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Changes in C stable isotopic composition of selected n-alkanes from the lipid fraction of a Rendollic Xerochrept affected by forest fire

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Forest fires are the main disturbance in the Mediterranean basin and exert both immediate and lasting environmental impacts. This is in part caused by the transformation of soil physical, chemical and biological characteristics associated to changes in soil organic matter (SOM) (González-Pérez et al., 2004, and references therein).

Within the framework of a coordinated multidisciplinary project where a variety of complementary analytical techniques were used, we were able to detect several markers surrogated to the effect of wildfires in SOM properties (González-Pérez et al., 2008).

In this communication we have analyse C stable ($\delta^{13}C$) isotopic composition of *n*-alkanes by gas chromatography isotope ratio mass spectrometry (GC-irMS). Previous work on this matter has focused the study in bulk $\delta^{13}C$ (Roscoe et al., 2000; Fernandez et al., 2004; Saito et al., 2007). However, this is the first attempt to study the effect of forest fires on C stable isotopic shifts composition in selected molecules.

Soils affected by wildfires were taken from a variety of scenarios from Andalusia (Southern Spain) that included different soil types under different vegetation and affected by wildfires between 1999 and 2005. As control (non-affected) samples were taken from nearby areas with similar soil characteristics and vegetation type but with no recent history of forest fires.

The soil lipid fraction was soxhlet extracted in the fine-earth samples with a mixture of dichloromethane/methanol. The accurate analysis of stable carbon isotope ratios of individual *n*-alkanes by GC–irMS requires previous separation from branched/cyclic hydrocarbons by conventional separation methods including urea adduction. GC–irMS analyses were performed on a Thermo Trace Ultra GC using a split less injector (280°C) via a Combustion III Interface linked to a Thermo Delta V+ IR-MS. The sample (1µl) in hexane was injected by a CTC auto sampler and the split opened after 1

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minute. The GC oven was programmed from 50-320°C at 5°C min and held at final temperature for 6 minutes with He as the carrier gas (flow 1ml/min, initial pressure of 50kPa, split at 20 mls/min). Chromatographic separation was performed on a fused silica capillary column (30m x 0.25mm i.d) coated with 0.25µm di-methyl Poly-siloxane (HP-5) phase. The acquired data was processed using the Isodat dynamic background integration Workspace software to give the peak retention times and isotope ratios as $\delta^{13}C$ values.

Carbon stable isotopic composition ($\delta^{13}C$) for odd carbon number *n*-alkane chains with length from 27 to 33 carbon atoms as obtained for the Cazorla (Jaen, Andalusia) site is shown in Table 1. The soil is a Rendollic Xerochrept formed on loess under *Pinus pinea* forest. An intense fire event occurred in August 2005 and the fire-affected and fire-unaffected soils were collected in 2005, 2006 and 2007. Alkane distribution in the control and burn samples collected in 2006 is shown in Figure 1.

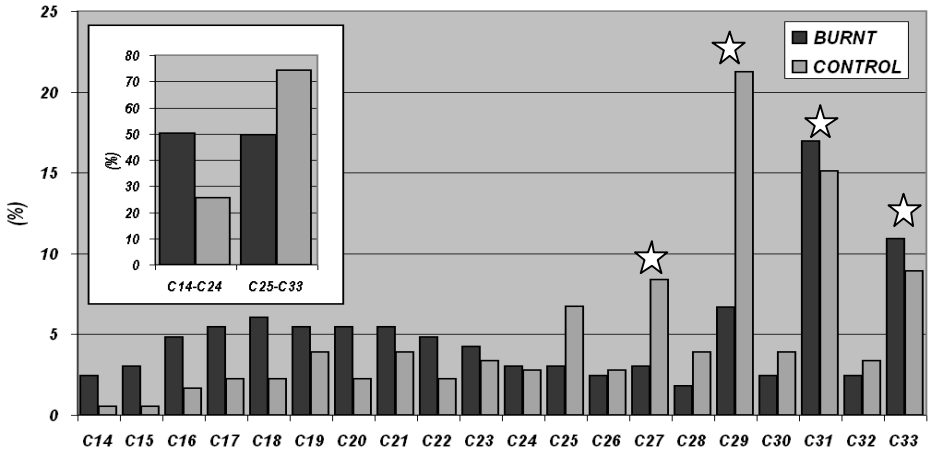

Figure 1. N-alkane distribution (m/z 85) as detected by GC/MS. Stars indicates the compound for which $\delta^{13}C$ was determined

Previously known effects of forest fires on soil *n*-alkane pattern include an increase in low MW homologues and in noun predominance in medium length chains (González-Pérez et al., 2008). Here a trend in $\delta^{13}C$ for odd carbon number *n*-alkane chains is also detected towards depletion in ^{13}C with time after the fire (Table 1).

The observed effect could be explained by a progressive addition of plant wax *n*-alkanes to the lipid soil pool from decayed hard wood vegetation (C3 type). Shortly after a wildfire, affected pine forest is known to produce a considerable amount of fresh or partially charred organic matter from the decayed vegetation. Elemental and isotopic studies have shown that bulk plant carbon and plant wax *n*-alkanes are incorporated into the soil, at least partly, via large particle-size fractions (Cayet and Lichtfouse, 2001).

Table 1: Stable isotope composition of n-alkanes (* mean values).

	Control ($\delta^{13}C$ in ‰)				
Year	C_{27}	C_{29}	C_{31}	C_{33}	C_{27-33}*
2005	-30.7	-34.4	-34.2	-31.1	-32.6
2006	nd	-30.5	-31.5	-30.4	-30.8
2007	-33.4	-34.5	-35.7	-31.1	-33.7
	Burnt ($\delta^{13}C$ in ‰)				
Year	C_{27}	C_{29}	C_{31}	C_{33}	C_{27-33}*
2005	-32.4	-35.0	-34.8	-32.9	-33.8
2006	-30.1	-32.0	-32.0	-30.4	-31.1
2007	-32.2	-33.5	-33.7	-32.4	-33.0
	Difference ($\delta^{13}C_{burnt} - \delta^{13}C_{control}$)				
Year	C_{27}	C_{29}	C_{31}	C_{33}	C_{27-33}*
2005	-1.7	-0.6	-0.6	-1.8	-1.2
2006	nd	-1.5	-0.5	0.0	-0.3
2007	1.2	1.0	2.0	-1.3	0.7

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