1 *Carbon in charcoals from pre-European garden soils*

2 **Detailed carbon chemistry in charcoals from pre-European Māori**
3 **gardens of New Zealand as a tool for understanding biochar stability**
4 **in soils**

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18 **Summary**

19 The stability of biochar, a form of charcoal intentionally made to be added to soil to
20 sequester carbon (C) and improve its function, remains unclear. As it is not feasible to
21 perform long-term (e.g., decades, centennial) laboratory experiments to assess biochar
22 evolution after soil amendment, the study of ancient archaeological charcoals can help
23 to identify characteristics (and possibly molecular markers) associated with the
24 decomposition and preservation dynamics of biochar in specific pedoclimatic
25 environments. In this study, the chemical composition of the organic carbon fractions
26 of three charcoals from pre-European Māori gardens of New Zealand (buried > 25 cm
27 depth) was thoroughly assessed. Complementary short-term incubations of charcoals
28 in sand were used to (i) evaluate the stability of C in the short-medium term, (ii)
29 model its mineralization process and (iii) estimate the C turnover. Elemental analysis,
30 thermogravimetric analysis (TG), X-ray photoelectron spectroscopy (XPS), solid-state
31 ¹³C nuclear magnetic resonance (NMR) and pyrolysis gas chromatography/mass
32 spectroscopy (Py-GC-MS) gave consistent results on describing the charring intensity
33 and the degree of polycondensation of these charcoals. The oldest buried deposit
34 (770±50 y BP) still retained un-charred or weakly charred lignocellulosic material,
35 indicating that such material survived decomposition processes for several centuries.
36 The amount of organic C mineralized in 109 d was <0.5% of initial charcoal-C. No
37 differences in MRT among samples were detected, in spite of inferred differences in
38 thermal impact. Longer term incubations are needed to obtain better estimates of C
39 turnover rates in charred material.

Introduction

Fire and the partly to severely charred material that remains in soil after vegetation fires have had an impact on soil fertility and soil genesis for millennia (Knicker, 2011). Contents up to 0.60 g pyrogenic carbon kg⁻¹ bulk soil can be found in very different soils (Brodowski *et al.*, 2006) , in spite of the large time span that in some cases has elapsed since the occurrence of a fire event (e.g., millennia; Knicker, 2011).

Fire, either natural or anthropogenic, has contributed to shape the landscape of New Zealand (McGlone & Wilmshurst, 1999). Polynesians settled in New Zealand *circa* AD 1200-1400 (McGlone & Wilmshurst, 1999) and made widespread use of fire for vegetation clearance of dwelling areas and cultivated fields. These pre-European gardeners cultivated mainly kumara, also known as sweet potato (*Ipomea batatas* L.), in a system involving planting mounds (pukes) directly formed by adding sand or gravel to the topsoil; other additives included ash, silt and clay materials, burnt scrub, shell and fireplace charcoal (Gumbley *et al.*, 2004; Hoffmann, 2011). Through these processes, Polynesians created anthropogenic soils currently known as “historical Māori gardens” (McFadgen, 1980) and also referred to as “plaggen soils” or Anthrosols in the literature (WRB, 2006). Archaeological remains of historical Māori gardens found in numerous locations of New Zealand have helped understand the functioning of these pre-European settlements (Gumbley *et al.*, 2004; Gumbley, 2011a; b; Hoffmann, 2011).

Excavated charcoal fragments used to establish the age of such settlements (McFadgen, 1980; Gumbley *et al.*, 2004) provide a unique opportunity to investigate the influence of pedoclimatic conditions on charcoal decomposition and preservation dynamics. This is of special interest in New Zealand as these gardens represent environments similar to those to which biochar is anticipated to be added. The use of

biochar, biomass thermo-chemically converted in an oxygen-limited environment, as soil conditioner has gained interest to sustainably sequester carbon and simultaneously improve soil functions without having a negative impact on the environment and human health in the short- and long-term (Verheijen *et al.*, 2009; IBI, 2012). Understanding the stability of biochar in specific soils is paramount for assessing its C sequestration capacity and potential. Once quantified, biochar may obtain monetary value, apart from its agricultural value, through the C credit market.

It is assumed that charred material (e.g., charcoal) is more recalcitrant than other types of organic compounds common in soil and this is attributed to the intrinsic chemical and biochemical stability of condensed aromatic groups (McBeath *et al.*, 2011). However, its origin, chemistry and survival in soils is related to a complex set of factors, as described by Czimczik and Masiello (2007) and Knicker (2011), including: i) fire conditions (oxygen availability, temperature) and fire frequency; ii) chemistry of the original plant material; iii) physical and chemical post-depositional mechanisms (e.g., leaching, erosion, protection by interaction with soil mineral fraction); v) the absence of efficient decomposers; and vi) human influence through land use and management practices.

This study aims to thoroughly assess the chemical composition of selected charcoals obtained from buried deposits of pre-European Māori gardens of New Zealand. For this, the organic fraction of three charcoals of different radiocarbon age has been analysed using elemental analysis, thermogravimetric analysis (TG), X-ray photoelectron spectroscopy (XPS), solid-state ^{13}C nuclear magnetic resonance (NMR) and pyrolysis gas chromatography-mass spectroscopy (Py-GC-MS).

Materials and methods

Materials

The three charcoals studied here were taken from distinct deposits of charcoal pieces in pre-European garden sites in New Zealand's North Island. These were identified with the naked eye and referred as "characteristic feature" in archaeological reports (Gumbley, 2011a; b; Hoffmann, 2011). One composite charcoal sample (considered as representative of each deposit) was obtained per archaeological site; the study was not intended to investigate the soil profiles at the archaeological sites. Horotiu-1 charcoal was obtained from the archaeological site S14/222, located in Horotiu, Waikato (37°42'43.7" S; 175°12'15"E; Hoffmann, 2011). The other two samples were obtained from Papamoa, Bay of Plenty: Papamoa-1 was obtained from the archaeological site U14/2860 (37°42'53.5" S; 176°19'26"E; Gumbley, 2011a) and Papamoa-2 from the archaeological site U14/2907 (37°40'58" S; 176°15'1.5"E; Gumbley, 2011b). Intact charcoal pieces were hand-picked and wet sieved (particle size 0.25-40 mm) by submerging the particles into a water bath from which charcoal was separated after floating off (Gumbley *et al.*, 2004). The origin of the charcoal can be either slash-and-burn clearance of the native vegetation by pre-European gardeners or firewood (direct human occupation) (Gumbley *et al.*, 2004; Gumbley, 2011a; b; Hoffmann, 2011). Each sample studied here contained charcoal from a mix of vegetal species. Primary forest vegetation in the area included tree species such as matai (*Prumnopitys taxifolia*), puriri (*Vitex lucens*), pukatea (*Laureli-novae-zelandiae*) and shrubs as mahoe (*Melyctus ramiflorus*), manuka (*Leptospermum scoparium*) or hebe (*Hebe spp.*) (Gumbley, 2011a; Hoffmann, 2011).

Horotiu-1 charcoal was sampled in a relict puke basin (at approx. 40 cm depth), filled with baked altered silt (Hoffmann, 2011). Numerous charcoal particles were found, constituting a rich mixed deposit of ca. 11 cm. The primary forest cover was

cleared shortly before the onset of gardening, around AD 1500-1600 (Hoffmann, 2011). The radiocarbon age of the specific site where the sample was located is, however, slightly more recent (329 ± 30 y BP; Table 1).

Papamoa-1 and Papamoa-2 charcoal samples were collected from the relict sand dune plain at Papamoa (Gumbley, 2011a; b). Garden soils at Papamoa are closely associated with large numbers of settlements marked by shell middens, located near the shoreline. Occupation of the Papamoa dune ridge plain occurred from AD 1400 to AD 1600. Papamoa-1 was obtained in a garden soil similar to that of Horotiu-1. The sample was collected from a horizontal black, charcoal-rich soil lens of 3-6 cm thick, at approx. 30 cm depth, described as a “linear burnt feature” or a blackish layer identified as different from the soil matrix, which included remains of volcanic tephra layers (Gumbley, 2011a). Charcoal, both as scattered lumps and as patches of fine particles, was present in the entire profile. The radiocarbon age of the site is 770 ± 50 y BP (Table 1). Papamoa-2 charcoal was obtained in an area close to shell middens in Papamoa (Gumbley, 2011b), from a 20-50 cm thick mixed soil at 25 cm depth. The reworked topsoil had a yellowish brown colour, whereas the subsoil consisted of pale brown sand, including charcoal and volcanic tephra. The charcoal (radiocarbon age of the site: 681 ± 30 y BP) had a variable particle size, including lumps visible to the naked eye and fine material concentrated in mottles (Gumbley, 2011b).

Chemical characterization and thermal analysis

One bulk charcoal sample was obtained per archaeological site, from which subsamples were taken. After homogenization, a representative subsample was obtained from each charcoal type and finely ground ($< 500 \mu\text{m}$) for the chemical characterization and thermal analysis. Charcoal pH and electric conductivity (EC)

were measured (n=2) using ground charcoal in deionized water (1:20 w:v) after 1.5 h shaking (IBI, 2012). Total C, H and N contents were determined using a vario MACRO cube CHNS elemental analyser (Elementar Analysensysteme GmbH, Hanau, Germany). The ash content was determined by thermal analysis using a thermogravimetry analyser (SDT Q600, TA Instruments, Melbourne, Australia) (Calvelo Pereira *et al.*, 2011). Oxygen content was estimated as follows: $O = 100 - (C + H + N + \text{ash})$ (all wt %). Traces of inorganic C (IC; i.e. CO_3^{2-}) were detected by the thermogravimetry analyser, as a small endothermic peak, in Papamoa-1 only. As the value was very low ($< 0.2\%$, below detection limit), total C was assumed to be all organic (C_{org} ; Table 1).

Thermogravimetric (TG) and derivative (DTG) curves were obtained using the SDT Q600 instrument described above and the volatile matter content (dry basis) and the stable, thermo-resistant fraction or fixed C (dry basis) determined (n=3) following the method described by Calvelo Pereira *et al.* (2011).

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was applied for surface analysis of a subsample of each charcoal, sieved (< 1 mm) as received, using a Phoibos 100 spectrometer (Specs, Berlin, Germany) with $\text{MgK}\alpha$ (1253.6 eV) radiation emitted from a double anode at 150 W. Charcoal subsamples were dried and kept for 2 d at 6×10^{-6} Pa. Afterwards, they were placed in the analytical chamber with the pressure adjusted to 1.5×10^{-7} Pa. Each charcoal was analysed in particulate (< 1 mm) form. Particles attached to a square sample holder (16 x 16 mm) with a non-interfering carbon adhesive of 12 mm diameter. Subsequently, the surface was cleaned with pure dried air to remove any loose particle. As the carbon adhesive was covered

completely, many < 1 mm particles (intact) were analysed. The survey spectrum was taken in ≈ 45 min; high resolution C 1s spectrum was taken in ≈ 1 h; and high resolution O 1s spectrum in ≈ 30 min.

Binding energies for the high resolution spectra (C 1s and O 1s) were calibrated by setting C 1s at 284.6 eV. A non-linear least-squares curve fitting with a Gaussian-Lorentzian mix function and Shirley background subtraction was used for deconvolution. Peaks were assigned to organic functional groups or moieties based on published data (Biniak *et al.*, 1997; Nishimiya *et al.*, 1998).

Solid-state CPMAS ^{13}C NMR spectroscopy

Solid-state ^{13}C CPMAS (cross polarization, magic-angle spinning) NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz with a Bruker AMX 200 MHz spectrometer (Rheinstetten, Germany). Finely ground charcoal subsamples were packed in a cylindrical zirconia rotor (7 mm diameter) with Kel-F end caps and spun at 4500 ± 200 Hz in a Doty Scientific MAS probe. Free induction decays were acquired with a 1 H 90° pulse of 5.5 μs and a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms, a cross polarization contact time of 1000 ms and a relaxation time of 3 s; 4000 scans were acquired. The spectra were zero filled to 8192 data points and processed by 100 Hz Lorentzian line broadening and 0.005 s Gaussian broadening. Chemical shifts were externally referenced to the ^{13}C resonance of glycine. As CPMAS ^{13}C NMR spectroscopy often under-detects aromatic C, an unequivocal quantification was not feasible.

Pyrolysis-gas chromatography-mass spectrometry

Pt filament pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was performed with a Pyroprobe 5000 (Chemical Data Systems, Oxford, USA) coupled to a 6890N GC and 5975B MSD GC-MS system (Agilent Technologies, Palo Alto, USA). Finely ground subsample (ca. 1 mg) was embedded in fire-polished quartz tubes that contained glass wool. The chars were pyrolysed at 750 °C for 10 s (10 °C ms⁻¹), which are conditions considered adequate for charcoal analysis by Py-GC-MS (Kaal *et al.*, 2009). The interface and the GC inlet (in splitless mode) were at 325 °C. The GC oven was heated from 50 to 325 °C (held 2 min) at 15 °C min⁻¹. The GC-MS transfer line was at 325 °C, the ion source (electronic ionization mode, 70 eV) at 230 °C and the quadrupole detector at 150 °C; scan range was *m/z* 50-500. The GC instrument was equipped with (non-polar) HP-5MS 5% phenyl, 95% dimethylpolysiloxane column (30 m x 0.25 mm i.d.; film thickness 0.25 µm). He was the carrier gas (1 ml min⁻¹).

A total of 109 pyrolysis products were identified and quantified using the peak area of their dominant fragment ion(s) (Table 2). This semi-quantitative dataset provides relative contributions of the pyrolysis products expressed as the proportion (%) of total quantified peak area (TQPA), which allows a more detailed comparison between samples and other techniques than visual inspection of pyrograms alone.

Sand-charcoal incubations

Incubation experiments using sand as substrate were performed to evaluate the short-term C stability of the two charcoals with the largest radiocarbon age difference (Horotiu-1 and Papamoa-1). For that purpose, 0.4 g of ground charcoal was thoroughly mixed with 10 g of sand (analytical grade from Unilab, Australia, acid-washed and pre-heated at 500 °C overnight in a muffle furnace; particle size < 500

µm) and placed in 500 ml Mason incubation jars. Un-amended sand was used as control. Distilled water, microbial inoculum and micronutrient solution were added to the jars to maintain biological activity following Cheng *et al.* (2008). Two treatments were considered for each charcoal: i) + inoculum, and ii) no inoculum. Microbial inoculum was obtained from an extract of a freshly-sampled fire-prone soil in the Manawatu area (New Zealand). One ml of inoculum obtained from a 1:50 w/v soil (A horizon) and deionized water filtrate was added for the + inoculum treatment; no inoculum treatment received 1 ml of deionized water instead. All the mixtures received 1 ml of micronutrient solution (Cheng *et al.*, 2008), with the pH adjusted to 6.5 using NaOH 0.1 M. All treatments were repeated (n=4).

The vials with experimental units were pre-incubated for 24 h at 4 °C in dark to avoid a CO₂ flush immediately after re-wetting dried sand and charcoal mixture (Christensen & Olesen, 1998). Vials were thereafter placed in jars, which contained a CO₂ trap (10 ml of 0.1 M NaOH) and an additional vial with 10 ml of deionized water, and sealed. The incubation was set for 109 d at 28 °C in the dark. After 3, 7, 11, 22, 33, 54, 70 and 109 d the CO₂ trap was replaced and the moisture content readjusted for each sample by using deionized water. After d 33, jars were vented regularly for 1 h for fresh air exchange. The evolved CO₂ trapped in the NaOH was precipitated by an excess of 1 M BaCl₂ solution and back titrated with standardized 0.1 M HCl using a TIM 865 Titration Manager (Radiometer Analytical, Lyon, France). Further calculations of C-CO₂ evolved were done following the specifications given by Pansu and Gautheyrou (2006) and references therein.

C mineralization model

Experimental data for the carbon mineralization were fitted by using the summation of two first order equations, i.e., the double exponential model (Sleutel *et al.*, 2005; Wang *et al.*, 2012). The model assumes the existence of two pools of C with different resistance against degradation and which are both mineralized according to first-order kinetics. In its general integrated form, the equation of the double exponential model expresses y , the fraction of C evolved at a time t , as:

$$y = a \cdot (1 - e^{(-k_1 \cdot t)}) + b \cdot (1 - e^{(-k_2 \cdot t)}) \quad (1)$$

where a and b refer to rapidly- and slowly-decomposable C pools, and k_1 and k_2 are their respective decomposition rate constants. As $a + b$ was set equal to the total amount of added carbon, only three parameters need to be estimated. SigmaPlot (version 11, Scientific Graphing Software, SPSS Inc.) was employed to perform nonlinear regression analysis. Then the half-life of the C was calculated considering the decomposition rate constants, according to the following equation:

$$t_{1/2} = \ln 2 / k \quad (2)$$

The mean residence time (MRT or turnover time) for each pool also depends on the decomposition rate constants. MRT was calculated following equation (3):

$$\text{MRT} = 1/k \quad (3)$$

Results

Chemical properties

Chemical properties of the Māori charcoals investigated here are shown in Table 1.

All charcoal showed an acidic pH, with values of 5.0, 6.0 and 5.5 for Horotiu-1, Papamoa-1 and Papamoa-2, respectively; EC values were below 4 mS m⁻¹ (Table 1).

Charcoals had a moderate C content (ranging between 485 and 613 g kg⁻¹) and low N (≤ 10 g kg⁻¹). The atomic H/C_{org} ratios ranged from 0.43 to 0.52. Papamoa-1 had the

highest atomic O/C_{org} ratio (0.52), whereas those of Horotiu-1 and Papamoa-2 were 0.48 and 0.43, respectively (Table 1). Ash contents were 244, 88 and 116 g kg⁻¹ for Horotiu-1, Papamoa-1 and Papamoa-2, respectively. Papamoa-1 was thus the charcoal with the highest C and O contents and lowest ash content (Table 1). Moisture content was similar among samples (17-18%); these high values were attributed to the hydrophilicity of weathered charcoals or the wet-sieving treatment.

Thermal analysis of charcoals

The TG and DTG curves are shown in Figure 1 and the data summarized in Table 1. The charcoals showed a similar thermo-degradability. All samples displayed an initial mass loss up to about 110 °C, attributed to water loss, and a gradual mass loss starting at 300 °C. Interestingly, Papamoa-1 showed an additional but small increase in mass loss around 600 °C. It cannot be ruled out the presence of carbonates, despite the low pH (Table 1) of the charcoal, but these, if present were in minor amounts. This peak could also be related to the loss of lignin or lignin-like moieties (Yang *et al.*, 2007). The relative contribution of fixed C to C_{org}, was 56, 62 and 53 % in Horotiu-1, Māori -2, and Papamoa-2, respectively.

Surface characteristics

Surface analysis indicated that charcoals were mainly composed of C and O, with small amounts of N (1.6-2.7 wt.%) and inorganic matter, such as Si (~1-20 wt.%), Al (~3-11 wt.%) and Ca (only present in minor amounts in Papamoa-1, 0.8 at. %; Figure 2). From the fitting of the C 1s core level XPS spectra (Figure 2), the following groups were identified: i) C bound to C in aliphatic and aromatic groups (CH_x, C-C

and C=C) at 284.6-284.7 eV, ii) O bound to C in hydroxyl and ether groups (–C-OR) at 286.0-286.4 eV, and iii) C bound to O in carboxylic, ester and lactone groups (–COOR) at 288.1-288.5 eV. The proportion of –C-OR groups was higher than that of –COOR in all samples (Table 3), the ratio –C-OR/–COOR being 1.52, 1.96 and 2.86 for Horotiu-1, Papamoa-1, and Papamoa-2, respectively. The O 1s spectra (data not shown) were poorly resolved but were consistent with the presence of the oxygen groups already identified in the C 1s spectra. Their broad and featureless appearance suggests the presence of other O-containing species, such as mineral matter, which agrees with the survey spectra. The surface O/C_{org} atomic ratios were 0.72, 0.46 and 0.73 for Horotiu-1, Papamoa-1, and Papamoa-2, respectively (Table 3).

Solid-state CPMAS ¹³C NMR spectroscopy

For all samples the chemical shift region with the greatest intensity was between 110 and 160 ppm, which corresponds largely to aromatic C (Figure 3). A small peak in the chemical shift region between 160 and 220 ppm, centred at ca. 175 ppm and associated to carboxyl moieties, could also be recognized. The broad band detected between 0 and 45 ppm corresponds to alkyl-C signal, but it was partially masked by spinning side bands of aromatic C (SSBs), especially for Horotiu-1 and Papamoa-2 (Figure 3). In addition, Papamoa-1 produced a considerable resonance at ca. 60 ppm from methoxyl C and at ~ 150 ppm from O-substituted aromatic C, both of which originate from aromatic methoxyl groups typical of lignin. The band at ~75 ppm is commonly assigned to O-alkyl C from polysaccharides (Figure 3).

Pyrolysis-GC-MS

The pyrolysis products were grouped according to probable source or chemical structure: i) carbohydrate products; ii) methoxyphenols; iii) N-containing compounds; iv) phenols; v) monocyclic aromatic compounds (MAHs); vi) polycyclic aromatic hydrocarbons (PAHs); vii) aliphatic components; and viii) other compounds.

Carbohydrates. Between 29 and 36 % of TQPA could be assigned to carbohydrate precursors (Table 2, Figure 4), represented by acetic acid, furans, pyrans, levoglucosenone and anhydrosugars (Pouwels *et al.*, 1989). Levoglucosan was abundant in the pyrolysate of Papamoa-1 only, indicating preservation of relatively intact polysaccharide (probably cellulose) (Poirier *et al.*, 2003). The presence of anhydrosugars and pyrans, which are indicative of the presence of un-charred or very weakly charred biomass (Kaal *et al.*, 2012) was interpreted as a key factor for describing the particular nature of this charcoal. The ratios of (pyrans+anhydrosugars)/furans were 0.03 (Horotiu-1), 0.36 (Papamoa-1) and 0.13 (Papamoa-1), confirming that the carbohydrates of sample Papamoa-1 are the least degraded and those of Horotiu-1 the most. Benzofurans were not included in this group because their origin is more ambiguous.

Methoxyphenols. 2-Methoxyphenols (guaiacols) and 2,5-dimethoxyphenols (syringols) were abundant (8% of TQPA) in the pyrolysate of sample Papamoa-1, while only traces of these lignin markers (Ralph & Hatfield, 1991) could be identified from Horotiu-1 and Papamoa-2 (< 1 % of TQPA).

N-containing compounds. Sixteen N-compounds accounted for 14-18% of TQPA, which was remarkable considering the low N content of these charcoals (Table 1, Table 2). These compounds have different origins: benzonitriles and (iso)quinoline originate from char-derived aromatic C and heterocyclic N compounds, whereas acetamide, a compound tentatively identified as 2-methoxy, 5/6-methylpyrazine and

acetylpyridone are specific of chitin (Stankiewicz *et al.*, 1998) and a 2,5/diketopiperazine is a dimerization product of proline-proline peptide linkage typical of chitin-entangled protein (Stankiewicz *et al.*, 1998). All other products share these sources, even though pyridines are probably largely from moderately charred biomass, whereas pyrroles, indole and diketodipyrrole originate primarily from non- or weakly charred proteinaceous biomass and chitin. In sample Horotiu-1 pyridine and benzonitrile were the most abundant (Table 2, Figure 4), whereas in sample Papamoa-1 pyridine, C₁-pyrrole and a chitin product (tentatively identified as 2-methoxy, 5/6-methylpyrazine) and in Papamoa-2 pyridine, C₁-pyrrole and benzonitrile were the most abundant. It is concluded that Horotiu-1 has a strongly charred black N fingerprint, Papamoa-2 has a moderately charred N fingerprint with the presence of some chitin whereas in Papamoa-1 chitin is more abundant than (weakly) charred N components. This interpretation is consistent with the benzonitrile/C₁ benzonitrile ratio, which was higher for Horotiu-1 charcoal (3.0) than for Papamoa-1 and Papamoa-2 charcoal (0.7 and 1.4, respectively; Figure 4). Beyond reasonable doubt, the chitin originates from fungal biomass and is thus an indication of microbial activity. The hypothetical presence fragmented shells present in the site (Gumbley, 2011b) contributing to chitin contents was discarded given the negligible amounts of inorganic C detected (Table 1).

Phenols. Phenols accounted for 4-10 % of TQPA. These compounds originate from many different biocomponents, including proteins, chitin, lignin and moderately charred biomass, and are therefore of little diagnostic value.

MAH. Benzene, toluene, C₂ benzenes, styrene and C₃-C₁₂ alkylbenzenes accounted for 15 to 30 % of TQPA, being most abundant in the pyrolysate of Horotiu-1 charcoal (Table 2). These compounds are common products of black C and especially benzene

and toluene often dominate its pyrolysates (Kaal & Rumpel, 2009). However, they are also produced upon of many types of non-pyrogenic components. For example, toluene may, in the present study, primarily originate from protein-derived materials (particularly in Papamoa-1). Theoretically, this would invalidate the benzene/toluene ratio as an indication of charring impact (alkyl bridges between aromatic groups) (Kaal & Rumpel, 2009). The C₄-C₁₂ alkylbenzenes originate from cyclization and aromatization of straight-chain aliphatic precursors during the fire that formed the charcoal (Wiesenberg *et al.*, 2009) but also during analytical pyrolysis (Saiz-Jimenez, 1994).

PAH. Polycyclic aromatic hydrocarbons include naphthalene, C₁ naphthalenes, fluorene, pyrene and others (Table 2), contributed 7 % of TQPA in Horotiu-1 and 2.5-3.2% in Papamoa-1 and -3 (Table 2; Figure 4). Because these compounds originate primarily from condensed aromatic moieties in black C (Rumpel *et al.*, 2007), the PAHs confirm the strongest thermal impact for Horotiu-1. This is further confirmed by the naphthalene/C₁ naphthalenes ratios, 5.2 for Horotiu-1 against ca. 1.7 for Papamoa-1 and Papamoa-2 (Figure 4). The benzene/toluene ratio gives a similar outcome (Figure 4), suggesting that toluene production from protein or chitin precursors did not severely affect this ratio, but its use is considered not adequate as it may lead to false interpretations (Fabbri *et al.*, 2012). This can constitute an indication of the original degree of thermal impact when post-depositional degradation does not alter the signal (Kaal & Rumpel, 2009).

Aliphatic components. Homologous series (C₁₃-C₂₁) of *n*-alkanes and *n*-alkenes, a set of alkane and alkene fragments of unknown structure (probably including branched compounds) and C₁₆-fatty acid combined accounted for 4-7% of TQPA (Table 2). The homologous series is dominated by short-chain compounds, which may be attributed

to charring (Wiesenberg *et al.*, 2009; Kaal *et al.*, 2012). The average chain length of the homologous series was similar for the three samples, i.e. 15.2-15.3, and there is no evidence of differential chain length shortening intensities. The contribution of C₁₆-fatty acid, which is an evaporation product of un-charred biomass, is highest in sample Papamoa-1 and lowest in Horotiu-1, which is consistent with previous statements, but the degree of branching (ratio of branched to linear alkanes and alkenes) was lowest for Horotiu-1, which contradicts previous observations (Kaal *et al.*, 2012).

Other compounds. Benzofuran, dibenzofuran and benzophenone had lowest contributions in Papamoa-1, which is indicative of a relatively low thermal impact for this sample. Alkylbenzofurans gave similar contributions for the samples analysed. Phthalic anhydride and benzoic acid might correspond to oxidized black C moieties; they were most abundant in Papamoa-1. The sources of minor contributions of acetophenone, an indanone compound, a compound tentatively identified as isopropenyltoluene and an unidentified compound with dominant *m/z* 131 and 142 are unknown. Interestingly, Papamoa-2 showed traces of a Br-compound, which can be an indication of biological bromination (Leri & Myneni, 2012).

Charcoal mineralization

Throughout the + inoculum incubation, Papamoa-1 charcoal evolved more CO₂-C expressed per g of initial charcoal than Horotiu-1 charcoal (3.0 vs. 1.8 mg CO₂-C g⁻¹ charcoal; Figure 5), but differences were not significant at *P* < 0.05. During the no inoculum treatment, both charcoals exhibited similar cumulative evolved CO₂-C after 109 d (Figure 5). Total evolved CO₂-C was equal or less than 3.0 mg CO₂-C g⁻¹ charcoal (or 0.3%) in all treatments (Figure 5). The model used here fitted well with

the C turnover data (adjusted $R^2 > 0.98$, $p < 0.001$; Table 4). The estimated rapidly-decomposable C pool was always very small, with a half-life ranging between 2 and 4 d. The slowly decomposing pool had values of half-lives ranging between 60 and 72 y, with 95% confidence intervals of 61-76 y for Horotiu-1 and 58-69 y for Papamoa-1 (Table 4).

Discussion

Detailed carbon chemistry in Māori charcoals: method comparison

The different methodologies applied produced consistent results regarding the main characteristics of the C fractions in the charcoals analysed. TG-DTG analyses showed a similar thermal degradation up to 600 °C for all samples and a relative greater stability of Horotiu-1 at higher temperatures (Horotiu-1 > Papamoa-2 > Papamoa-1). This is consistent with NMR, which showed that Horotiu-1 and Papamoa-2 are composed of partially carboxylated aromatic structures with a small contribution of alkyl C while Papamoa-1 charcoal additionally contains un-charred or weakly charred lignin and polysaccharides. These differences were confirmed by the pyrolysis fingerprints, with Papamoa-1 being characterized by having a substantial contribution of recognizable and therefore un-charred or weakly charred lignin and polysaccharides, in addition to chitin from biological activity. Horotiu-1 has the largest relative proportions of MAH, PAH and benzonitriles from relatively strongly charred biomass (Kaal *et al.*, 2012) and may therefore be expected to have been subjected to a more intense charring regime. The Papamoa-2 pyrolyzate exhibited intermediate characteristics. All charcoals showed a small residual aliphatic C fraction, which probably corresponds to the alkyl C resonance in ^{13}C NMR. The

charring intensity parameters indicate a degree of polycondensation (e.g., more complete carbonization) in the order Horotiu-1 > Papamoa-2 > Papamoa-1. Note that Py-GC-MS overestimates the abundance of fungal biomass and non- and weakly-charred components, most likely because of differences in pyrolyzability between these fractions and the predominant presence of condensed aromatic C fraction which is less amenable to pyrolytic fragmentation. This is in agreement with the low level of mineralization of the charcoal C after 15-week of incubation (< 0.5%; Figure 5) suggesting that the actual survival of these materials can be related to an inherently stable chemical composition. Similar mineralization levels have been reported from 50-d incubations of manufactured charcoals in sand (Cheng *et al.*, 2008). Incubations in sand of fresh, low temperature, wood-derived chars for a period of 150 d, also rendered a relatively low level of mineralization (< 2%) of charred-wood C produced at temperatures below 350 °C (Baldock & Smernik, 2002).

The inferred differences in thermal impact of the charcoals investigated here can be explained as follows. Horotiu-1 charcoal was found in the basal layer of a puke feature (Hoffmann, 2011), which also contained pebble-to cobble size heat-altered oven-stones used by Māori people. In contrast, Papamoa-1 and Papamoa-2 charcoals were associated with remains of slash-and-burn practices considered key for the initial stages of development of the ancient gardens studied (Gumbley, 2011a; b), which apparently produced charcoal at lower intensity, presumably at lower temperatures.

Comparison of elemental composition and XPS assists in elucidating the spatial distribution of C fractions within the charcoal particles (Figure 2; Tables 1 and 3). For all charcoals, the O/C_{org} atomic ratio obtained from XPS was higher than that calculated from the elemental analysis of the bulk sample (Table 1, Table 3), indicating that the oxygen tends to be distributed at the surface, in agreement with a

dominance of oxidized surface functional groups. However, a surface contribution from the mineral matter cannot be discarded, as the ash content obtained from the elemental analysis and XPS were very similar for Horotiu-1 and Papamoa-1, whereas for Papamoa-2 XPS data indicated a higher surface concentration of ash (mainly as SiO₂).

It is concluded that the aromatic C moieties in the charcoals were relatively oxidized. Freshly-produced biochars do not show such elevated content of O-containing functional groups, unless if specifically targeted through surface activation procedures (Hina *et al.*, 2010). A relatively high degree of surface oxidation, comparable to that one found in the charcoals investigated here, has also been found in charcoals of different ages from Brazilian Anthrosols (Liang *et al.*, 2008).

In this study it was found that the Horotiu-1 charcoal, found in a deposit of ≈ 329 y BP of age, and possibly produced at a relatively high temperature, had no evidence of microbial degradation, although surface oxidation was evident. The original soils were often dry during summer (Hoffmann, 2011), forming a hard layer that may have hampered the downward water flow thus favouring seasonal wetting-drying cycles. These changes in redox conditions may have enhanced the formation of carboxylic C content, as reported by (Cao *et al.*, 2006) working with Neolithic charred material.

Papamoa-1 and Papamoa-2 are relatively old chars (> 680 y BP) with noticeable amounts of markers of chitin and possibly that of an organobromine compound (Figure 4; Table 2), which suggests some microbial (oxidative) activity. As indicated above, Papamoa-1 and Papamoa-2 were presumably formed at relatively low temperature (less carbonization, less condensed aromatic structure), and therefore being more prone to microbial attack than Horotiu-1. Thus, while this explains the presence of microbial fingerprints, it does not help understand the long-term stability

shown by this poorly charred material. Both samples were found in visible layers of large charcoal particles buried under shifting sand dunes (Gumbley, 2011a; b). It is thus hypothesized that, while the charcoal particles were at the soil surface they were partly decomposed, but this decomposition was drastically slowed down after burial. The effect of the tephra, common in the soil where Papamoa-1 was located (Gumbley, 2011a), deserves further attention.

Limitations to the use of charcoal-C studies in understanding biochar stability

The study of archaeological charcoals to infer information on the long-term biochar-C stability in soil presents specific shortcomings of using this approach (e.g., lack of knowledge of the extent of carbon loss prior to sampling). The original biomass type, degree of charring, the environmental conditions as temperature and water content, and the type of soil where the biochar is applied are key factors influencing biochar-C longevity once deployed (Knicker, 2011). The charcoals under study differed widely in key properties related to C stability: the Horotiu-1 underwent a relatively high thermal impact, whereas Papamoa-1 was poorly carbonized. All had in common a long-term post-depositional exposure to biotic and abiotic oxidation under similar environmental conditions.

Mean residence times (MRT) for the slow-decomposable pool of C when incubated under ideal conditions ranged between 87 and 104 y, which are comparable to those reported in recent publications on fresh biochars produced at relatively low temperatures (Singh *et al.*, 2012; Wang *et al.*, 2012). No differences in MRT among samples were detected, in spite of inferred differences in thermal impact. It is evident that longer incubations are needed for a better prediction of MRT and to discern differences between types of charcoals. Nonetheless, (i) the location and nature of the

O groups (surface vs. internal; phenolic vs. carboxylic), (ii) the role of sources of recalcitrant C as aliphatic moieties, and (iii) porosity differences between charcoals affecting microbial access to the substrate, may have also had a role in mitigating differences in MRT among samples.

Conclusions

Elemental analysis, thermogravimetric analysis (TG), X-ray photoelectron spectroscopy (XPS), solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) and pyrolysis gas chromatography-mass spectroscopy (Py-GC-MS) gave explicable results on describing the characteristics of the C fractions in the charcoals of different age. The charring intensity parameters obtained by Py-GC-MS and NMR were lowest for the oldest sample (770 ± 50 y BP), which appeared to contain recognizable lignocellulosic material, indicating that un-charred or weakly charred material survived decomposition processes for several centuries. Surface deposition of Papamoa-1 and Papamoa-2 through slash-and-fire activities followed by the burial of these charcoals in an active sand dune system may explain (i) the presence of markers of microbial activity (e.g. chitin) and (ii) the subsequent preservation of un-charred or weakly charred material through post-depositional protection mechanisms such as anoxia (either permanent or seasonal). The amount of organic C mineralized in 109 d was $<0.5\%$ of initial charcoal-C. No differences in MRT among samples were detected, in spite of inferred differences in thermal impact. More research is needed to assess the importance of underlying biological processes contributing to biochar chemical and biological degradation.

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FIGURE CAPTIONS

Figure 1 Thermogravimetric (TG) and derivative (DTG) curves of the charcoals: H-1 is Horotiu-1, P-1 is Papamoa-1 and P-2 is Papamoa-2.

Figure 2 X-ray photoelectron spectra for (a) survey spectra and (b) C 1s core level of the charcoals: H-1 is Horotiu-1, P-1 is Papamoa-1 and P-2 is Papamoa-2.

Figure 3 Solid-state CPMAS (cross polarization, magic angle spinning) ^{13}C NMR spectra of the charcoals: H-1 is Horotiu-1, P-1 is Papamoa-1 and P-2 is Papamoa-2. *, spinning side bands, SBBs, from aromatic C.

Figure 4 Total ion current pyrograms of charcoals. Numbers refer to pyrolysis products in Table 2. Ratios of pyrolysis products (benzene to toluene, naphthalene to C_1 naphthalene and benzonitrile to C_1 benzonitrile) are reported. * indicates a peak that is mostly related to contamination and not a real pyrolysis product.

Figure 5 Cumulative carbon mineralization ($\text{mg CO}_2\text{-C g}^{-1}$ charcoal-C) of charcoal samples (H-1 is Horotiu-1, P-1 is Papamoa-1), incubated at 28 °C for 109 d. Treatments: presence (+ inoculum) and absence (no inoculum) of soil inoculum. Values are the mean $\pm$ standard error of mean (n=4).

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580 **TABLES**

581 **Table 1** Chemical characteristics of the Māori charcoals. Radiocarbon age indicates the age of the layer where charcoal was sampled.

Charcoal	Radiocarbon Age (y BP)	pH	EC ^a mS m ⁻¹	C _{org} ^b	N ^b	H ^b	O ^b	Ash ^{b,c}	Fix. C ^{b,d}	VM ^{b,e} %	Moist. ^f %	Atomic ratio (bulk charcoal)	
												H/C _{org}	O/C _{org}
Horotiu-1	329±30	5.0	2.4	485	4	20	248	244	272	31.7	16.8	0.48	0.38
Papamoa-1	770±50	6.0	1.7	613	4	27	267	88	381	35.4	17.7	0.52	0.33
Papamoa-2	681±30	5.5	4.0	609	10	22	243	116	322	38.3	17.8	0.43	0.30

582 ^a Electric conductivity

583 ^b Dry basis.

584 ^c At 900 °C

585 ^d Fixed C

586 ^e Volatile matter

587 ^f Moisture

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589 **Table 2** Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) products,
590 fragment ions for quantification, tentative biocomponent assignment (group) and
591 relative contribution (TPQA, total quantified peak area) for charcoal samples.

n	Pyrolysis product	Group	RT ^a	m/z	TPQA		
					Horotiu-1 %	Papamoa-1 %	Papamoa-2 %
1	Acetic acid	Carbohydrate	1.236	60	5.04	4.17	4.47
2	Furan compound	Carbohydrate	1.247	82	5.92	4.59	3.85
3	Benzene	MAHs	1.366	78	12.04	3.54	4.95
4	n-Methylpyrrole	N Compounds	1.543	80+81	1.65	0.57	1.05
5	Pyridine	N Compounds	1.590	79	3.19	2.38	4.29
6	Pyrrole	N Compounds	1.595	67	1.32	0.95	1.42
7	Acetamide	N Compounds	1.601	59	0.00	0.33	0.32
8	Toluene	MAHs	1.704	91+92	8.89	5.86	8.03
9	2-Furaldehyde	Carbohydrate	1.803	95+96	0.27	1.94	2.07
10	Furan compound (2-methylfuran?)	Carbohydrate	1.902	82 (+53)	1.70	1.17	1.09
11	3-Furaldehyde	Carbohydrate	1.902	95+96	11.81	9.17	8.99
12	C1-Pyrrole (DP) ^c	N Compounds	2.047	80+81	1.42	2.35	2.15
13	C1-Pyridine	N Compounds	2.151	93+66	0.97	0.68	0.92
14	C2-Benzene (DP)	MAHs	2.256	91+106	2.39	1.45	1.86
15	Styrene	MAHs	2.391	78+104	1.44	1.06	1.35
16	C2-Benzene	MAHs	2.422	91+106	1.05	0.97	0.80
17	5-Methyl-2-furaldehyde	Carbohydrate	2.775	110+109	2.92	4.85	4.34
18	C3-Alkylbenzene	MAHs	2.879	91	0.33	0.27	0.29
19	Benzonitrile	N Compounds	2.942	103+76	3.33	0.50	1.51
20	Phenol	Phenols	3.020	94+66	3.62	5.57	7.94
21	Unidentified N-compound	N Compounds	3.150	95+94+66?	0.67	1.03	1.00
22	Benzofuran	Other	3.191	118+89	2.26	0.90	2.65
23	C4-Alkylbenzene	MAHs	3.451	91	2.13	0.93	1.96
24	2-Methoxy, 5/6-methylpyrazine?	N Compounds	3.581	124+123+95?	0.53	1.74	1.00
25	Indene	PAHs	3.597	115+116	0.80	0.34	0.56
26	C1-Phenol	Phenols	3.659	107+108	0.32	0.94	0.40
27	Acetophenone	Other	3.680	105+77+120	2.09	1.14	0.93
28	C1-Phenol	Phenols	3.841	107+108	0.63	1.99	1.17
29	Guaiacol	Lignin	3.901	109+124	0.12	4.34	0.25
30	Levogluconone	Carbohydrate	3.909	98+68	0.84	2.47	3.82
31	Isopropenyltoluene?	Other	4.028	117+132 (+115)	0.51	0.31	0.32
32	Unidentified carbohydrate compound	Carbohydrate	4.059	126	0.00	0.39	0.18
33	C1-Benzofuran	Other	4.169	131+132	0.53	0.46	0.51
34	Unidentified compound	Other	4.169	131+142 (+103+133?)	0.33	0.41	0.32
35	C1-Benzonitrile	N Compounds	4.189	117+90 (+116)	1.12	0.70	1.05
36	Alkane	Aliphatics	4.540	57+71	0.05	0.79	0.93
37	Alkene	Aliphatics	4.553	55+69	0.14	0.72	0.82
38	C5-Alkylbenzene	MAHs	4.678	91+92	0.31	0.30	0.29
39	Benzoic acid	Other	4.710	105+77+122	0.40	1.32	0.81
40	Unidentified carbohydrate compound	Carbohydrate	4.725	69+57	0.02	0.52	0.71
41	C1-Guaiacol?	Lignin	4.767	123+138	0.01	0.28	0.03
42	Naphthalene	PAHs	4.850	128	3.58	0.90	1.03
43	Undidentified carbohydrate compound	Carbohydrate	4.865	69+57	0.18	1.26	0.74
44	4-Methylguaiacol	Lignin	4.886	123+138	0.00	1.41	0.05
45	Chitin marker	N Compounds	4.970	109+81+137 (+95?)	0.04	0.74	0.39
46	Unidentified compound	N Compounds	5.105	91+131	0.50	0.32	0.49
47	4-Vinylphenol?	Phenols	5.131	120+91	0.12	0.61	0.46
48	C2-Benzofuran	Other	5.157	145+146	0.34	0.32	0.34
49	Alkane	Aliphatics	5.209	57+71	0.20	0.19	0.16
50	Indenone compound?	Other	5.557	104+132	0.17	0.23	0.20
51	Isoquinoline/benzonitrile derivative (Propenenitrile-Phenyl comp)	N Compounds	5.607	129+102	0.29	0.36	0.39
52	C6-Alkylbenzene	MAHs	5.625	91+92 (+162)	0.21	0.16	0.16
53	Indole	N Compounds	5.697	117+90	0.36	0.75	0.65
54	Phthalic anhydride	Other	5.718	104+76+?148?	0.83	1.83	1.52
55	Br-compound?	Other	5.791	225+223+227	0.00	0.06	0.38
56	C1-Naphthalene	PAHs	5.853	142+115	0.35	0.32	0.26
57	4-Vinylguaiacol	Lignin	5.957	150+135	0.06	0.86	0.18
58	Alkane	Aliphatics	5.968	57+71	0.16	0.00	0.11
59	C1-Naphthalene	PAHs	5.989	142+115	0.35	0.22	0.29
60	Alkene (homologous)	Aliphatics	6.020	55+69	0.16	0.18	0.26
61	Alkane (homologous)	Aliphatics	6.108	57+71	0.21	0.11	0.14
62	Syringol	Lignin	6.202	154+139	0.00	0.43	0.04

63	Alkene	Aliphatics	6.207	55+69	0.11	0.19	0.15
64	Alkane	Aliphatics	6.373	57+71	0.14	0.03	0.05
65	C7-Alkylbenzene	MAHs	6.540	91+92 (+176)	0.15	0.20	0.18
66	Biphenyl	PAHs	6.561	154(+153)	0.50	0.28	0.29
67	Alkene (homologous)	Aliphatics	6.888	55+69	0.11	0.25	0.21
68	Alkane (homologous)	Aliphatics	6.987	57+71	0.18	0.12	0.16
69	4-Methylsyngol	Lignin	7.044	168+153	0.00	0.16	0.01
70	C3-Guaiacol	Lignin	7.117	164+149	0.00	0.22	0.02
71	Levogluconan	Carbohydrate	7.299	60+73	0.49	5.70	1.05
72	C8-Alkylbenzene	MAHs	7.413	91+92	0.09	0.13	0.13
73	Dibenzofuran	Other	7.684	168+139	0.83	0.16	0.76
74	Alkene (homologous)	Aliphatics	7.725	55+69	0.10	0.25	0.18
75	Alkane (homologous)	Aliphatics	7.798	57+71	0.16	0.15	0.17
76	Alkene	Aliphatics	8.167	55+69	0.17	0.07	0.08
77	Alkane	Aliphatics	8.172	57+71	0.23	0.14	0.15
78	Fluorene	PAHs	8.198	166	0.17	0.08	0.14
79	C9-Alkylbenzene	MAHs	8.250	91+92	0.09	0.13	0.13
80	Benzophenone	Other	8.479	105+77+182	1.48	0.43	1.85
81	Alkene (homologous)	Aliphatics	8.505	55+69	0.08	0.06	0.09
82	Alkane (homologous)	Aliphatics	8.588	57+71	0.14	0.11	0.11
83	Diketodipyrrole	N Compounds	8.963	186+93	0.47	0.85	1.23
84	Alkene	Aliphatics	9.020	55+69	0.03	0.08	0.08
85	C10-Alkylbenzene	MAHs	9.035	91+92	0.09	0.11	0.12
86	Alkene (homologous)	Aliphatics	9.254	55+69	0.05	0.04	0.07
87	9H-flouren-9-one	PAHs	9.259	180+152	0.81	0.13	0.35
88	Alkane (homologous)	Aliphatics	9.332	57+71	0.18	0.12	0.09
89	Alkane	Aliphatics	9.462	57+71	0.14	0.12	0.04
90	Phenanthrene/Anthracene	PAHs	9.613	178	0.36	0.20	0.24
91	C11-Alkylbenzene	MAHs	9.748	91+92	0.13	0.11	0.11
92	Alkane	Aliphatics	9.763	57+71	0.20	0.34	0.15
93	Alkene (homologous)	Aliphatics	9.966	55+69	0.11	0.11	0.11
94	Alkane (homologous)	Aliphatics	10.044	57+71	0.12	0.10	0.09
95	Alkane	Aliphatics	10.122	57+71	0.10	0.11	0.08
96	2,5-Diketopiperazine	N Compounds	10.371	70+194	0.05	0.33	0.35
97	C12-Alkyl Benzenes	MAHs	10.533	91+92	0.06	0.08	0.09
98	Alkane	Aliphatics	10.704	57+71	0.06	0.08	0.09
99	Alkane	Aliphatics	10.933	57+71	0.14	0.23	0.09
100	C16-Fatty acid	Aliphatics	10.964	60+73	0.05	0.72	0.23
101	Alkane	Aliphatics	11.188	57+71	0.12	0.30	0.12
102	Alkane	Aliphatics	11.245	57+71	0.08	0.13	0.05
103	Alkene	Aliphatics	11.286	55+69	0.04	0.09	0.12
104	Pyrene	PAHs	11.448	202	0.11	0.04	0.07
105	Alkene?	Aliphatics	12.051	55+69	0.00	0.51	0.00
106	Alkane	Aliphatics	12.259	57+71	0.00	0.12	0.11
107	Alkane	Aliphatics	12.503	57+71	0.08	0.23	0.17
108	Alkene	Aliphatics	12.503	55+69	0.00	0.15	0.11
109	Alkene	Aliphatics	13.616	55+69	0.00	0.10	0.06

592 ^a Retention time, min.

593 ^b Benzene, toluene, ethylbenzene, styrene and xylenes.

594 ^c Double peak (two isomers).

Table 3 Percentage of oxygenated functional groups, and surface O/C_{org} atomic ratio

values of the charcoals.

Charcoal	–C-OR, %	–COOR, %	Atomic ratio, O/C _{org}
Horotiu-1	26.1	17.2	0.72
Papamoa-1	34.4	17.6	0.46
Papamoa-2	31.2	10.9	0.73

Table 4 Estimation of C turnover dynamics of decomposable fraction of C in charcoals fitted to a two component decay model. R_a^2 is the adjusted R^2 . Numbers within parenthesis give 95 % confidence intervals.

Charcoal	Treatment	C pool I ^a		C pool II ^b			R_a^2	p	C_{100y}^c
		%	$t_{1/2}^d$ (d)	%	$t_{1/2}$ (y)	MRT ^e (y)			
M1	+	0.10	2	99.9	72	104	0.987	< 0.0001	38
	inoculum				(69-76)	(99-110)			(36-40)
	no	0.09	4	99.9	64	93	0.990	< 0.0001	34
M2	+	0.13	3	99.8	60	87	0.989	< 0.0001	32
	inoculum				(58-64)	(83-92)			(30-34)
	no	0.10	3	99.9	66	95	0.995	< 0.0001	35
	inoculum				(62-69)	(90-100)			(33-37)

^a Rapidly decomposable pool.

^b Slowly decomposable pool.

^c Model-based estimation of the C remaining after 100 y.

^d Half-life.

^e Mean residence time.

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