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Short Paper

8000 yr of black carbon accumulation in a colluvial soil from NW Spain

Joeri Kaal [a,*], Antonio Martínez-Cortizas [b], Peter Buurman [c], Felipe Criado Boado [a]

[a] *Laboratorio de Arqueología del Paisaje (LAr), Instituto de Estudios Gallegos Padre Sarmiento, IEGPS-CSIC-XuGa, Rúa San Roque 2, 15704 Santiago de Compostela, Spain*
[b] *Departamento de Edafología y Química Agrícola, Fac. Biología, Universidad de Santiago de Compostela, Campus Universitario Sur, 15782 Santiago de Compostela, Spain*
[c] *ESS-CC (Earth System Science-Climate Change), Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands*

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Abstract

Analytical pyrolysis-GC/MS and solid-state ^{13}C NMR (nuclear magnetic resonance) were applied to the NaOH-extractable organic matter fraction of a colluvial soil from Galicia (NW Spain) that represents more than 8500 yr of accumulation. While molecular indicators of vegetation change were looked for, it seemed likely that any such signal was disturbed by the intense fire regime of the area. This conclusion was drawn from (1) the presence of three charcoal layers, (2) the high proportion of aryl C in NMR spectra (non-quantitative) and (3) the prevalence of benzenes and polycyclic aromatic hydrocarbons (PAHs) in the chromatograms (38±6% of total identified peak area), also in charcoal-poor samples. If this conclusion is accurate, the area has been subjected to burning episodes for at least 8000 yr. Additionally, the results indicate that biomass burning residues (black carbon; BC) may become NaOH extractable after long periods of degradation in mineral soil. These results add to our knowledge of the long-term fate of BC in soil, which is a potential agent in the global C cycle.

Keywords: Fire record; Black carbon; Pyrolysis-GC/MS

Introduction

Black carbon (BC) is the product of incomplete combustion of organic matter. It is a continuum of highly aromatic components ranging from weakly charred plant material through charcoal to soot. Black carbon is among the most recalcitrant terrestrial organic matter pools on Earth, and therefore potentially important in global C cycling (Goldberg, 1985). Nonetheless, owing to the chemical and physical diversity of BC and the related lack of a widely accepted quantification technique, the concentration and fate of BC in terrestrial soils are poorly understood (Schmidt and Noack, 2000). Degradation of BC creates problems in palaeorecords. For instance, while charring involves the loss of carboxylic functional groups (Almendros et al., 1992), the BC formed is susceptible to rapid oxidative degradation in the soil environment (Knicker et al., 2006). Consequently, the oxidation products of BC are highly aromatic carboxylated structures that are chemically similar to highly aromatic humic substances (e.g. Kumada, 1983; Haumaier and Zech, 1995; Shindo et al., 2004). The lack of straightforward evidence of a BC contribution to such humic substances is a significant limitation in our understanding of the role of fire in recalcitrant soil organic matter formation.

The Campo Lameiro area (Pontevedra, NW Spain) harbours one of the largest concentrations of rock art (petroglyphs) in the northwest of the Iberian Peninsula. By means of the creation of the *Rock Art Park of Campo Lameiro*, it is designed to become a major tourist attraction. However, the history of the area is poorly understood due to the scarcity of archaeological remains encountered in the surrounding soil. The soils comprise several meters of up to more than 8500 yr old colluvium. Stone and charcoal layers in these soils are indicative of episodes of soil redistribution by erosion/accumulation, probably linked to forest fires (Costa Casais et al., in press). The parent rock, migmatitic granite, yields large amounts of poorly crystalline aluminum hydroxides ("active Al") upon weathering, that is thought to be responsible for the stabilisation and accumulation

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[*] Corresponding author. Fax: +34 981547104.
E-mail address: joeri@samage.net (J. Kaal).

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of organic matter through sorptive processes (Carballas et al., 1967). This feature is typical of the thick organic-rich colluvial soils of NW Spain, referred to as Atlantic rankers, "cryptopodzolic Podzols" and aluminic soils which sometimes exhibit andic properties (Duchaufour, 1982; Delvaux et al., 2004; García-Rodeja et al., 2004).

Chemical fingerprinting of soil organic matter, using pyrolysis-GC/MS, did not prove to be useful for tracing vegetation changes in Campo Lameiro soil. Instead, results provide evidence of fires in the area throughout the Holocene. ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS NMR) was employed to support pyrolysis results. In addition, we aim at demonstrating the usefulness of CPMAS NMR and pyrolysis-GC/MS in studies concerning ancient BC, despite of inherent drawbacks: NMR underestimates the proportion of ^{13}C in condensed aromatic structures when CPMAS is used (Smernik et al., 2002) and an unknown fraction of BC may be non-pyrolysable or produce pyrolysis products that are not amenable to GC (Islas et al., 2002).

Materials and methods

The study site is located on an isolated hill at 320 m a.s.l. in NW Spain (U.T.M.: X: 538797; Y: 4710597). The parent rock is overlain by 40 cm of "inorganic" colluvium made of transported saprolite that dates back to the late Pleistocene–early Holocene ($C=6.4\pm4.2$ g kg^{-1} soil), and 110 cm of strongly humic colluvium ($C=72\pm34$ g kg^{-1} soil). Carbon and extractable Al contents are presented in Kaal et al. (in press), while a description of the geomorphology of the study site can be found in Costa Casais et al. (in press).

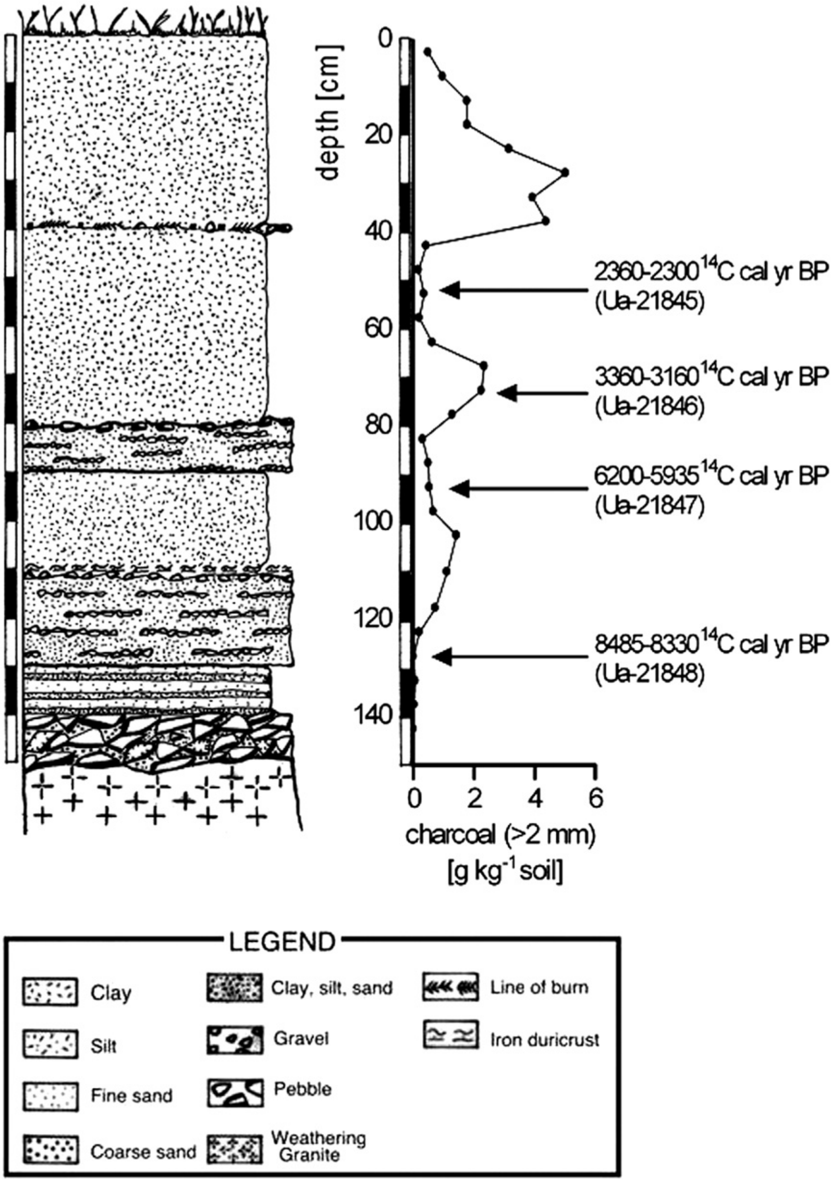

Figure 1. Soil profile (courtesy of M. Costa Casais), with to the right the macroscopic charcoal (>2 mm) profile with radiocarbon datings of the organic matter fraction (given as 2σ cal yr BP range).

A soil monolith from the surface to the base of the loose material at 145 cm was sliced into 5-cm sections to collect soil samples. An exception was made for the material between 105 and 115 cm, involving a stone layer, which was analysed as one sample. The material was air-dried and sieved over 2 mm to isolate the fine earth fraction. Macroscopic charcoal (>2 mm) was collected by means of wet sieving and weighed after drying. Figure 1 shows a representation of the soil profile, macroscopic charcoal content and radiocarbon dates of the organic matter fraction (Ångström Laboratory, Division of Ion Physics, ^{14}C-lab, Uppsala, Sweden).

Since pyrolysis-GC/MS of four selected soil samples (fine earth fraction, <2 mm) gave low-quality chromatograms and mass spectra, soil organic matter was separated from the fine earth fraction by extraction with 0.1 M NaOH for 5 min (twice) and water (3–5 times, until the supernatant was colourless) for further analysis (Nierop et al., 2001). Decanting of extracts was preceded by centrifugation at ~1000×*g* for 15 min. Extracts were then combined and acidified to pH 1.5–2.0 with HF/HCl (0.3/0.1 M), gently manipulated through a 63-μm mesh-size sieve to remove fine roots and buoyant smaller (63 μm–2 mm) charcoals, dialysed against distilled water and freeze-dried. The fine roots and the 63-μm to 2-mm charcoals accounted for a small yet undetermined proportion of non-extractable C and were omitted from analysis. Extraction yields were 82±12% of total C, as estimated from the difference of C content of the residues and that of the sample prior to extraction. The organic matter species discussed here are thus the NaOH-extractable fraction (2–123 g kg^{-1} soil; possibly containing some particulate matter <63 μm) and charcoals >2 mm (up to 50 g kg^{-1} soil; Fig. 1).

The NaOH-extractable organic matter was pyrolysed using a Curie-Point pyrolyser (600 °C) connected to a Carlo Erba GC 8000 gas chromatograph. The pyrolysis products were separated on a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51b (film thickness 0.40 μm), with helium as the carrier gas. The initial oven temperature was 40 °C, the heating rate 7 °C min^{-1}. The final temperature of 320 °C was maintained for 20 min. The GC column was connected to a Fisons MD 800 mass spectrometer (mass range *m*/*z* 45–650, cycle time 1 s). Replicates were obtained for two samples only.

The 94 pyrolysis products used for the quantification accounted for all major peaks in the total ion current. These compounds were generally quantified using the two major fragment ions. Relative response factors were assumed to be unity, which means the results are only semi-quantitative. The compounds were grouped according to their probable origin into the following component classes: benzenes *sensu lato* (benzene, C_1- and C_2-benzenes, naphthalene, C_1-naphthalene, benzofuran, dibenzofuran, biphenyl, anthracene/phenanthrene, fluorene and pyrene/fluoranthene), carbohydrates (acetic acid, 2-methylfuran, 2H-furan-3-one, 3/2-furaldehyde, 5-methyl-2-furaldehyde and levoglucosan), lipids (C_{10}-C_{33}-alkanes, C_{11}-C_{28}-alkenes, C_3-C_{20}-alkylbenzenes and a C_3-naphthalene), phenols (phenol and methylphenols), N-compounds (pyrrole, 3-methylpyrrole, diketodipyrrole, indole, pyridine, 2- and 3-methylpyridine, benzonitrile and (iso)quinoline) and lignins (guaiacol and 4-vinylguaiacol). The C_3-C_{20}-alkylbenzenes and the C_3-naphthalene showed concentration profiles that were similar to that of the lipid markers and were not found among the products of thermally assisted hydrolysis and methylation (THM; this technique can be envisaged as pyrolysis-GC/MS with preliminary addition of a methylating agent to protect functional groups from secondary pyrolysis reactions; Challinor, 2001) of selected samples (unpublished results). Therefore, these pyrolysis products were assumed to be cyclisation products of lipids (Saiz-Jiménez, 1995). We focus on the contributions of component classes rather than individual pyrolysis products to facilitate a comprehensive discussion.

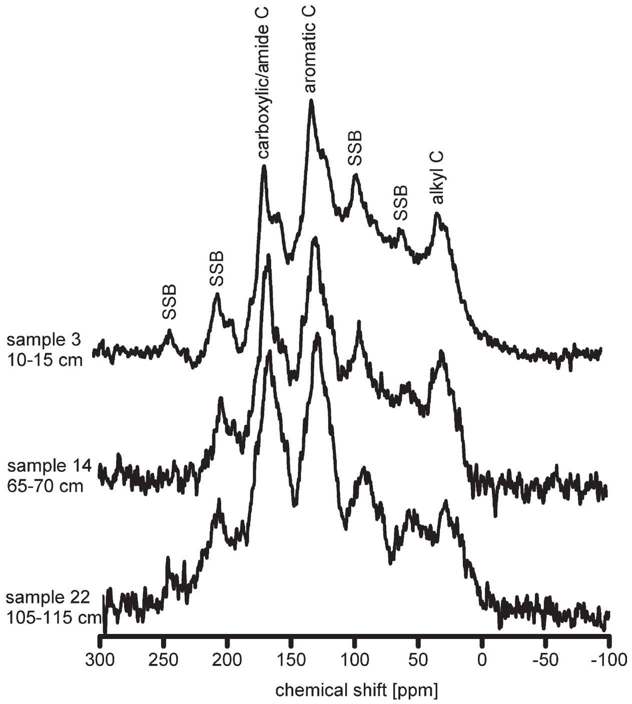

Figure 2. Solid-state ^{13}C CPMAS NMR spectroscopy of selected samples. Note the dominance of aromatic (128 ppm) and carboxyl/amide C (166 ppm). Most other peaks were not assigned due to possible overlap with spinning side bands (SSB; see text).

Solid-state ^{13}C CPMAS NMR of five selected samples of extractable organic matter was performed on an Inova 750 MHz spectrometer (Varian Inc., Palo Alto, CA, USA). Contact time was set as 1 ms, recycle delay was 1 ms and the spinning rate 7 kHz. Fourier transformation using a line broadening of 60 Hz was applied to the free induction decay files prior to manual phase and baseline corrections.

Results

The NMR spectra are distorted by significant spinning side bands (SSB) at ±74 ppm of the parent signals of aromatic (130 ppm) and carboxylic C (166 ppm; possibly including some amide C). The high degree of side-spinning is caused by the dominance of aromatic and carboxylic C (Fig. 2), which are most prone to side-spinning (Conte et al., 2004), and the high energy of the spectrometer. Although SSB can normally be easily mathematically relocated to their parent resonance, the

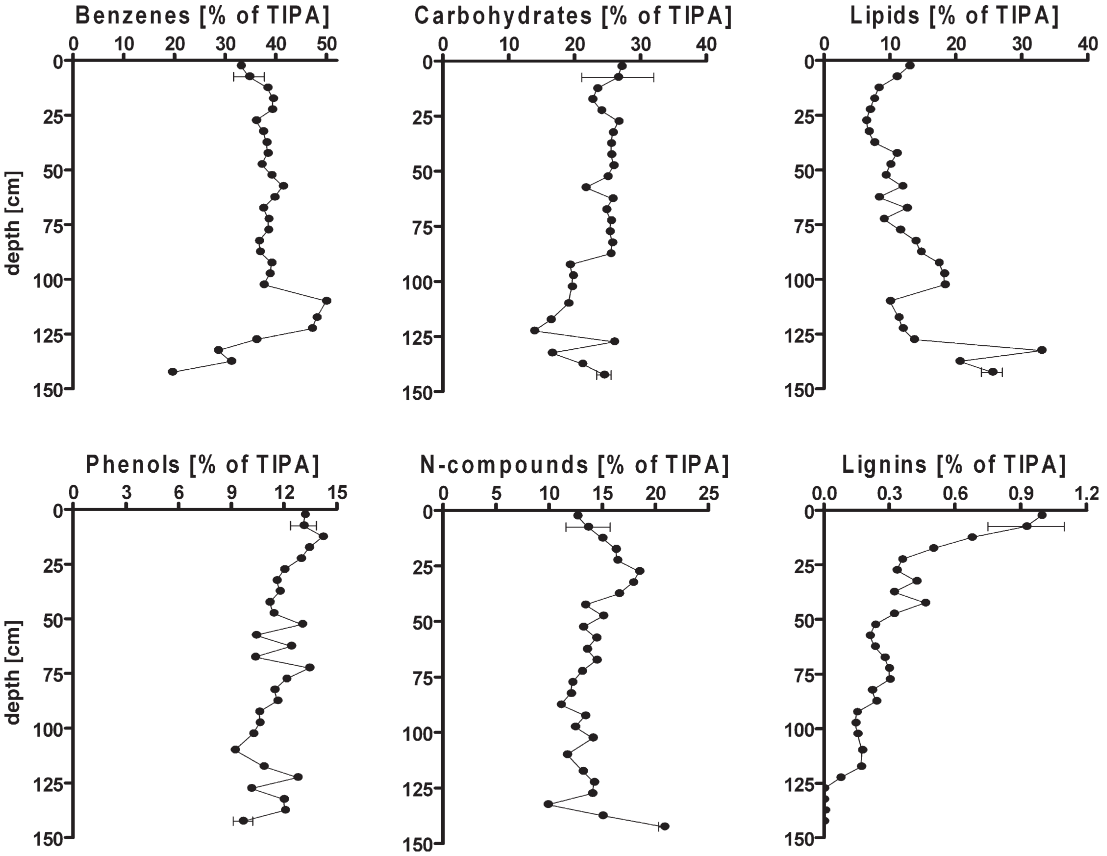

Figure 3. Component class distribution of quantified pyrolysis-GC/MS chromatograms, expressed as percentage of total identified peak area (TIPA). Note the differences in *y*-axis scaling. Error bars represent the standard error of the mean of duplicates (of two samples only).

SSB seem to have significant contributions to the remaining chemical shift regions, especially to those of di-*O*-alkyl and *O*-alkyl C (by carboxyl SSB) and methoxyl/*N*-alkyl C (by aromatic SSB), while the second order SSB of carboxyl C may even bias methyl C estimations (at 20 ppm). Hence, these results are not quantitative and serve only as evidence of the unusually large contribution of aromatic and carboxylic C.

The pyrolysis component class distribution confirms the large quantity of benzenes (Fig. 3). Three samples in the lower part of the profile display a benzenes contribution approaching 50% of total identified peak area. Carbohydrates have a significant contribution, even in the oldest samples at the bottom of the profile. The contribution of levoglucosan is 2.5% at the surface but it disappears towards the bottom of the profile ($r^2=0.75$, $P<0.001$, $n=30$; data not shown). The remaining carbohydrate markers are essentially furans (including furfurals), i.e. heterocyclic aromatic compounds. The lipid component class is dominated by *n*-alkane/alkene doublets. Lipids increase with depth ($r^2=0.50$, $P<0.001$, $n=30$) and thus age. Major negative excursions from this depth trend coincide with elevated macroscopic charcoal contents ($r^2=0.30$, $P<0.01$, $n=30$). Nitrogen-containing pyrolysis products are abundant (14.4±2.6%), despite of the poor observability of proteinaceous structures in complex mixtures using conventional pyrolysis-GC/MS (Chiavari and Galletti, 1992). Phenols show a small gradual decrease with depth. The soil is virtually devoid of lignin markers (0.30±0.28%). The lignin signature declines exponentially with depth.

Discussion and conclusions

As shown by ^{13}C CPMAS NMR, the main features of the organic matter are the preponderance of aromatic and carboxylic C. Using pyrolysis-GC/MS, benzenes are also the main component class, but pyrolysis products with carboxylic groups are scarce. The latter is presumably due to decarboxylation during the pyrolysis step (Martín et al., 1994) or the poor chromatographic properties of polar compounds in a non-polar GC column (Dignac et al., 2006). Indeed, preliminary experiments using THM showed large peaks of the methyl esters of benzenecarboxylic acids with up to six carboxylic groups. We believe that the benzenes, of which an unknown fraction is heavily carboxylated, represents the pyrolysis of partially oxidised BC.

One explanation for the inverse relation between the contribution of NaOH-extractable compounds yielding aliphatic pyrolysis products and macroscopic charcoal content is the selective consumption of lipid biomolecules during a fire. The effect of fire on lipids is highly variable, and Fernández et al. (2001) inferred that the lipid fraction may consist of a thermally labile and a fire-resistant fraction.

The N-containing pyrolysis products were mainly benzonitrile and heterocyclic aromatic N-compounds (92±3% of the total contribution of N-compounds), which are reportedly associated with charring (Alcañiz et al., 1994; Almendros et al., 2003; Knicker et al., 2005). Lignin markers are virtually absent

(<1.0%), which can be attributed to the loss of the methoxyl functionality during charring (González-Pérez et al., 2004), confirmed by the weak signal of methoxyl C (ca. 45–60 ppm) in the ^{13}C NMR spectra.

From the pyrolysis-GC/MS analyses, the carbohydrates were mainly furans. Although these products may form upon the pyrolysis of intact cellulose, the small contribution of the latter's dominant pyrolysis product, i.e. levoglucosan (Poirier et al., 2005), indicates that the carbohydrates had lost most of their (di-)*O*-alkyl C groups. Therefore, the carbohydrate compartment is strongly degraded. The extensive rearrangement of carbohydrate structures to furan-based (hence aromatic) structures is a well-known product of charring when analysed by pyrolysis-GC/MS (e.g. Pastorova et al., 1994) or ^{13}C NMR (Baldock and Smernik, 2002). Alternatively, the degraded state of the carbohydrate class indicates non-thermal (e.g. microbial) degradation. The decreasing levoglucosan contribution with depth very likely represents the decay of uncharred polysaccharide material.

Altogether, we consider the pyrolysis-GC/MS fingerprint indicative of the presence of large amounts of NaOH-extractable BC. We are not aware of any process other than charring to cause the accumulation of highly aromatic organic matter dominated by domains of benzenes and PAHs (38 ± 6% of total identified peak area), heterocyclic N compounds and benzonitrile. The sum of these probably BC-derived pyrolysis products is 51 ± 6%. This is of course only a rough estimate of BC content due to the possible BC origin of the furans and aforementioned drawbacks in the pyrolysis-GC/MS technique. We consider pyrolysis-GC/MS capable of assessing BC in NaOH-extractable organic matter, but obviously not for its quantification. CPMAS NMR and pyrolysis-GC/MS are more likely to under represent BC than overestimate its proportion because of the lack of protons for ^{1}H-^{13}C cross polarisation in condensed aromatic structures and the possible formation of a non-pyrolysable residue, respectively.

The pyrolysates of the samples from the bottom of the profile (125–145 cm) exhibit lowest benzenes (Fig. 3) and total aromaticity contributions (not shown), which may indicate the absence or a smaller contribution of BC to the organic matter. The sample taken at a depth of 125–130 cm was dated 8435–8330 cal yr BP. Therefore, we hypothesise that the area was subjected to at least 8000 yr of burning episodes.

Some studies in Galicia showed that charcoal layers coincide with periods of known human activity from the mid-Holocene onwards (Martínez Cortizas et al., 2005). Radiocarbon dating combined with pyrolysis-GC/MS suggests that also before that time (ca. 8000 BP and after), fire had an important effect on the soil and landscape evolution. Whether the fires were natural or produced by past societies has yet to be elucidated. Additionally, the abundance of highly aromatic organic matter in almost all samples indicates that the macroscopic charcoals provide an incomplete picture of the fire history.

Finally, the results invoke the question whether the large amount of "active Al" is responsible for the long-term stabilisation of the organic matter in the study area (see Introduction). A complementary cause is that the carboxylic groups on the intrinsically recalcitrant BC-derived organic matter, combined with its large surface area and porosity, allows it to undergo strong interactions with mineral phases, thereby further protecting the BC against biodegradation (Brodowski et al., 2005; Knicker et al., 2006). The sorptive interaction between heavily functionalised BC-derived recalcitrant organic matter and "active Al" could perfectly explain why thousands of years old material exhibits organic C contents of up to 14% in a humid temperate climate such as that of Galicia.

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