Fire Mediated Geochemical Alterations in Andosol's SOM under Canarian Pine (*Pinus canariensis*) Forest

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Introduction and Objectives

Soils in the Midlands slopes of the Tenerife Island (Canary Islands) are mainly allophanic andosols that sustain Canary pine forest-type vegetation. Andosols are usually formed from volcanic substrates, having a typical A horizon (melanic epipedon) [1] that accumulates high quantities of organic carbon (80-300 g C/kg) [2]. The peculiar properties of these variable-charge soils are due to the occurrence of materials such as allophanes, imogolite and other Fe and Al oxyhydroxides prone to form organo-mineral structures with a high degree of stability that in turn contribute to an efficient protection of organic C [3 and references therein].

Although many areas of the Tenerife Island are subjected to intense human activities, the *Pinus canariensis* forests are under environmental protection laws and wildfire is the main threat. However, studies on the effects of fire on andic soil properties are scarce [4].

Fire exerts ecological and environmental impacts that lead to changes in the quantity and quality soil organic matter (SOM) [5, 6]. Fire induce "de novo" formation of highly condensed pyrogenic products including highly recalcitrant forms such as black carbon [7] that contribute to long term C and N sequestration in soils [8].

The main objective is to elucidate changes exerted by fire to the SOM fraction of an andosol from the island of Tenerife affected by a high intensity fire. A number of complementary analytical tools *i.e.* elemental analysis, analytical pyrolysis (Py-GC/MS) and solid state nuclear magnetic resonance spectroscopy (CP MAS ^{13}C NMR) were used to trace descriptors for SOM alterations. These techniques have been recently used to detect fire derived alterations on Mediterranean soils [9-11] and to monitor their recovery [12].

Methodology

Samples were collected during February 2007 in "Monte de la Esperanza", located in Northern Tenerife (28°25′ 44'' N; 16°23′40'' W. 10-15 % slope and 1333 m a.s.l.). The area was affected by an intense wildfire in June 1995 when *c.* 2000ha burnt. The soil is an Andosol (ash soil) on volcanic parent material and the vegetation is dominated by *P. canariensis* with nearly 80 % coverage in the fire un-affected area, made up of very old and tall trees. In the burnt area *Erica arborea* and *Cistus symphytifolius* are the most abundant species.

Fire-affected soil (BS) and a neighbouring site with similar characteristics but not affected by fire (CS) were sampled, the latter was used as a control. Composite soil samples combining four sub-samples (within an area of ca. 20 m^2) taken from the first 10 cm of soil after removal the litter layer were taken. The soil material was then transported in glass containers, dried at room temperature and sieved to fine earth (<2 mm).

Elemental analysis

Total C and N were measured in duplicate by dry combustion (975 ºC) using an Elementar Vario EL microanalyzer detecting N as N$_2$ and C as CO$_2$. Organic carbon was eliminated from the bulk soil by combustion for 4 hours at 450 ºC and the remaining inorganic carbon (IC) was measured. Total Organic Carbon (TOC) was then estimated as the difference between TC and IC, after prior correction for weight loss. In addition the maximum water-holding capacity (WHC) of the samples was measured in triplicate.

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

Pyrolysis was performed in a micro-furnace Double-shot Pyrolyzer (Frontier Lab., model 2020) attached to a GC/MS system Agilent 6890. Between 1 to 2 mg of soil sample were used for analysis in a two step pyrolysis experiment; in a first step, a thermal desorption was carried out by increasing the initial temperature of 100 °C at a rate of 20 °C min^{-1} to a final temperature of 340 °C for 3 min, in a second step the sample was heated at a temperature of 600 °C for 1 min. GC/MS conditions were previously described by the authors [3]. Identification of individual compounds was carried out by single ion monitoring, low-resolution mass spectrometry and comparison with published and stored data (NIST and Wiley libraries).

^{13}C NMR spectroscopy

Samples were pre-treated with hydrofluoric acid for enrichment in organic material by removal of the mineral matrix including interfering paramagnetic compounds. Dry samples (10g) were treated with 10% HF (50ml) 5 times, stirred (2 hours) and centrifugated. After the HF treatment, samples were washed and centrifugated repeatedly with deionized water and freeze-dried. The samples were confined in a zirconium oxide rotor with an external diameter of 7 mm. The variable amplitude cross polarization magic angle spinning (CPMAS) technique was applied with a contact time of 1 ms, spinning speed of 6.8 kHz and pulse delay of 1 s. The spectra were subdivided into different chemical shift regions [13]. The relative ^{13}C intensity distribution was determined by integrating the signal intensity in the different chemical shift regions. Corrections concerning the intensity distribution of spinning side bands were made [11].

Results and Discussion

Elemental and physical Fire-induced alterations

Burnt sample (BS) lost over 50 % of N and OC contents as compared to the fire un-affected control soil (CS), which exhibit typical C and N contents for andosols [1] (Table 1). Significant OC and N losses have been reported for soils affected by high severity fires [10, 14, 15] and heated in the laboratory (>50 % OC loss at 220 °C [16]). OM lost after intense fires are likely a result from soil vulnerability to splash and entrainment by overland flow [17]. In addition a moderate degree of erosivity by rain in the area has been reported [18]. The CEC and WHC decreased probably as a consequence of OM destruction. The observed 9% in BS pH increase could be attributed to the ash liming effect in high-severity wildfires [4, 11]. Alternatively the loss of organic acids during fire may add to the ashes liming effect increasing soil pH [19].

Table 1: Elemental and physical parameters

	TC (%)	OC (%)	N (%)	C/N (in H20)	pH	CEC (µs/cm2)	WHC* (ml/g soil)
Burnt Soil (BS)	9.9	9.8	0.6	16.3	6.26	120.6	1.10 ± 0.02
Control Soil (CS)	19.5	19.4	1.1	17.6	5.75	149.4	1.80 ± 0.03

*WHC; Water Holding Capacity

Analytical Pyrolysis

The thermal input, at sub-pyrolysis temperature (340 °C) usually releases compounds associated by low thermal stability links to the macromolecular structure of the more thermostable material. These thermovaporized products could correspond to substances of recent origin with poorly condensed structure and peripheral attachment to the most condensed soil organic matter [20]. Fire un-affected soil (CS) presented a wide variety of compounds typically found in soil OM and a greater abundance of released compounds at 340 °C than BS. TIC of CS was dominated by carbohydrate and lignin derived compounds. Also present were N-containing products from peptides and aromatic structures. In addition alkane/ene doublets and fatty acids (FAs), including fatty acid methyl esters, were also observed in both samples. A wide range *n*-alkanes was found with a bi-modal distribution, maxima at C_{19} and C_{26}, and a slight even-carbon-numbered compounds (>C_{24}). In general plant lipids are characterised by the

predominance of long chain odd-carbon-numbered *n*-alkanes in the C_{23-33} range and microbial alteration results in enhanced accumulation of even-carbon-number homologues [21]. Carbohydrate derived compounds, which are dominant in CS, are thermally-labile soil OM compounds, their absence in the BS pointed to a thermal transformation of the fire affected soil OM. A conspicuous reduction in *n*-alkanes and fatty acids abundance in burnt soils has been previously observed [22]. In addition, FAs short chain/long chain ratio between burnt and unburnt soils is an indicator for soil recovery after wildfires [12]. In this case, the absence of fatty acids methyl esters in the BS probably indicates not only the remarkable alteration of the soil OM due to the fire event but also the absence of a natural recovery.

The second thermal input, at pyrolysis temperature (600 ºC), is dominated by aromatic compounds, *n*-alkanes and some N-containing structures. Quantitative differences were observed with a substantial increase in the amount of pyrolized material in BS as compared to CS. The reason may be the presence of recalcitrant and refractory OM in BS formed during the fire event. Aromatic compounds detected are mainly polycondensed structures (PAHs) and other aromatic rich components that are components of recalcitrant OM usually present in biochar and black carbon. N-containing structures, including benzonitriles are more abundant in BS.

^{13}C NMR Spectroscopy

The CPMAS ^{13}C NMR spectra of demineralized soil samples are in Fig. 1. Table 2 shows the integration values of the main ^{13}C NMR spectral regions. The spectra in both CS and BS was characterised by a dominant signal in the *O*-alkyl region (60-110 ppm), more intense for BS (39.08%) compared to CS (35.60%). This contrasts with previous findings reporting *O*-alkyl structure losses as the effect of SOM heating [10,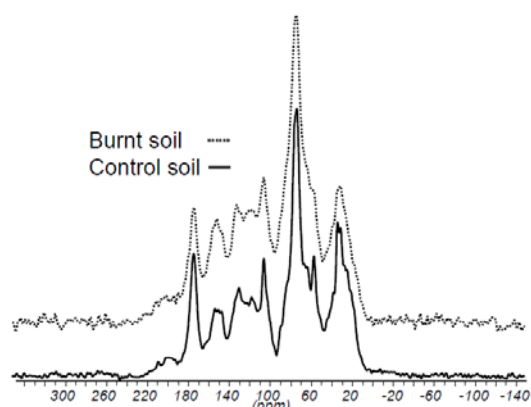 23]. The dominant peak in this region (74 ppm) together with the peak at 106 ppm corresponds to polysaccharides [24]. The increase in the *O*-alkyl intensity in BS may be attributed to inputs of fresh litter from post fire bush vegetation. Signal at 54 ppm is attributed to methoxyl C derived from lignins and α-C of proteins, this is weak in BS, which is in agreement with the Pyrolysis results. There is a conspicuous decrease of alkyl C material (0-45 ppm) in the BS (16.37 vs. 21.50 %). This region is generally assigned to lipids, waxes and other plant or microbial derived aliphatic biomolecules [25]. On the contrary, an increase in BS was found for the aryl C and O-substituted aromatic C regions (140-110 and 160-140 ppm respectively) that pointed to the formation of condensed, refractory material, such as black carbon during the fire event. Signals typically assigned to carboxyl and amide C (185-160 ppm) were also detected in both samples (9.71 (CS) and 8.51 (BS)). The *O*-Alkyl-C/Alkyl-C ratio has been reported as an indicator of OM transformation: carbohydrates are transformed, producing newly-formed alkyl structures while lipids are more recalcitrant to degradation [26]. The depletion in this ratio from 2.4 (BS) to 1.7 (CS) is associated with the ongoing degradation of plant residues, decreasing the relative contribution of *O*-alkyl C and the relative increase of alkyl-C, this result agreed with the even-carbon number predominance of *n*-alkenes detected in the pyrolysis results.

Fig. 1. Solid state ^{13}C NMR spectra of demirelaized (HF treated) soil samples.

Table 2. Semi-quantitative assessment (%) of the different C types as seen by 13C NMR integration regions.

	Ketone, Aldehyde (245-185)	Carboxyl, Amide (185-160)	*O*-subst, Aromatic (160-140)	Aromatic (140-110)	*O*-alkyl (110-60)	*n*-alkyl, Methoxyl (60-45)	Alkyl (45-0)	*O*-alkyl/Alkyl
CS	2.92	9.71	7.43	14.78	35.60	8.07	21.50	1.7
BS	3.89	8.51	8.57	15.88	39.08	7.70	16.37	2.4

C region values are given in ppm; CS: Control soil; BS: Burnt soil.

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