol (trans)	10,945	164+149	LIG
51	e15	C15:1 alkene	11,002	55+69	MCC
52	a15	C15:0 alkane	11,070	57+71	MCC
53	C4-naph	C4-dihydronaphthalene	11,475	173(188)	PAH
54	4ag	4-acetylguaiaicol	11,635	151+166	LIG
55	uni3	unidentified sugar compound	11,859	116	CARB
56	chitin3	3-acetamido-6-methyl-x-pyrone	11,936	125+167	NCOMP
57	e16	C16:1 alkene	12,004	55+69	MCC
58	a16	C16:0 alkane	12,066	57+71	MCC
59	fluorene	fluorene	12,273	166+165	PAH
60	e17	C17:1 alkene	12,953	55+69	MCC
61	levogl	levoglucosan	13,000	60+73	CARB
62	pristene	prist-1-ene	13,296	56	MCC
63	C3s	C3:1-syringol (trans)	13,425	194+179	LIG
64	dkdp	Cyclo(Pyr-Pyr) (diketodipyrrole)	13,669	186+93	NCOMP
65	e18	C18:1 alkene	13,856	55+69	MCC
66	a18	C18:0 alkane	13,908	57+71	MCC
67	phen/ant	Phenanthrene/anthracene	14,219	178	PAH
68	e19	C19:1 alkene	14,717	55+69	MCC
69	a19	C19:0 alkane	14,764	57+71	MCC
70	squa	squalene	14,869	81+95	MCC
71	e20	C20:1 alkene	15,532	55+69	MCC
72	a20	C20:0 alkane	15,542	57+71	MCC
73	f16	C16:0-fatty acid	15,542	60+73	MCC
74	dkpz	Cyclo(Pro-Pro)	15,952	70+194	NCOMP
75	e21	C21:1 alkene	16,321	57+71	MCC
76	a21	C21:0 alkane	16,321	55+69	MCC
77	e22	C22:1 alkene	17,073	57+71	MCC
78	f18	C18:0-fatty acid	17,073	60+73	MCC
79	a22	C22:0 alkane	17,083	55+69	MCC
80	e23	C23:1 alkene	17,794	57+71	MCC
81	a23	C23:0 alkane	17,794	55+69	MCC

82	uni4	alkylcyclohexane compound	18,256	83+280	OTHER
83	e24	C24:1 alkene	18,484	57+71	MCC
84	a24	C24:0 alkane	18,484	55+69	MCC
85	e25	C25:1 alkene	19,154	57+71	MCC
86	a25	C25:0 alkane	19,154	55+69	MCC
87	e26	C26:1 alkene	19,792	57+71	MCC
88	a26	C26:0 alkane	19,792	55+69	MCC
89	e27	C27:1 alkene	20,414	55+69	MCC
90	a27	C27:0 alkane	20,430	57+71	MCC
91	e28	C28:1 alkene	21,006	55+69	MCC
92	a28	C28:0 alkane	21,022	57+71	MCC
93	e29	C29:1 alkene	21,587	55+69	MCC
94	a29	C29:0 alkane	21,597	57+71	MCC
95	e30	C30:1 alkene	22,142	55+69	MCC
96	a30	C30:0 alkane	22,153	57+71	MCC
97	e31	C31:1 alkene	22,682	55+69	MCC
98	a31	C31:0 alkane	22,692	57+71	MCC
99	e32	C32:1 alkene	23,201	55+69	MCC
100	a32	C32:0 alkane	23,206	57+71	MCC
101	e33	C33:1 alkene	23,720	57+71	MCC
102	a33	C33:0 alkane	23,782	55+69	MCC

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Mound - Sector 1

Mound - Sector 5

La1 - Lagoon infilling

La2 - Younger lagoon

Canal-East Profile

Earthen mound Em-1 (50 cm depth)

**Lagoon
La-1 (30 cm)**