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Wildfire and black carbon in Andalusian Mediterranean forest

J.A. González, F.J. González-Vila & O. Polvillo
Instituto de Recursos Naturales y Agrobiologia, CSIC, P.O. Box 1052, 41080 Sevilla, Spain
G. Almendros
Centro de Ciencias Medioambientales, CSIC, Serrano 115 bis, 28006 Madrid, Spain
H. Knicker
Lehrsthul für Bodenkunde, TU München, 85350 Freising-Weihestephan, Germany
F. Salas & J.C. Costa
Centro Operativo de Prevención y Extinción de Incendios, Consejería de Medio Ambiente, Junta de Andalucia, Manuel Siurot 50, 41013 Sevilla, Spain

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ABSTRACT: The recent history of wildfires in forested and natural areas from Andalusia is studied in terms of BC and soot production. An estimation of the potential BC emissions in Andalusia Autonomous Community, Spain is presented. The main forms of refractory carbon present in selected soils affected by wildfires are described as studied by pyrolytic (Py-CG/MS) and spectroscopic (^{13}C NMR) techniques. It is estimated that up to 31221.8 t of refractory materials can be formed by forest fires in Andalusia every year. Among the Andalusian provinces, those in the coastal area (Malaga, Almeria, Huelva, Cadiz & Granada) show the higher potential for BC production in the range of 7.52-3.36 kg ha^{-1} year^{-1}, whereas BC production figures are lower in the the Guadalquivir Valley provinces (Seville, Jaen & Cordoba) with a BC potential production in the range of 1.94-0.72 kg ha^{-1} year^{-1}. Using direct pyrolysis, most of the pyrolysis products present in undisturbed natural soils (sugars, furans, lipids, peptidic derivatives, etc) vanishes and charred "non pyrolyzable" refractory carbonous materials dominate the pryrograms of the forest soils affected by fire. This dominant presence of condensed carbon in the soil organic carbon pool after a forest fire is again apparent when studying the CPMAS ^{13}C NMR spectra. A neat increase in the intensity of the aromatic C region is observed while that of the O-alkyl C region decreases drastically. For a better understanding of the global C cycle and turnover in Mediterranean forest soils, the identification and quantification of refractory carbonous materials is necessary. The effect of different forest management practices (*ie.* prescribed fires) in soil refractory C forms, and in restoring some of other functional qualities of Mediterranean ecosystems deserves investigation.

1 INTRODUCTION

The soil is the largest terrestrial pool of carbon (2157–2293 Pg), of which ca. 70 % is organic carbon and the remain corresponds to C in carbonates (Batjes 1996). Soil organic carbon pool doubles that present in the atmosphere (760 Pg) and is about 2–3 times larger than that in living organisms in all terrestrial ecosystems (Prentice et al. 2001, Post et al. 1990). Depending on the turnover time in soil, three conceptual fractions of carbon can be distinguished: active labile and active intermediate that may remain in the soil for years or some decades, and passive or refractory remaining in soil for centuries to millennia (Belesdent & Mariotti 1996). Small deviations in the different forms of carbon in the soil may have a significant effect in the global climate change.

In certain well–aerated tropical soil environments, charcoal and oxidation resistant elemental carbon (OREC) can be significantly degraded on decadal to centennial timescales, only a fraction of the total production of OREC from biomass burning and fossil fuel combustion is likely to be sequestered in the slow-cycling "geological" carbon reservoir (Bird et al. 1999). However, in the Mediterranean regions where extreme environmental conditions alternate along the year, biological activity is not favourable to humification processes but to intense mineralization. Under such conditions, the importance of abiotic constraints such as fire and dehydration favoured by intense solar radiation are important factors in the formation of stable organic matter in the soil.

Fire is a regular factor affecting the evolution of the Mediterranean ecosystem; wildfires occur at a high frequency liberating large amounts of CO_2 to the atmosphere. As the burned ecosystem regrows, CO_2 is again removed from the atmosphere *via* photosynthesis and incorporated into the new vegetative growth with a net C balance that has been considered null (Levine *et al.* 1995). However, vegetation fires produces a considerable amount of refractory organic carbon, mainly in the form of black coal (BC), which is composed of polyaromatic and relatively inert carbon forms produced by incomplete combustion processes. After a wildfire an increase of C in soil is observed, this has been attributed in part to the sequestration of this recalcitrant, hydrophobic organic matter (Johnson & Curtis 2001).

2 METHODS

An estimation of potential black coal (BC) production per year by forest fires in Andalusia was calculated for each province. This was based on previously published historical data on forest fires and on estimations of carbon stored in Mediterranean forest biomass, from the following formula:

$$BC = BA \times ACC \times BCE$$

where BA = burnt area in ha (mean 1991-2000); ACC = average forest carbon content (for Spain is 29.7 t/ha)*; BCE = black carbon emissions factor**

(*) About 45% of biomass by weight is made up of carbon. The average biomass in forests for Spain is estimated in 66 t/ha (FAO 1995a,b), corresponding to *c.* 29.7 t of carbon/ha. (**) Calculated from the estimates of black carbon emissions described in Kuhlbusch 1998 and of global biomass burned from forest (consOolidated data for: savannas, tropical, temperate and boreal forests and agricultural waste) in Levine *et al.* 1995. In residues of vegetation fires: BCE Min = 0.0135; BCE Max = 0.0593. In the form of aerosols (soot): BCE Min = 0.0015; BCE Max = 0.0018.

Natural pine forest soils (*Pinus halepensis*, *P. pinea*, *P. pinaster*) were sampled in the first 15 cm of the soil profile in recently burned and unburned sites. Five soil samples were randomly collected from each site. Air dried samples were sieved through a 2 mm screen, liofilized and grinded.

Pyrolysis analysis was performed using a Curie Point Pyrolyzer (Horizon Inst.) connected in tandem with a GC-MS (Varian Saturn 2000). Raw samples were placed in a Fe-Ni filament and flash pyrolized at 600 °C for 5 seconds. Solid-state NMR was performed in the raw soil samples using a Bruker DMX 400 instrument with a triple resonance probe with a zirconium rotor of 7 mm ∅ topped with a KEL-F cap. The ^{13}C resonance was 100.61 MHz and the specra were acquired using a pulse delay of 300 ms and a spinning speed of 5.5 kHz.

3 BLACK CARBON PRODUCTION BY FOREST FIRES IN ANDALUSIA

Global BC production by vegetation burning is estimated to account for as much as 0.2 Pg year-1, 2.7 times the average total fossil fuel emissions of Spain and Portugal (0.0602 and 0.0137 Pg C year-1) for the period 1988–1998. BC is affecting the net C balance and may constitute a substantial fraction of the "missing carbon" in the global C budget i.e. BC is reducing net CO2 release caused by permanent deforestation by up to 18 % (Kuhlbusch 1998) and C emissions by biomass burning by up to 5.1 %.

For the period 1992–1997, up to 91 % of all forest fires in the EU occurred in the Mediterranean countries and 40.6 % of the total burnt area corresponded to Spain. Over this period, 75 824 ha were burned each year accounting for a 0.61 % of all forests and other wood land of the EU Mediterranean countries (Zanatta *et al.*, 2000). For the period 1991–2000, the mean area affected by fires in the Andalusian Autonomous Community was 17 205 ha year^{-1} (Table 1) equivalent to 1.97 % of the total area and a 3.74 % of all forested and natural areas (Ministerio de Medio Ambiente 2001).

A summary of the recent forest fire history (1991-2000) in Andalusia Autonomous Community as well as an estimation of the total carbon affected is ahown in Table 1. An Estimation of the maximum and minimum production of black coal in the form of particulate residues or aerosols emitted (soot) by forest fires during one average year in Andalusia is shown in Table 2.

It is estimated that up to 31221.8 t of refractory materials can be formed by forest fires in Andalusia every year, at a rate of 1.815 t burnt ha^{-1}. Part of this BC, between 766.5 and 919.8 t year^{-1}, is emitted in the form of aerosols (soot) to the atmosphere and after some time (40 hours to 1 month) will be deposited and incorporated into sediments worldwide, and a small part of submicrometer size particles will remain airborne as part of the background planetary aerosol. However, most BC, a maximum of 30302 t year^{-1} for Andalusia, will remain as fire residues and eventually incorporated into the soil, in or nearby, the place of the fire.

Among the Andalusian provinces, those in the coastal area (Malaga, Almeria, Huelva, Cadiz & Granada) show the higher potential for BC production in the range of 7.52-3.36 kg ha^{-1} year^{-1}, whereas BC production figures are lower in the the Guadalquivir Valley provinces (Seville, Jaen & Cordoba) with a BC potential production in the range of 1.94-0.72 kg ha^{-1} year^{-1} (Fig. 1).

Table 1. Forest fires in Andalusia Autonomous Comunity during the period 1991-2001

Year	Fires (nr.)	Burnt Area (ha)	% Area Burnt	Total C*
1991	2110	65252	0.74	1937.98
1992	1559	18857	0.22	560.05
1993	1288	17344	0.20	515.12
1994	1671	36135	0.41	1073.21
1995	1389	12972	0.15	385.27
1996	739	1259	0,14	37.39
1997	750	2953	0.03	87.70
1998	1137	5240	0.06	155.63
1999	892	6627	0.08	196.82
2000	938	5413	0.06	160.77
Average	**1247**	**17205**	**0.20**	**510,99**

Source: MMA (2001).

(*) Average biomass affected by fire in tx1000 of carbon

Table 2. BC production (particulate residues or aerosols) emitted by forest fires in Andalusia

	BC in vegetation fires residue (t/year)		BC in soot (t/year)		Total BC (t/year)	
Province	Min	Max	Min	Max	Min	Max
Almeria	1414.7	6214.1	157.2	188.6	1571.9	6402.7
Cadiz	695.5	3055.2	77.3	92.7	772.8	3147.9
Cordoba	218.4	959.5	24.3	29.1	242.7	988.6
Granada	939.3	4125.8	104.4	125.2	1043.6	4251.0
Huelva	1327.8	5832.6	147.5	177.0	1475.4	6009.6
Jaen	486.6	2137.2	54.1	64.9	540.6	2202.1
Malaga	1213.8	5331.9	134.9	161.8	1348.7	5493.7
Seville	602.3	2645.7	66.9	80.3	669.2	2726.0
Andalusia	**6898.4**	**30302.0**	**766.5**	**919.8**	**7664.9**	**31221.8**

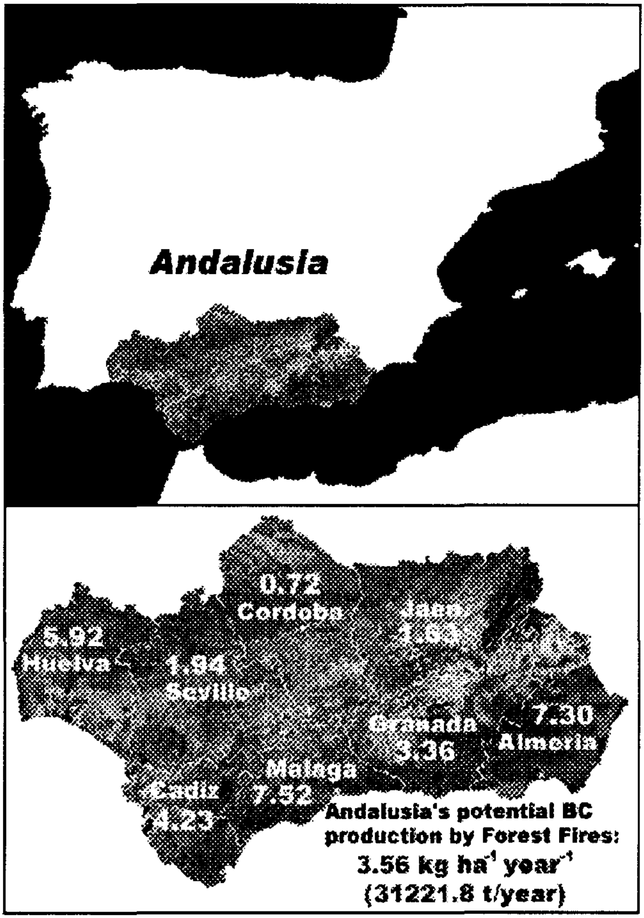
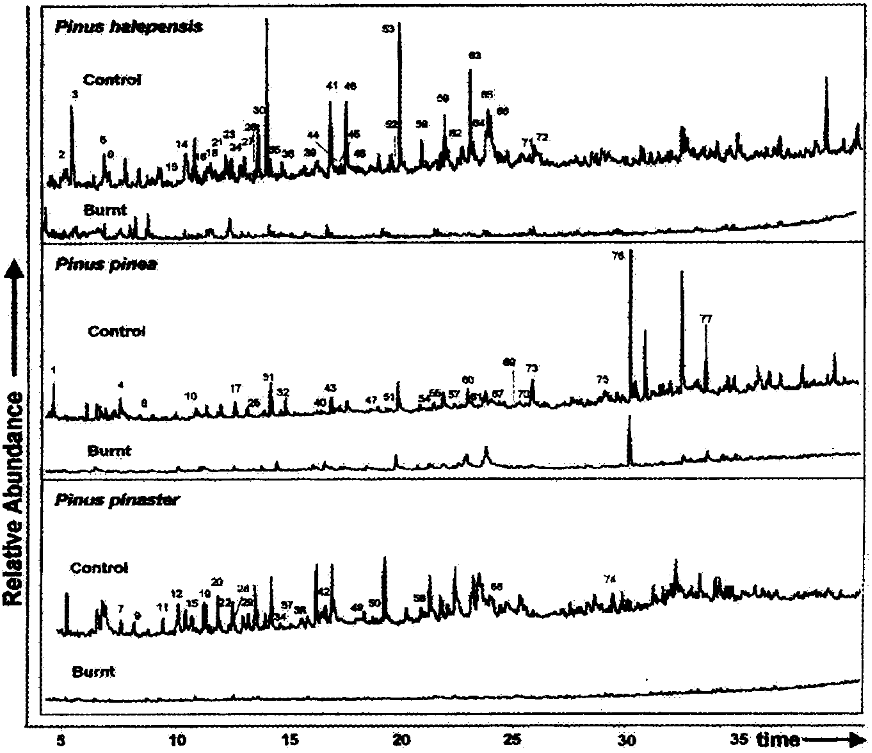


Figure 1. Location and map of Andalusian Autonomous Community with an indication of the potential BC production by forest fires by area unit (kg ha^{-1} year^{-1})

4 CONVERSION OF ORGANIC CARBON TO REFRACTORY FORMS DURING FIRE

Upon pyrolysis the control soils release a wide variety of typical organic soil pyrolysis compounds. Thus, anhydrosugar and furan compounds as well as a wide ser of nitrogen-containing products, arising respectively from carbohydrate and peptidic domains; typical methoxyphenols with both guaiacyl and syringyl skeletons, indicating the presence of microbually-reworked lignin and alkyl molecules are suggesting a moiety of recalcitrant, insoluble lipidic geopolymers already present in the unburnt soil profile. On the contrary, in the forest soils affected by fire, most pyrolysis products present in undisturbed natural soils vanishes and the dominance of charred "non pyrolyzable" refractory carbonous material is clear (Figure 2).

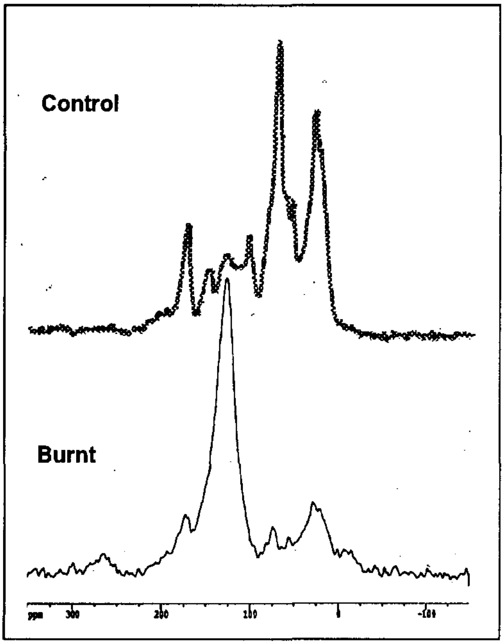


IDENTIFIED COMPOUNDS BY PY-GC-MS

1 benzene
2 2-methyl-2-cyclopentene-1-one
3 toluene
4 furfural
5 1H pyrrole 3 methyl
6 2-hydroxymethylfuran
7 styrene
8 cyclopente-1-ene-3,4-dione
9 2-methyl-2-cyclopente-1-one
10 2-acethylfuran
11 2,3-dihydro-5-methylfuran-2-one
12 5-methyl-2-fufuraldehyde
13 benzylalcohol
14 benzaldehyde
15 phenol
16 5-methyl-2-fufuraldehyde
17 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one
18 5,6-dihydropyran-2,5-dione
19 3-hydroxy-2-methyl-2-cyclopenten-1-one
20 2,4-dihydropyran-3-one
21 2-methoxytoluene
22 2-hydroxy-3-methyl-2-cyclopenten-1-one
23 4-isopropyltoluene ó mentatriene
24 2,3-dimethylcyclopenten-1-one
25 hydroxymethyldihidropyranone
26 5-ethyl-2-fufural
27 o-cresol
28 2-furoic acid methyl ester
29 4-methylphenol,pcresol
30 2,6 dimethylphenol
31 guiacol
32 levogluconone
33 3-hydroxy-2-methyl-(4H)-pyran-4-one
34 dimethyldihydropyranose
35 phenylacetonitrile
36 3-hydroxy-2methyl-(4H)-pyran-4-one
37 2,4-dimethylphenol
38 benzoic acid
39 4-ethylphenol
40 catechol
41 2-acetoxy-5-ethylfuran
42 3,5-dihydroxy-2-methyl-(4H)-pyran-4-one
43 methylguaiacol
44 5-hydroxyl-2-fufuraldehyde
45 metoxymethylbencene
46 4-vinylphenol
47 4-methylcatecol
48 4ethyl-2-methylphenol
49 4-ethylguiacol
50 4-hydroxybenxyl alcohol
51 indole
52 1,4-dideoxy-D-glycerohex-1-enopyranos-3-ulose
53 vinylguiacol
54 trans propenylphenol
55 2,6-dimethoxypenol
56 eugenol
57 4-propylguiacol
58 3-methylindole
59 vanillin
60 cis isoeugenol
61 4-hydroxyacetophenone
62 homovanillin
63 isoeugenol trans
64 1-(4-hydroxy-3-methoxyphenyl)propyne
65 acetovanillone
66 vanilliv acid methyl ester
67 4-ethyl-2,6-dimethoxyphenol
68 guaiacylacetone
69 2,6-dimethoxy-4-vinyphenol
70 1,6,anhydro-b-glucofuranose
71 guaiacylpropan-2-one
72 propiovanillone
73 guaiacyl vinylketone
74 trans coniferaldehyde
75 retene
76 myristic acid
77 palmitic acid

Figure 2. Changes in pyrograms and compounds identified by GC/MS of raw soil samples from *Pinus halepensis*, *P. pinea* & *P. pinaster* forest soil: control soil and soil affected by forest fire (Burnt)

The formation of condensed refractory materials after a forest fire is again apparent in the CPMAS ^{13}C NMR spectra. A neat increase in the intensity of the aromatic C region (160 to 110 ppm) is observed while that of the O-alkyl C region (110 to 60 ppm) decreases drastically. CPMAS ^{13}C spectra of samples from a *Pinus halepensis* forest soil and intensity distribution (% of total signal intensity) is shown in Fig. 3.



Integrated Region (ppm)	Control	Burnt
325.88 – 301.44	0.35	0.11
301.44 – 244.72	0.68	3.34
244.72 – 186.72	3.37	2.87
186.72 – 160.27	7.92	7.75
160.27 – 140.39	5.41	11.89
140.39 – 109.93	11.57	42.33
109.93 – 90.78	6.99	5.46
90.78 – 60.32	26.97	5.98
60.32 – 45.55	8.23	3.04
45.55 – 0.50	27.71	13.88
0.50 – -40.17	0.78	3.34

Figure 3. Changes on CPMAS ^{13}C spectra and intensity distribution of raw soil samples from a *Pinus halepensis* forest: control soil and soil affected by forest fire (Burnt)

5 CONCLUSIONS

Fire is often perceived as a destructive force, however under certain circumstances, fire is a natural and necessary component of native and human influenced ecosystems (Komarek 1974; Caldararo 2002). It is well known the beneficial effects of fire on native plant germination and growth and by eliminating the organic litter accumulated in the forests.

After a forest fire, an increase in soil carbon is observed. New carbon species, mainly in the form of charcoal and other charred materials, enters the soil organic pool, and the organic matter already present in the soil experiments molecular modifications that affects structural and colloidal (condensation, aromaticity and solubility) properties. This conduces to the formation and stable sequestration of highly refractory charcoal and recalcitrant, hydrophobic organic matter in the forest soil, as described in previous work (Almendros *et al.* 1990; Johnson & Curtis 2001) and confirmed by the results presented here.

Under the Mediterranean environmental conditions, characterized by drastic temperature and moist differences along the year influencing, in part, a high frequency of forest fires, the phenomena conducing to the formation of black carbon and charred materials in the soil are particularly favored. These forms of carbon are highly resistant to oxidation and represents a relevant part of the long-term geological soil's carbon pool. The potential for black carbon formation only from forest fires in the form of residues of vegetation fires (mainly charcoal) and soot (aerosols) for Andalusia is estimated in up to 0.31 x 10^5 t/year. For a better estimation of the most stable soil carbon pool, black carbon inventories must be tuned including soil charred materials and geopolymers and this shall rely on data obtained from experimental evidence.

In order to be able to forecast C turnover in soil and for a better understanding of the global C cycle, a proper identification and quantification of refractory carbonous materials is necessary. There is also a need to study the real size and turnover rates of the refractory carbon pools in a range of Mediterranean forest soils, and the effect of different forest management practices (*ie.* prescribed fires) in sustaining or increasing long-term organic matter, as well as in restoring some of other functional qualities of Mediterranean ecosystems.

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