**Medium term effects of fire induced soil organic matter alterations on Andosols under
Canarian pine (*Pinus canariensis*)**

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ABSTRACT

Andosols are characterised by high organic matter (OM) content defining the specific properties of these soils and representing an efficient carbon (C) sink within the global C cycle. In the present study, the medium-term alterations of the soil organic matter (SOM) pool of the topsoils of burnt and unburnt Andosols taken eleven years after a severe wildfire were evaluated. The soils derived from *Monte la Esperanza* in Tenerife Island, Spain and were covered predominantly by *Pinus canariensis*. The double shot pyrolysis Gas Chromatography/Mass Spectrometry (GC/MS) was applied after optimising the suitable temperatures by thermogravimetry. Analytical pyrolysis was complemented by solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy. Soil OM content decreased harshly in fire-affected soil, leading to a noteworthy reduction of the water holding capacity. Generally, surface horizons of control and burnt Andosols have a rather similar SOM composition as analysed by Py-GC/MS. In addition, this technique illustrated i) the presence of markers of conifers and angiosperms in the burnt soil, which points to the recovery of the vegetation; ii) the increase in short chain *n*-alkanes due to thermally induced breakdown processes during fire; iii) the dominance of furans in contrast with the low contribution of C6-based polysaccharide specially in the BS indicate the alteration of the carbohydrates, and iii) a relative enrichment of aromatic compounds released at 600 °C in the burnt soil when compared to that unaffected by fire. The latter points to the formation of black carbon like

material during the fire event, which was also detected by thermogravimetric analyses and evidenced by the increase in the signal in the aromatic region of the ^{13}C NMR spectrum.

The high content of polysaccharides derived products and the low alkyl C /O-alkyl C ratio determined by NMR spectroscopy in the fire affected soil clearly indicate the inputs of plant material during the post fire recovery time.

The results suggest that the severe wildfire causing the loss of large quantities of organic C which decreased the recalcitrant C pool but also led to a destruction of the A horizon to an extent unexpected for fire-affected soils without andic properties. Although this study cannot exclude that the present A horizon contains still pre-fire remnants, analytical pyrolysis complemented by NMR spectroscopy provided strong evidence that post-fire pedogenesis determined the quality of its SOM. Most tentatively a quick development of a new vegetation cover prevented a complete removal of the mineral soil by erosion and provided enough new organic material for a fast partial recovery of the C stocks in the A horizon.

Keywords

Wildfire, analytical pyrolysis, black carbon, ^{13}C NMR spectroscopy, thermal cracking, pyrophyte

INTRODUCTION

Soils in the northern slopes of the Tenerife Island (Canary Islands; Spain) are mainly allophanic Andosols, which are usually formed from volcanic substrates, having a typical thick dark-colored A horizon (melanic epipedon) [1]. They accumulate high quantities of organic carbon (80–300 g C kg⁻¹) [2], occurring mainly in the form of stabilised humic material. The peculiar properties of these variable-charge soils are due to the occurrence of poorly crystalline materials such as allophanes, imogolite and other Fe and Al oxyhydroxides. Such materials are prone to form organo-mineral structures with a high degree of stability. All those facts contribute to a strong resistance to water erosion and an efficient protection of organic C against microbial decomposition [3]. Despite their small contribution to the total of soils in the world, their C sequestration potential is essential for the global C cycle. On the other hand, during vegetation fires, the characteristic high amount of organic matter (OM) in their A horizons provides an efficient fuel which can easily be combusted. This is in contrast with non-andic soils in which the low heat conductivity of the mineral phase prevents the occurrence of temperatures high enough for OM combustion. Therefore fire over Andosols constitutes an additional risk to destroy the protecting topsoil and subsequently promotes erosion.

A further unique condition of most forest systems growing on the Andosols on the Tenerife Island is that they sustain Canary pine (*Pinus canariensis*) forest-type vegetation, which is endemic to the Canary Islands. They are still well preserved ecosystems and the only noteworthy natural disturbances affecting them are wildfires. This pine is one of the most fire-resistant conifers in the world due to its pyrophytic characteristics. For instance, its bark is thick and formed by different layers of hard wood which protect the tree from an occasional forest fire. The new shoots can grow directly from the lower trunk, and the cones frequently remaining closed for several years (serotinous cones) are opened usually as a consequence of fire. Canary Pine trees can often rejuvenate themselves and sprout again even though they have been burned in forest fires [4].

71 In general, the effect of fire on the SOM content is very variable and greatly depends upon
 72 the fire intensity and the accessibility and size of the fuel load [5-9]. They range from a total
 73 destruction of the OM after very intense fires to increases of up to 30% in the surface layers
 74 [10]. In addition to alteration of the size of the OM pool, fire can change its quality. It is
 75 generally accepted that fire leads to the formation and accumulation of condensed products,
 76 commonly referred to as black carbon (BC) [11]. This material is assumed to have a high
 77 biochemical recalcitrance and thus to contribute to the long term C and N sequestration in
 78 soils [12]. Previous studies devoted to the effect of fire in andic soils are very scarce and
 79 were mostly dedicated to the fast changes in physical properties, mineralogical or elemental
 80 composition [13, 14]. Only few is known about the effects of BC input on the quality, quantity
 81 and function of OM in soils with andic properties. Thus, in order to fill this gap, we used
 82 analytical pyrolysis complemented by elemental analysis, thermogravimetry and ^{13}C nuclear
 83 magnetic resonance spectroscopy to decipher fire induced alterations of SOM in an Andosol
 84 from Tenerife Island, which was affected by fire in 1995. Thermal analysis methods and
 85 specifically thermogravimetry-differential scanning calorimetry (TG-DSC) was applied to
 86 determine bulk changes in the OM fractions in terms of thermal stability [11]. Soil OM can be
 87 divided in three groups according to resistance to thermal oxidation [15]: labile OM (200–380
 88 °C), recalcitrant OM (380–475 °C), and refractory OM (475–650 °C) respectively, which
 89 includes BC. The results of the TG-DSC have been used to decide the temperatures at
 90 which analytical pyrolysis was carried out. A two-step analytical pyrolysis (Py-GC/MS) was
 91 developed at 340 °C and 600 °C (desorption and pyrolysis step respectively) in order to
 92 improve the chemical characterization of the SOM. In general, the pyrochromatogram
 93 provides information on macromolecular structures [16], however the double shot pyrolysis
 94 allows thermal desorption of samples (at sub-pyrolysis temperature) prior to pyrolysis, and so
 95 allows the sequential examination of the products released by thermal desorption and by
 96 thermal cracking from the same sample [17]. This technique has been recently useful to
 97 detect fire effects on Mediterranean soils [5, 17] and to monitor their recovery [18]. Solid-
 98 state ^{13}C nuclear magnetic resonance spectroscopy (CP MAS ^{13}C NMR) was applied to

complement the pyrolysis data by providing information about the bulk chemical composition of the samples [19].

2. AREA OF STUDY AND METHODOLOGY

2.1 Area of study and sampling

Samples for this study were taken in February 2007 in the “*Monte la Esperanza*”, located in the northern slopes of the island of Tenerife (latitude: 28°25' 44" N; longitude: 16°23'40" W) with an average slope between 10–15 % and an altitude of 1,333 m above sea level. This zone is under the influence of the *alisio* trade winds and is characterised by a thermo-Mediterranean mesophytic subhumid bioclimate [4], with average precipitation of 730 mm year⁻¹. The mean annual temperature is 16 °C and the potential evapotranspiration is 750 mm year⁻¹ [20]. The soil is an Andosol, with volcanic origin, and its evolution is closely related to weather conditions. The location of the sampling site in the Island of Tenerife is shown in Fig. 1. This area was affected by an intense wildfire, starting on the 21st of July 1995 and burning around 2,000 ha during one week.

The vegetation is dominated by *P. canariensis*, with nearly 80 % coverage in the fire-affected area and is composed of very old (up to 700 years old) and tall trees (20–30 m). The understory is dominated by *Erica arborea* and *Cistus symphytifolius*.

The experimental design was based on sampling a fire-affected soil (BS) and a neighbouring site unaffected by fire, which was used for comparative purposes (CS). In both cases, composite soil samples were prepared by combining four sub-samples taken within an area of ca. 20 m² from the fire affected and unaffected site. Samples derived from the first 10 cm of soil after removal of the litter layer. The soil material was then transported in glass containers, dried at room temperature, sieved to fine earth (<2 mm) and homogenised for analytical determinations.

2.2 Elemental and physical analysis

Soil pH in water (soil-water ratio 1:2.5) was measured with a Crison microPH 2000 pH meter. Total C and N were determined in duplicates by dry combustion (975 °C) using an Elementar Vario EL microanalyser detecting N as N₂ and C as CO₂. Organic carbon was eliminated from the bulk soil by combustion for 4 hours at 450 °C [20] in a muffle oven and the remaining inorganic carbon (IC) was identified by elemental analysis. Total organic carbon (TOC) was then estimated as the difference between TC and IC, after considering the weight loss. In addition, the maximum water-holding capacity (WHC) of the samples was measured in triplicate according to [21]

2.3 Thermogravimetric analyses

TG-DSC was carried out using a Netzsch STA 449C Jupiter thermal analysis system in which the gas outlet is coupled by a capillary via a PDZ ANCA S/L interface module to a PDZ Europa 20:20 isotope ratio mass spectrometer system. The soil sample (30mg) was placed in an Al₂O₃ crucible, and heated at 20 °C min⁻¹, from 30 to 650 °C under a flow of 20% O₂ in He (50 cm³ min⁻¹) and from 650 to 1000 °C under a flow of He only. The TG and DSC signals were exported to the NETZSCH software for analysis versus temperature.

2.4 Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

A double-shot pyrolyser PY2020iD (Frontier Lab Ltd., Fukushima, Japan) attached to a GC/MS system Agilent 6890 was used. For bulk soils (control and burnt), 1 mg of each sample was placed in small crucibles. In the case of samples demineralised with 10% hydrofluoric acid, approximately 0.7 mg were used. A two-step pyrolysis was developed for this study. In a first step, a thermal desorption was settled by increasing the initial temperature of 100 °C at a rate of 20 °C min⁻¹ to a final temperature of 340 °C which was kept for 3 min. In a second step, the sample was heated at pyrolysis temperature of 600 °C for 1 min. The GC/MS conditions were the same for both desorption and pyrolysis experiments. The GC was equipped with a split-less injector, and a fused silica capillary column DB5 MS (J&W Scientific) (30 m×250 µm× 0.25 µm film thickness). The oven

temperature was held at 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 300 °C for 10 min. The carrier gas was helium with a flow rate of 1 mL min⁻¹. The detector consisted of an Agilent 5973 mass selective detector and electron impact mass spectra were acquired with a 70 eV ionizing energy measuring fragments in the m/z 50–500 range. The length of the capillary column was shortened in 30 cm due to cleaning and maintenance purposes before the measurement of the HF-treated soils. The identification of individual compounds was carried out by ion chromatography for different homologous series, low-resolution mass spectrometry and comparison with published and stored data (NIST 05 and Wiley libraries).

2.5 ¹³C NMR spectroscopy

The solid-state NMR spectra were obtained using the variable amplitude cross polarisation magic angle spinning (CPMAS) technique using a Bruker DSX 200 with a ¹³C Resonance frequency of 50.3 MHz. To concentrate the OM and to remove paramagnetic material, the bulk soil samples were treated with 10% (v/v) hydrofluoric acid (HF) prior to solid-state NMR analysis. This is a useful approach to increase the signal-to-noise ratio of solid state ¹³C NMR spectra of soils and to reduce interference from paramagnetics [22]. In brief, dry sample material (10 g) was filled in polyethylene bottles and treated with HF (50 mL). After stirring for 2 hours and centrifugation the supernatant was discarded. The procedure was repeated five times and subsequently, the demineralised samples were washed with deionised water to remove excess salts and finally freeze-dried. As shown in earlier studies, no NMR detectable changes in the OM composition are induced by this treatment performed at room temperature [19, 22]. Frequently, alterations of the intensity distribution of CPMAS NMR spectra of bulk soils are observed. They are caused by selective reduction of the cross polarisation efficiency and thus of signal intensity of carbons which are in close neighbourhood to protons interacting with paramagnetic iron. A more detailed description of the theoretical background of this fact is given in Knicker et al [19]. After the

HF treatment, the remaining soil material accounted for 26.1 ± 0.2 % (BS_HF) and 46.3 ± 3.6 % (CS_HF), comprising 79 % and 90 % respectively of the initial OC content.

The samples were confined in a zirconium oxide rotor with an external diameter of 7 mm. Applying a contact time of 1 ms, between 5,000 and 10,000 scans were accumulated using a spinning speed of 6.8 kHz and a pulse delay of 300 ms. The ^{13}C chemical shifts were referenced to external tetramethylsilane (= 0 ppm) and adjusted with glycine (= 176.04 ppm) as an external standard. For quantification, the spectra were subdivided into different chemical shift regions according to [22]: alkyl C (0–45 ppm), *N*-alkyl/methoxyl C (45–60 ppm), *O*-alkyl C (60–110 ppm), aromatic C (110–160 ppm), carboxyl/amide C (160–185 ppm) and carbonyl C (185–245 ppm). The relative ^{13}C intensity distribution was determined by integrating the signal intensity in different chemical shift regions with an integration routine supplied with the instrument software. Corrections concerning the intensity distribution of spinning side bands were made [5]. On the basis of these data, the ratio of *O*-alkyl C/alkyl C is calculated as indicator of the degree of OM decomposition and alteration [23].

3 RESULTS AND DISCUSSION

3.1 Elemental and Physical Fire-Induced Alterations of the Soil

As shown in Table 1, the organic C and N contents of the burnt soil (BS) are about 50% and 45% lower than those determined for fire-unaaffected soil (CS). The latter exhibits typical C and N contents for Andosols, characterised by a high organic C content (80 to 300 g kg⁻¹) due to stabilisation of OM by short-range ordered minerals (allophane, imogolite, and ferrihydrite), which have a large surface area capable of adsorbing organic molecules or forming Al-humus complexes [1]. Considerable organic C and N losses have been reported for soils affected by high severity fires [8, 12, 24] and for soils heated under laboratory conditions (>50 % organic C loss at 220 °C; [25]) due to release of combustion gases and small volatile degradation products. In natural environments, additional post-fire losses of OM can occur because of the removal of the protective litter and vegetation cover, thus intense fires turns the soil highly vulnerable to splash and entrainment by overland flow,

which have been reported in the study area [26]. The C/N ratios were similar in both samples (16.3 for BS and 17.6 for CS; Table 1), whereas the WHC decreased strongly (~40%) as a direct consequence of the disappearance of OM (Table 1). In acid soils, the release of hydroxides, carbonates, and numerous cations by the ashes from plant tissues [13, 14] contribute to an increase in their pH which can cause a further loss of organic acids after the fire [7, 27]. A slight increase from 5.8 in the CS to 6.3 in the BS was also observed at our study site. Greater changes have been reported by other authors, being attributed to the so-called liming effect [28]. The liberation of minerals together with the liming effect [26] is likely to have contributed to a fast vegetation recovery, which could have mitigated further OM loss by erosion.

3.2 Thermogravimetric Analyses

Thermogravimetric measurements show a lower total weight loss in BS (31.1%) than in CS (49.9 %) (Fig. 2). This result is in agreement with the greater content of OC in CS than in BS. In addition to the observed weight losses, in both samples, DSC exothermic peaks at 250 to 350 °C (Fig. 2) can be attributed to decomposition of labile materials, including depolymerisation of cellulose molecules. This is typically reported for the thermal analysis of higher plants [29] and indicates the recovery of the vegetation in the BS. Peaks at 400–500 °C are attributed to combustion of recalcitrant OM [30]. Both samples also show an endothermic peak at 70–90 °C that can be explained by a loss of water from clays. The only qualitative difference between the DSC traces of the fire-affected and unaffected soil is a shoulder at 500–550 °C in the thermogram of BS that may indicate the presence of BC-like material.

3.3 Analytical Pyrolysis

Product distributions corresponding to the total ion current chromatograms (TIC) of bulk and HF-treated soils of the desorption (340 °C) and pyrolysis (600 °C) step are presented in

Figures 3 and 4 respectively. Identified compounds are separated in groups according to their source or structure and are listed in Table 2.

3.3.1 First shot (340 °C)

The first thermal input, at sub-pyrolysis temperature, usually releases compounds associated through low thermal stability links, loosely joined to the macromolecular structure of the thermostable material [11]. As observed for the untreated and HF-treated Andosols, the fire-unaaffected soils released a greater amount of pyrolysis products than the burnt soils (Fig. 3). Although variations in distributions can be noted (especially a strong decrease in C2 and C3 abundances), the same pyrolysis products are detected in bulk and HF-treated samples. They are dominated by carbohydrate compounds (C), lignin-derived compounds (L), doublets of *n*-Alkane/*n*-alkene and aromatic compounds (A). The major differences caused by the HF treatment in the pyrochromatograms are the relative increase in some short-chain *n*-alkanes/enes and the presence of a number of terpenoids.

Carbohydrate-derived products are considered thermally-labile soil OM compounds-[31]. Furans and furfurals may originate from fresh and/or degraded carbohydrates [32]. However, the dominance of 2-furaldehyde and 5-methyl-2-furaldehyde (C2 and C3; Fig. 3) indicate degradation of the polysaccharide fraction [33]. D-glucopyranose and specially D-allose (C7 and C11 respectively) largely originate from polysaccharides being protected against thermal degradation [34]. Their absence in the BS confirms that fire altered the polysaccharidic structures. In general, there is a dominance of furans, which contrast with the low contribution of C6-based polysaccharide pyrolysis products. However, the thermal alteration caused by the wildfire occurred in 1995 cannot be considered the only reason of the furan dominance, since this is also observed in the CS.

Levogluconan was not identified in the studied soils and according to Evans and Milne [35], this may be due to the presence of a high content of alkali-metals in the samples, which inhibit its formation.

Besides, the high contents in polysaccharides in the pyrochromatograms of the HF-treated samples of these allophanic soils highlight their binding capacity as well as the importance of polysaccharide contribution to organo-mineral complexes.

Lignin derived structures are more evident for CS. The dominance of guaiacyl units indicates the woody coniferyl lignin origin [36], still vinylphenols which are markers of coumaryl lignin in grasses [37], are present in all the samples (see L2, L3 in Fig 3). Phenols and C₁-C₂ alkylphenols, are identified only in low amounts and can originate from any phenolic precursors including lignin, tannin, proteinaceous biomass, partially charred biomass and carbohydrates [38].

Methylanthracene and methylated phenanthrenes (A8–A10) exist in both samples. The origin of these polycyclic aromatic hydrocarbons (PAHs) is uncertain. They were discussed to be evidence for condensation reactions [39], or formed through cyclisation [40]. However released at this temperature, they are not considered as specific markers of BC in SOM [41].

The N-compounds have been mainly found in the form of pyridine, methylhydantoin, indole and benzonitriles which are common pyrolysis products from SOM derived from peptides [42]. Specifically, pyridines are largely resulting from alanine, whereas indoles are derived from tryptophan and aromatic nitriles from phenylalanine [43]. In general, N-compounds are very scarce, especially in the pyrochromatograms of the HF-treated soils. The latter is probably due to the high pH-dependence of the adsorption of amino groups and carboxyl groups through hydrogen bonds to organo-mineral complexes [44]. In addition, pyrolysis-GC/MS tends to underestimate the contribution of N-containing biomolecules [43].

Doublets of *n*-alkanes/*n*-alkenes ranging from C₁₀ to C₃₁ with a slight odd-over-even C predominance and maxima at C₁₃ (CS) and C₁₁ (BS) are present. Figures 5a and 5b show the distribution of *n*-alkanes in bulk soils detected by the average area of the selected ion monitoring (SIM) (m/z 57) at 340 °C. The average chain length (ACL) decreased fairly from 17.8 (CS) to 16.2 (BS), whereas the ratios of short-to-total *n*-alkanes ($(\sum C_{10}-C_{17})/(\sum C_{10}-C_{31})$) and short-to-long *n*-alkanes ($(\sum C_{10}-C_{17})/(\sum C_{24}-C_{31})$) increased (0.5 to 0.7 and 2.9 to 6.7 respectively; Table 3). These alterations are due to thermally induced break-down processes

of *n*-alkanes, which were previously observed for fire-affected soils [14, 45]. Such a decrease in the relative abundance of long chain *n*-alkanes in burnt soils has been previously reported [5, 18, 46]. Doublets of *n*-alkanes/*n*-alkenes are constituents of aliphatic biopolymers such as cutans and suberans found in the outer layers of aerial and belowground parts of higher plants [47], therefore they are commonly observed in soils [48].

Concerning the *n*-alkanoic acids, although in a lower amount in BS, they are present in both soils showing the typical even-over-odd C predominance. They ranged between C₁₄–C₂₆ with maxima at C₁₄ and C₁₆. In addition, the hexadecanoic acid methyl ester (FAME-C₁₆) was detected in CS, CS_HF and BS_HF, and according to [3] it is of bacterial origin.

Concerning terpenoids and other lipids, β -Sitosterol and Terpinene (peaks 2 and 4 respectively; Table 2) are ubiquitous in both samples. β -Sitosterol is widely distributed among the plant kingdom and is one of the most common steroids in the wax and gums of higher plants [49]. Terpinene is characteristic of conifers [50]. Its presence in the BS, although with lower abundance than in the CS, could be indicative of on-going recovery of the vegetation, which agreed with the fact that pinecones of Canarian Pine open and release the seed when exposed to the heat of fire (pyrophyte species). However, the major difference observed is the presence of a number of triterpenoids in the pyrolysis products of BS_HF (peaks 6–9; Table 2). Triterpenoids are characteristic biomarkers for angiosperm waxes [51], their occurrence exclusively in the BS supports the recovery of the vegetation in the burnt area. A fire usually opens an area to greater sunlight and warmth stimulating germination of some seeds. It is well known that Gramineae are the most common producers of pentacyclic triterpenes bearing a methoxyl group at C-3 [52] thus many grass species probably regenerated readily after fire.

3.2.2 Second shot (600 °C)

The second shot, up to 600 °C, releases additional products formed through the pyrolysis of structural domains with a higher thermal stability, resulting in extensive cracking of the macromolecular network. On the other hand, the HF-treatment increased the concentration of OM and released compounds from organo-mineral complexes. Thus, the

pyrochromatograms of bulk and HF-treated Andosols, albeit fairly similar, presented noticeable differences and will be studied separately.

3.2.2.1 Pyrochromatograms of bulk Andosols

Pyrochromatograms of bulk soils at 600 °C are similar and briefly consisted of aromatic compounds, long chain *n*-alkanes, a few carbohydrate-derived structures and some N-containing compounds (Fig. 4).

The main difference between CS and BS is the relative increase in several aromatic compounds in the latter. The detected aromatic compounds (An compounds; Table 2) were mainly PAHs. Unsubstituted PAHs (indene, naphthalene, phenanthrene, anthracene, fluorine, biphenyl, etc) are derived from dense aromatic structures present in black carbon [53, 11]. They have been previously reported in Andosols with fire history [3]. Still, the presence of such products in CS is not unexpected considering that forest fires occur frequently on the island. They may be related to charcoal buried after the deposition of hot volcanic ash which burnt the vegetation. Alternatively, they may derive from erosion processes which transported burnt biomass to the control area. Several di- and tri-methylbenzenes (A13, A14) are present in all the samples. They are commonly observed in the pyrolysis products of natural macromolecular materials. However, they also may have been formed during pyrolysis by secondary cyclisation/aromatisation reactions [11, 54]. Toluene, pyrrole, (alkyl)-phenols, probably phenol and N-containing-compounds such as indole and methylindole may result from a contribution of proteinaceous and peptide-like material but could also have been formed during the natural charring process [55].

Figures 4c and 4d show the distribution of *n*-alkanes at 600 °C for CS and BS, respectively. Series of *n*-alkanes are present in the range C₁₀–C₃₁. Their intensity maxima were at C₁₃ and C₁₅ for BS, whereas the contribution of homologues with more than 15 C atoms decreased drastically with molecular weight. In addition to the C₁₁–C₁₅ maxima, a high relative abundance of C₁₉–C₂₂ homologues was observed for CS. The relative abundance of short *n*-alkanes (Σ C₁₀–C₁₇) increased from 0.50 (CS) to 0.61 (BS), the ratio between short chain (Σ C₁₀–C₁₇) and long chain (Σ C₂₄–C₃₁) enlarged from 2.8 (CS) to 5.9 (BS). Thus, the

ACL decreased from 18.1 (CS) to 16.8 (BS) (Table 3). These changes can also be attributed to thermally induced cracking processes of long chain *n*-alkanes occurred during fire [5, 45, 46]. The distribution patterns of the aliphatic compounds in the pyrochromatograms obtained from andic CS agrees with the occurrence of a major, stable aliphatic domain [3].

Carbohydrates are not the dominant compounds of the pyrochromatograms. However, their presence, mainly as benzofurans (C13–C16; Fig. 4) has been previously reported as residues from leaves, roots, and fresh litter, which is in agreement to the recovery of vegetation. Comparable to other andic soils of the island [3] furan and glucopyranose, derivatives are also present in both samples.

Only few N-containing structures, including benzonitriles (P5, P6; Table 2) were identified. They are more abundant in the BS, which may be explained by accumulation of charring products formed from N-rich source material. Still, they may have been formed from proteinaceous compounds during the pyrolysis.

3.2.2.2 Pyrochromatograms of HF-treated Andosols

The HF-treatment caused a high mass loss, however the removed material was mainly composed of mineral phases, consequently the net C loss occurred was very low and the yielded material was enriched in C. At a molecular level it released compounds from organo-mineral complexes. Thus, in addition to the series of compounds described for bulk soils, the released pyrolysis products are mid-chain *n*-alkane/alkene doublets, lignin derived structures, polysaccharide molecules, *n*-alkanoic acids and a few triterpenoids (BS_HF sample). On the contrary, the signals of f N-containing structures were hardly identified in the TIC of the HF-treated soils (Fig. 4). Aside from this no significant qualitative differences are observed between the pyrochromatograms of control and fire affected Andosols after the HF treatment (CS_HF and BS_HF respectively; Fig 4).

As for the bulk soils, series of *n*-alkanes in the range C₁₀–C₃₁ were revealed. The long-chain (C₁₈–C₃₁) aliphatic lipids identified in the HF-treated Andosols originate from three major vascular plant sources: wax esters, suberin, and cutin [58, 59]. Similarly to TIC obtained after the desorption step, doublets of *n*-alkanes/*n*-alkenes appear in the TIC of the

HF-treated soils. They correspond to secondary compounds formed by degradation of aliphatic biopolymers of higher plants [49]. The C₁₂, C₁₄ and C₁₆ *n*-alkanoic acids identified in both HF-treated Andosols are typical products of bacteria and fungi [56].

The high lignin contribution is characteristic of both HF-treated soils. The guaiacyl monomer is the main phenolic compound present in the pyrochromatograms, in addition other guaiacyl structures (vanillyl) are present. According to Bahri et al. [58] the guaiacyl structure, which has only one methoxyl group, is more easily accessible for binding to mineral phases than syringyl units. The removal of the mineral matrix during the HF-treatment of the Andosols may have caused that those compounds are less protected from being released during pyrolysis. In addition, the “grass lignin” signature was still noticeable as reflected by the high relative abundance of 4-Vinylguaiacol (L3), a pyrolysis product of ferulic acid [36].

β-Sitosterol (peak 4; Table 2) derived from higher plants is present in both samples [49]. Similarly to the desorption step, the pentacyclic triterpenes (characteristics of angiosperms vegetation) are more abundant in the BS_HF, pointing to the recovery of the vegetation in the burnt area and the dominance of grass species.

With respect to the untreated soil, the relative abundance of 5-methyl-2-furfural (C3) and D-allose (C11) released upon pyrolysis increased in both HF-treated samples. Possibly, removal of the mineral phase facilitated the pyrolysis of carbohydrates formerly protected within organo-mineral complexes.

3.4 ¹³C NMR spectroscopy

The CPMAS ¹³C NMR spectra of the HF-treated soils and their intensity distribution are displayed in Fig. 6. They reveal a comparable chemical composition of SOM in the fire affected and unaffected soil. Both spectra are characterised by a dominant signal in the O-alkyl C region (60–110 ppm). The main peak in this region at 74 ppm together with the resonance line at 106 ppm supports the assignment to polysaccharides [59]. Slightly higher intensity in this region was found for BS (39%) compared to the CS (36%). This result seems

to be in contrast with other reports showing that the effect of heating on SOM leads to a loss of O-alkyl C structures [6, 24]. However, one has to bear in mind that new vegetation developed during the recovery of the fire-affected ecosystems and that such a vegetation is mainly composted of herbs and shrubs. Relative to a pine forest the latter is expected to produce a higher amount of litter. Thus, if in the burnt system, litter production is more intense than litter and SOM degradation, a relative enrichment of carbohydrates is observed [60]. In the aromatic C regions (160–110 ppm) a slightly higher intensity was found for BS than for CS. Possibly this is an indication for the incorporation of charred residues into the SOM after the fire event. Nevertheless, this region also comprises the signal corresponding to phenolic C, which appears as a resolved peak in the range 160–140 ppm. The O-alkyl C/alkyl C (45 to 0 ppm) ratio has been reported as an indicator of OM transformation, since carbohydrates are preferentially used as energy and C source for the build-up of microbial biomass. The latter contains high amounts of alkyl C such as peptides and lipids contributing to the signal intensity in the chemical shift region between 45 to 0 ppm. Additionally, the accumulation of recalcitrant waxes contributes to a relative enrichment of this region [24]. The fact that this ratio is higher for BS (2.4) than for CS (1.7) supports the suggestions that in the former the proportion of less degraded litter is higher, either because of a high litter production during the recovery period or because the post-fire soil conditions reduced the degradation efficiency [59].

4. CONCLUSIONS

The comparison of pyrograms of HF-treated and untreated soil samples indicated that mineral complexes may protect the release of compounds during pyrolysis. The study of those Andosols sampled eleven years after a fire from the Tenerife Island confirms that in such soils fire-induced thermal breakdown processes exert appreciable medium-term alterations of the quantity and quality of OM. Possibly the ecologically most relevant change consisted in a strong decrease of the OM content in the A horizon after fire, showing that here the fire has decreased the sequestered C pool. In our study site, an A horizon was still

identified, possibly because it newly developed by post-fire pedogenic processes. Such a scenario could explain the greater abundance of indicators for litter or scarcely degraded OM in the burnt than in the fire unaffected soil. In addition, the abundance of pentacyclic triterpenoids in the pyrochromatogram of burnt soils suggests the recovery of the vegetation in the area and the dominance of grass species. Our results clearly underline that in particular in soils with andic properties a fast recovery of the vegetation is essential for avoiding desertification.

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- 609

FIGURES CAPTIONS

Figure 1. Sampling site location at “*Monte la Esperanza*”, Tenerife (Canary Islands).

Figure 2. Weight loss thermograms (TG) and differential scanning calorimetric (DSC) curves of A horizons of a fire-unaffected (CS) and a fire affected (BS) Andosol within the range from 0 to 900 °C.

Figure 3. Py-GC/MS Total ion current chromatogram from the bulk and HF-treated A horizons of the fire-unaffected (CS) and fire affected (BS) Andosols at 340 °C (First shot). Labels over the peaks refer to compounds listed in Table 2.

Figure 4. Py-GC/MS Total ion current chromatogram from the bulk and HF-treated A horizons of the fire-unaffected (CS) and fire affected (BS) Andosols at 600 °C (second shot). Labels over the peaks refer to compounds listed in Table 2.

Figure 5. Relative abundances of *n*-alkanes corresponding to the selected ion monitoring (SIM) chromatogram (*m/z* 57) released from Py-GC/MS at 340 and 600 °C.

Figure 6. Solid-state ¹³C NMR spectra and intensity distribution (%) of HF-treated A horizons of fire-unaffected (CS) and a fire affected (BS) Andosols.

630

Table 1. Elemental analysis (C, OC and N), pH (H₂O) and water holding capacity (WHC) of material from the A horizons of a fire-unaffected (CS) and fire affected (BS) Andosol eleven years after a severe fire.

Sample	C (g kg ⁻¹)	OC (g kg ⁻¹)	N(g kg ⁻¹)	C/N	pH (1:2.5 H ₂ O)	WHC (ml g ⁻¹)
Control Soil (CS)	195±7	194±7	11±2	17.6	5.8±0.1	1.8±0.2
Burnt Soil (BS)	99±5	98±5	6±1	16.3	6.3±0.2	1.1±0.1

631

632

Table 2. Peak identification of pyrolysis gas chromatography-mass spectrometry products by component classes

Carbohydrates (Polysaccharidic-derived structures)		Lignin derived structures	
<i>Peak label</i>	<i>Compound</i>	<i>Peak label</i>	<i>Compound</i>
C1	x-Methylfuran	L1	Guaiacol
C2	2-Furfural	L2	Vinylphenol
C3	5-Methyl-2-furfural	L3	4-Vinylguaiacol
C4	x,x-Dimethylfuran	L4	Eugenol
C5	Maltol	L5	Isoeugenol
C6	x-Furanmethanol	L6	Vanillin
C7	D-Glucopyranose	L7	x-Methoxy-2-[1-methyl-2-propenylbenzene]
C8	x,x-Dimethylfuranone	L8	Vanillic acid, methyl ester
C9	x-Hydroxymethyl-x-furfural	L9	Acetovanillone
C10	Dimethyl-2-furanone	L10	x-Ethylguaiacol
C11	D-Allose	L11	x--Methylguaiacol
C12	Octylfuran	Aromatic compounds (including PAHs)	
C13	x-Ethyl-dibenzofuran	<i>Peak label</i>	<i>Compound</i>
C14	Benzofuran	A1	Styrene
C15	Dibenzofuran	A2	Phenol
C16	x-Methyl-dibenzofuran	A3	p-Cresol
Alkanes and alkenes		A4	o-Cresol
<i>Peak label</i>	<i>Compound</i>	A5	p-Ethylphenol
o●10	Decane/ene	A6	Trimethylphenol
o12	1-Dodecene	A7	x,x-Dimethylnaphthalene
●13	Tridecane	A8	x-Methylantracene
●15	Pentadecane	A9	x-Methylphenanthrene
●16	Hexadecane	A10	x,x-Dimethylphenanthrene
●17	Heptadecane	A11	Benzene
o●18	Octadecane/ene	A12	Toluene
o●19	Nonadecane/ene	A13	Xylene
o●20	Eicosane/ene	A14	Trimethylbenzene
o●21	Heneicosane/ene	A15	Indene
o●22	Docosane/ene	A16	x-Methylindene
o●23	Tricosane/ene	A17	Naphthalene
o●24	Tetracosane/ene	A18	x,x-Dimethylphenol
o●25	Pentacosane/ene	A19	x-Methylnaphthalene
o●26	Hexacosane/ene	A20	1,1'-Biphenyl
o●27	Heptacosane/ene	A21	1,1'-Biphenyl-x-methyl
o●28	Octacosane/ene	A22	x-H-Fluorene
o●29	Nonacosane/ene	A23	Benzonaphthalene
o●30	Tricontane/ene	A24	Phenanthrene
o●31	Hentriacontane/ene	A25	Anthracene
Fatty acids		A26	Fluoranthene
<i>Peak label</i>	<i>Compound</i>	A27	Pyrene
FA14	Tetradecanoic acid	A28	Chrysofluorene
FA15	Pentadecanoic acid	A29	Chrysene
FAME16	Hexadecanoic acid methyl ester	A30	Benzopyrene

FA16	Hexadecanoic acid	Other structures (terpenoids and other lipids)	
FA17	Heptadecanoic acid	<i>Peak label</i>	<i>Compound</i>
FA18	Octadecanoic acid	1	Acetic acid
FA20	Eicosanoic acid	2	Terpinene
FA22	Docosanoic acid	3	Ergosterol
FA26	Hexacosanoic acid	4	β -Sitosterol
Nitrogenated compounds (including peptide-derived structures)		5	α -Tocopherol
<i>Peak label</i>	<i>Compound</i>	6	A-Neooleana-x,x-diene
P1	Pyridine	7	Olean-12-ene
P2	x-Methylhydantoin	8	A-Friedo-oleana-x-ene
P3	Indole	9	Urs-12-ene
P4	x-methylpyridine		
P5	Benzonitrile		
P6	Methylbenzonitrile		
P7	Quinoline		

Peak labels C, FA, P, L and An refers to molecules derived from carbohydrates, fatty acids, peptides, lignin and aromatic structures, respectively.

634

Table 3. Comparison of parameters calculated from *n*-alkanes released by analytical pyrolysis at 340 and 600 °C.

Sample	Short/Total <i>n</i> - alkanes ratio: $\Sigma C_{10}-C_{17}/\Sigma C_{10}-$ C_{31}	Short/Long <i>n</i> - alkanes ratio: $\Sigma C_{10}-C_{17}/\Sigma C_{24}-$ C_{31}	Average Chain Length (ACL)
CS-340 °C	0.5	2.9	17.8
BS-340 °C	0.7	6.7	16.2
CS-600 °C	0.5	2.9	18.1
BS-600 °C	0.6	5.9	16.8

ACL; Average chain length is the weighted average number of C atoms. Values were calculated from the integration of peaks shown in Fig 5.

635

636

636 Highlights:

- 637 • Medium-term alterations in the soil organic matter (SOM) of the topsoils of burnt
638 Andosols
- 639 • Pyrolysis–GC/MS, thermogravimetric analysis and ^{13}C NMR spectroscopy used to
640 study changes into the SOM due to fire
- 641 • Thermally induced breakdown processes and BC formation due to fire
- 642 • Markers of vegetation recovery in HF-treated burnt Andosols shown by Py-GC/MS
- 643

Figure 2

Figure 6