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Effects of fire on soil organic matter quality along an altitudinal sequence on Mt. Etna, Sicily

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Abstract

Soil organic matter (SOM) can directly be affected by wildfires, both in terms of quantity and quality. The combustion is often incomplete, leading to the formation of pyrogenic organic matter (PyOM), a highly heterogeneous material with prevailing aromatic nature. Focusing our attention

on PyOM, we investigated an altitudinal soil sequence on Mount Etna, Italy, ranging from 500 m to 1800 m asl, where the fire frequency is assumed to have been higher at lower elevations due to a warmer and drier climate. We evaluated the effect of fire on the chemical and physical characteristics of SOM along the altitudinal sequence. At two sites at a similar altitude but having a different recent fire history, we also examined the effect of fire frequency on SOM. Chemical oxidation of SOM with acid dichromate was used to evaluate the contribution of pyrogenic organic carbon to total SOC. Furthermore, four SOM density fractions were separated and characterised for principal composition, spectroscopic properties by Diffuse Reflectance Infrared Fourier Transform (DRIFT) and Nuclear Magnetic Resonance (NMR), and particle morphology by Scanning Electron Microscopy (SEM). The stocks of C and N as well as the chemical oxidation resistant carbon (COREC) increased with decreasing altitude, hence supporting the hypothesis of higher fire frequency at lower altitudes. The highest C concentrations were found in the density fraction 1.0-1.6 g cm⁻³. At the lower sites, a considerable amount of aromatics, and hence a significant part of COREC, was found in the density fraction 1.0-1.6 g cm⁻³ except for (macro)charcoal that occurs in the lightest fraction (<1.0 g cm⁻³). The properties of this latter density fraction seemed to be well related to vegetation characteristics.

The dichromate oxidation procedure, however, has methodological restrictions. This procedure resulted here to be poorly specific for PyOM in the investigated soils, since it isolated a fraction rich in lipids. The lack of specificity for PyOM is most likely due to the rather low content of aromatics in SOM, although fire frequency was relatively high.

Keywords: wildfires, soil organic matter, density fractionation, pyrogenic carbon, ¹³C NMR, dichromate oxidation, Mt. Etna.

1 **Introduction**

2 Mediterranean landscape has been shaped by wildfires over millennia, so much that the indigenous
 3 vegetation became adapted to face the deleterious effects and acquired the ability to grow and
 4 reproduce quickly (Scarascia-Mugnozza et al., 2000). At the beginning of the Holocene, high
 5 climate seasonality favoured fire expansion in the Mediterranean region. Human impact also
 6 affected fire regimes and especially fire frequencies since the Neolithic (c. 8000-4000 y BP;
 7 Vanniere et al., 2008; Noti et al., 2009). Burning as a consequence of anthropogenic activities
 8 became more frequent after the onset of the Bronze Age (c. 3800-3600 y BP) and appears to be
 9 synchronous with the development of settlements in the region, slash-and-burn agriculture, animal
 10 husbandry, and mineral exploitation (Vanniere et al., 2008). This finally caused significant changes
 11 in the vegetational communities (e.g. temporal decline of *Quercus ilex* forests and expansion of
 12 shrublands and maquis; Vanniere et al., 2008).

13 In the near future a higher fire frequency is expected in the Mediterranean basin due to increasing
 14 temperature and decreasing precipitation (IPCC Fourth Assessment Report, 2007; Moriondo et al.,
 15 2006). As a consequence of climate warming, new areas with high structural continuity will
 16 increase the risk of extreme fire behaviour. Furthermore, the fuel types are strongly influenced by
 17 climate (Alvarez et al., 2012). Soils, which suffer many consequences of the occurrence of fires
 18 (Certini, 2005), will probably experience marked C losses because of combustion (Certini et al.,
 19 2011) or post-fire erosion (Shakesby, 2011). Of the soil components, soil organic matter (SOM) is
 20 in fact the one most directly affected by fire being the fuel in soil. When the fire intensities are not
 21 extreme, heating turns SOM to pyrogenic organic matter (PyOM) that was defined by Masiello
 22 (2004) as a continuum of combustion products ranging from slightly charred degradable biomass to
 23 highly condensed refractory soot. Although modern studies have demonstrated that PyOM is not so
 24 resistant to decomposition as previously assumed (Bird et al., 1999; Hamer et al., 2004; Knicker et
 25 al., 2006), it can still be considered as the most recalcitrant component of SOM (Kuhlbusch and
 26 Crutzen, 1995; Schmidt et al., 2011; Singh et al., 2012). The PyOM structure is highly

1 heterogeneous, mostly depending on the plant materials composition and burning conditions. It is
2 characterised by hetero-aromatic forms (González-Pérez et al., 2004; Knicker et al., 2006, 2008a).
3 Since SOM fractions have a narrower range of properties compared to the bulk, a physical
4 fractionation can be useful to study such a complex mixture of thermally altered
5 biomacromolecules. In particular, density fractionation allows to obtain a light SOM fraction,
6 consisting of slightly decomposed plant and animal residues with a rapid turnover, and a heavy
7 SOM fraction, which includes the SOM involved in organo-mineral complexes that is thought to
8 contain more humified residues with a lower C/N ratio and a lower turnover rate (Glaser et al.,
9 2000). PyOM is usually reported to be mainly concentrated in the light pool (Skjemstad et al., 1990;
10 Golchin et al., 1997; von Lützow et al., 2007).

11 The aim of this work is to assess the effect of fire on SOM content and composition along an
12 altitudinal and climatic sequence on Mount Etna (Sicily) where Egli et al. (2012) found evidences
13 that fire activity was higher at lower elevated sites by studying the radiocarbon age of charcoal
14 particles and the stable fraction of soil organic matter. Our hypothesis is that the higher fire
15 frequency at lower elevated sites left a strong fingerprint on SOM, mostly detectable by the
16 accumulation of aromatic compounds. In such an environment, fire is a principal factor of soil
17 formation and a higher fire frequency is expected for the near future. Our study of SOM from this
18 sequence shall help to provide predictions on the fate of OM in the soils at higher elevated sites. In
19 this regard, we intended also to look for signals of a direct effect of fire frequency by comparing
20 two sites of the topo-climosequence having similar altitude and properties, except the recent fire
21 history.

22 To accomplish this purpose, soil samples were separated on a density basis into four fractions,
23 which were analysed for principal chemical composition (organic C, total N) and spectroscopic
24 properties and observed by a scanning electron microscope (SEM). Additionally, a chemical
25 oxidation of SOM using acid dichromate was performed to determine the amount of pyrogenic
26 carbon in each fraction.

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Materials and Methods

Study sites

The study area is Mount Etna, Sicily (Italy), the largest active volcano of Europe with a maximum elevation of 3323 m asl. The Etna landscape is characterised by lava-flows stratigraphically placed according to ages. Poli Marchese (2004) recognised in the Etna region the following vegetation zones:

- a) basal-mediterranean zone with a thermo-mediterranean subzone (*Oleo-Ceratonion*, below 500-600 m asl), a meso-mediterranean subzone (*Quercion ilicis*; between 600 and 1100 m asl) and a supramediterranean subzone (*Quercetalia pubescentis*; between 1100 and 1500 m asl)
- b) montane-mediterranean zone between 1500 and 2400 m asl (*Fagetalia sylvaticae* with *Astragaletum siculi*, *Pinus nigra* ssp., *Laricio* (*Quercus-Fagetea*), etc.)
- c) Mediterranean high-alpine zone above 2400 m asl (*Rumici Anthemidetum aetnensis*)

Human impact is an important environmental factor in the Etna region. Large areas around the volcano have been disturbed over centuries by human activities, in particular by agriculture. Pristine soils are exclusively found at high altitudes, on unproductive sites and/or on relatively young (< about 5 ky) lava flows.

We investigated six sites along an elevational gradient on the northeast flank of the volcano ranging from Mediterranean (551 m asl; warm, semi-arid to sub-humid climate) to subalpine (1772 m asl; cold, humid climate) climate zones (Table 1, Fig. 1). Soil moisture and temperature regimes vary between xeric to udic and thermic to frigid, respectively (Raimondi et al., 1999). All selected sites were north-facing and the chemical and mineralogical composition of the parent material was similar (cf. Table 2). Five sites were located on a lava flow and a sixth one (site 6) on another lava flow having (Fig. 1), however, the same composition. The lava flows were trachy-basalts (alkali mugearite) that can be attributed to the recent Mongibello chronozone (8 ky) or the ancient

Mongibello chronozone (about 15 ky) (Egli et al., 2012). Dating of lava flows in the Etna region was done by chronostratigraphic studies (Romano, 1979; 1983) and radiometric dating ($^{230}\text{Th}/^{238}\text{U}$ in Condomines et al., 1982; K-Ar in Gillot et al., 1994). Independent of climate, lava flows induced in several cases forest fires (as soon as they flowed through forests), hence contributing to some extent to fire dynamics. Such a contribution is not related to a particular vegetation or climate zone: adventitious craters and flank eruptions occur in all vegetation zones (Pichler, 1984). The risk of a forest fire due to a lava flow is, however, higher in pine forest than in oak forest (due to the lower flammability; Forest service, personal communication). Such risks are however, in recent times, better foreseeable and controllable than a common bush fire.

To discriminate the effects of fire frequency on soil organic matter, we compared sites 4 and 6, both having similar vegetation, altitude, topography and morphological soil properties – but substantially differing in the recent fire history. In fact, during the last 30 years, site 4 burned approximately once per decade while site 6 burned almost every year (Forest Service, personal communication).

At each site, three soil profiles were opened and sampled at 0-10 and 10-30 cm depth intervals. This procedure has been chosen for a better comparability of the results; it however neglects the genetic soil horizons. One to three kg of soil material were taken from either depth interval; such unusually large amounts are actually needed for coarse-textured soils to be representative samples (Hitz et al., 2002). Soil bulk density was determined by a core sampler (100 cm³), taking 2-4 replicates for each depth interval or, when the stoniness was high, by excavating holes backfilled with quartz sand (irregular hole method, as described in Howard and Singer (1981)). All of the investigated soils did not exhibit any marked sign of erosion or human disturbance. Additional information about the sites and soil properties is reported in Egli et al. (2012).

C and N contents

The soil samples were air-dried and sieved to 2 mm. Total C and N contents of the fine earth (the less than 2 mm fraction) were measured by a C/H/N Analyser (Elementar Vario EL, Elementar

1 Analysensysteme GmbH, Hanau, Germany) on oven-dried (70 °C for 48 h) and ball-milled
2 material.

4 *Density fractionation*

5 Density fractionation was performed on a composite sample (combining aliquots from the 3 profiles
6 per site) following a procedure adapted from Christensen (1992), which is based on the use of Na-
7 polytungstate solutions with different concentrations. The following fractions were separated: <1.0
8 g cm⁻³, 1.0-1.6 g cm⁻³, 1.6-2.0 g cm⁻³ and >2.0 g cm⁻³. In brief, 40 g of fine earth was put in 400 mL
9 of deionised water, slightly stirred for 12 h, then centrifuged for 10 min at 5,000 g. The supernatant
10 was skimmed off and evaporated, so obtaining the <1.0 g cm⁻³ fraction. The residual sample was
11 dried at 40 °C and mixed to a sodium polytungstate solution with a density of 1.6 g cm⁻³. After an
12 ultrasonic treatment of 50 J mL⁻¹ for 40 s, we centrifuged the suspension for 30 min at 3000 g. The
13 supernatant was skimmed off and evaporated, so obtaining the 1.0-1.6 g cm⁻³ fraction. The same
14 procedure was finally applied to the residue using a polytungstate solution with a density of 2.0 g
15 cm⁻³, so as to separate the 1.6-2.0 g cm⁻³ fraction from the >2.0 g cm⁻³ one. All of the fractions were
16 washed three times with deionised water, centrifuging and discarding the supernatants, hence dried
17 at 40 °C.

19 *Hydrofluoric acid treatment*

20 A hydrofluoric acid (HF) treatment according to Gonçalves et al. (2003) was carried out on aliquots
21 of both bulk samples and density fractions before performing the ¹³C NMR analysis, so as to
22 remove paramagnetic minerals, which strongly reduce the signal-to-noise ratio of the spectra. A HF
23 treatment is also required as pretreatment for black carbon quantification by dichromate to allow a
24 complete oxidation of labile SOM, including the physically protected one. In brief, 5 g of soil were
25 shaken at room temperatures with 50 mL of 10% (w/w) HF for 12 h in polyethylene bottles, then

centrifuged and the supernatant discarded. The procedure was repeated five times, thereafter the residue was washed five times with 40 mL distilled water and dried at 50 °C.

Although the hydrofluoric acid treatment usually causes some C and N removal, selective losses of specific groups should not occur, as supported by the findings of Rumpel et al (2006a) and Knicker et al. (2008b).

Dichromate oxidation

The contribution of PyOC to total SOC was estimated by assuming the chemical oxidation resistant carbon (COREC) to be PyOC as proposed by Knicker et al. (2007).

Following Rumpel et al. (2006b), 250 mg of HF-treated sample was mixed with 40 mL of a potassium dichromate solution (0.1 M $K_2Cr_2O_7$ in 1L of 2M H_2SO_4) in a thermal bath at 60° C for 6 h. The solution was checked during the treatment to detect a possible premature saturation that is revealed by a greenish colour. In this case the oxidation had to be repeated with a larger quantity of sulphochromic solution. To prevent such a problem as much as possible we referred to a C_{org} -to-acid ratio of 2 mg mL⁻¹ as suggested by Knicker et al. (2007). Thereafter, the sample was washed at least four times with 50 mL distilled water. The residue was then dried at 50 °C and the mass loss was determined. The C and N recovered were calculated by mass balance.

DRIFT measurements

Diffuse Reflectance Infrared Fourier Transform (DRIFT) measurements were performed on bulk soil and density fractions samples using a Tensor 27, Bruker. Spectra were recorded from 4000 to 250 cm⁻¹ on pulverised samples dried at 60 °C.

To quantify the relative contribution of single C moieties, we divided the intensity (area) of each peak of the DRIFT spectra by the sum of the intensities of all peaks taken into account (see Table 3) using the software OPUS 6.

1 *NMR spectroscopy*

2 ¹³C solid-state cross-polarisation/magic angle spinning nuclear magnetic resonance (CP/MAS
3 NMR) spectra of HF-treated samples were recorded on a Bruker AMX300-WB spectrometer at
4 75.47 MHz, equipped with a 4-mm CP-MAS probe. The 90° pulse was 3.2 µs; 20000 scans were
5 acquired, depending on the sample, with a 4 s repetition time, using a contact pulse of 2 ms and a
6 60-kHz radiofrequency field. All spectra were recorded at room temperature, spinning at the magic
7 angle at 5.0 kHz.

8 We applied this technique to the density fractions, combining equal aliquots from the top 10 cm of
9 the soil at the highest altitudes (subjected to a lower fire frequency), 1 and 2, and, separately, of the
10 lower sites, 4 and 6 that are subjected to a high fire frequency. The fractions < 1, 1-1.6 and 1.6-2 g
11 cm⁻³ were analysed.

12 A semiquantitative determination of the main C forms was done integrating the chemical shift
13 regions of the spectra and expressing them as percentages of the total area between 0 and 220 ppm:
14 0 to 45 ppm (alkyl C), 45 to 110 ppm (O-alkyl C, subdivided in methoxyl/N-alkyl, 45 – 60 ppm; O-
15 alkyl, 60 - 90 ppm; di-O-alkyl, 90 – 110 ppm), 110 to 165 ppm (aryl C, subdivided in aromatic C-H
16 and C-C, 112 – 140 ppm and O substituted, 140 – 165 ppm), 165 to 185 ppm (carboxyl C), and 185
17 to 220 ppm (aldehydes, ketones) (Wilson, 1987).

18

19 *SEM-EDX*

20 Bulk, loose (uncoated) fine earth was observed by a scanning electron microscope (SEM). The
21 principal chemical composition (total elemental contents) of the focused specimen was assessed by
22 a Dual Beam Quanta 200 3D FEI, equipped with an energy-dispersive spectrometer (EDS) with a
23 Dual BSD detector and a W emitter operating at an accelerating voltage of 20 kV.

24

25 *Statistics*

Datasets were first checked for normal distribution by a Shapiro-Wilk test (SigmaPlot 11.0, Systat Software Inc.; Jann, 2005), using a two-tailed test for significance. However, since most of them did not show a normal distribution, the Spearman rank correlation coefficient was taken into account.

Results and Discussions

Carbon and nitrogen in bulk soil and density fractions

The mean concentrations of carbon and nitrogen tended to slightly decrease with altitude in both the 0-10 and 10-30 cm soil layers (Table 4). The C and N stocks showed the same trend, especially for the deep layer (10-30 cm) (Fig. 2). Egli et al. (2007; 2012) found the same elevational trend for soil organic matter in the Etna region. These authors partly correlated the results to the climate and vegetation, inferring that in such an environment higher temperatures should lead to an increase of SOM and higher precipitation to a better mineralisation and consequently a decrease in SOM. Higher temperatures usually should enhance mineralisation, but in this case higher temperatures are correlated to aridity that decelerate the degradation processes and to fire events that promote C sequestration.

Climate (temperature and precipitation and, as their ramification, fire and aridity) obviously influenced the concentration and stocks of SOC. A correlation between SOC and climate has been found also in other investigations (e.g. in Burke et al., 1989). A contrary trend was, however, found by Chiti et al. (2012): conifers and broadleaf forests showed a trend in SOC stock distribution, with the stocks decreasing with increasing Mediterranean conditions. Additional driving factors of the SOC trend must be attributed to the type and structure of vegetation cover that changes along the investigated toposequence. The coniferous sites have only little understorey (due to the lack of light) compared to the oak forests. The maquis finally consists to a large extent of understorey (as big trees become less abundant). Vegetation can, however, not be considered as a fully independent factor (in terms of the soil forming state factors; Jenny, 1941) as it reacts to climate. Other

1 investigations (Percival et al., 2000) reported that annual temperature and precipitation explained
2 only partially the variation in soil C content. Under Mediterranean climate conditions, soil
3 properties achieve a notable relevance in enhancing organic matter protection. The soil carbon
4 storage is favoured by large organic matter inputs, high soil clay contents, a calcium-saturated soil
5 matrix and reduced summer aridity (González González et al., 2012). In the Etna region, the clay
6 content and a Ca-saturated soil matrix are of minor importance because the clay content is low and
7 the soils and parent material are acidic.

8 Therefore, the elevational trend of the SOC stocks must be also related to the accumulation of fire-
9 derived OM at lower sites, where fire is more frequent.

10 The increasing C and N stock trend with decreasing altitude was much more evident in the deeper
11 layer (Fig. 2). Here, more C seems to be stored at lower altitudes. As observed in the field, charcoal
12 (macrocharcoal) was able to migrate through macropores to deeper layers due to a good aeration
13 and infiltration rate of volcanic soils (Rivas et al., 2012). Combustion material from the topsoil was
14 probably exported into deeper horizons by water percolation, mesofauna activity, and other causes
15 that finally increases the C stocks in the subsoil, a mechanism that has been observed also in other
16 areas (Schmidt and Noack, 2000; Rumpel et al., 2004; Gonzalez-Perez et al., 2004; Djukic et al.,
17 2010; Knicker, 2011).

18 The elevational trend is more evident for N than for C in these soils (Fig 2); this could be a further
19 clue of a large contribution of PyOM. In fact, a relatively N-rich biomass (e.g. grass vegetation)
20 during charring shows an efficient incorporation of N into the soil (Knicker, 2010). The lower sites
21 actually have a vegetation cover richer in grass compared to the higher sites which are dominated
22 by pine stands having a poorly developed understorey. Consequently, the more distinct altitudinal
23 trend of N, particularly for the deep layer, could also be due to fire effect.

24 However, fire can affect the presence of nitrogen in opposite ways. Bárcenas-Moreno and Bååth
25 (2009) showed that heating to about 200°C induces a preferential loss of nitrogen over carbon, thus

increasing the C/N ratio, whereas heating at higher temperatures, up to 400-500°C, leads to a preferential loss of carbon over nitrogen.

The two sites at the same elevation and with a different recent fire history, site 4 and site 6, did not show any relevant differences in terms of soil C and N concentrations and stocks (Table 4, Fig. 2).

The SOC concentration in the density fractions usually decreased with increasing density in both soil depths, with a single exception for the fraction 1.0-1.6 g cm⁻³ that, on average, had the highest C concentration (Table 5). Site 6, where nearly a fire per year occurred in the last two decades, had the highest C concentration in the fraction 1.0-1.6 g cm⁻³ in both investigated soil layers. This effect does not seem to be due to climate/vegetation properties but rather to the fire frequency, because site 4, having the same altitude and vegetation, had a much lower C concentration in this fraction than site 6. In this regard several authors report that fire-derived carbon is mainly concentrated in the 1.0 – 2.0 g cm⁻³ fraction (e.g. Skjemstad et al., 1990; Golchin et al., 1997; von Lützow et al., 2007).

In the various density fractions (all soils) nitrogen followed quite similar concentration trends to those observed for C. In particular, also for N the highest concentrations were found in the 1.0-1.6 g cm⁻³ fraction (Table 5).

The lighter fractions often showed a higher C/N ratio than the heavier ones, supporting the expectation that the light fractions mainly contained slightly decomposed plant-derived polysaccharides, lignin, cutin, suberin and/or (macro)charcoal (Sollins et al., 2006). Golchin et al. (1997) attributed such a difference in the C/N ratio between density fractions of soil also to preferential adsorption of N-rich organic compounds onto inorganic surfaces in the heavier fractions. The C and N content in the four SOM fractions is given in Fig. 3. Although the lighter fractions had higher C and N concentrations, more than 50% of total SOC and N were in the >2.0 g cm⁻³ fraction due to the higher mass of this fraction. This finding is in apparent contrast with that reported by Golchin et al. (1997) who measured, in three Typic Malanudands dominated by allophane (Japan), an average contribution of 13% to total SOC in the heavy fraction (>2.0 g cm⁻³).

1 The Japanese Andosols however contained a high amount of allophane (that has a low density of
2 1.9 g cm^{-3}). Consequently, most C was found in the fraction $1.6 - 2.0 \text{ g cm}^{-3}$ (about 65% of total
3 SOC).

4 The amount of C and N in the lightest fraction of SOM often depends more on the
5 vegetation/climate effects than on soil properties, since this fraction has little interaction with
6 minerals. In our altitudinal sequence, the highest sites showed the largest amount of C and N in the
7 lightest fraction, probably due to accumulation of pine litter, which is notoriously a poor quality
8 litter. In forests, humus type and organic matter input strongly depends on the tree types. Díaz-Pinés
9 et al. (2011) clearly demonstrated that the larger C stocks in coniferous forests (when compared to
10 oak trees) are due to a high litter input and the poorer chemical quality of the soil organic matter
11 under pine stands. Similar to our case, the differences between pine and oak were mainly found
12 with respect to the particulate soil organic matter that is not associated to mineral particles (Díaz-
13 Pinés et al., 2011). At the mid site at 1090 m asl the lightest fraction is less abundant, probably due
14 to better environmental conditions for decomposers. Finally, at the lowest elevations, where drought
15 becomes a limiting factor for microorganisms, the lightest fraction increases again.

16

17 *DRIFT analysis*

18 As inferred by DRIFT analysis, aliphatic C-H stretching (aliphatic methyl and methylene groups),
19 C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers and phenols and C-OH
20 stretching of aliphatic alcohols appeared to be the dominant groups in the bulk samples from all
21 sites (Table 6). Only small differences seemed to occur with respect to the relative proportion of
22 functional groups.

23 Also the 'twin' sites 4 and 6 showed only minor differences: in particular, site 4 had less intense
24 signals related to phenolic and aliphatic components and an apparently higher contribution from
25 carboxylic groups than site 6 (Table 6).

1 The C-OH stretching of aliphatic, alcoholic O-H showed a marked difference in intensity between
 2 the more elevated sites (1 and 2) and the others, especially in the top 10 cm of soil. This difference
 3 could be caused by the change in the vegetation type, *i.e.* to the transition from conifer stands to
 4 maquis/oak tree vegetation (Table 6).

5 The relative proportion of methyl and methylene groups in the top soil layer increased with altitude
 6 (Fig. 4). Since Simkovic et al. (2008) detected a decrease in intensity of the FTIR peaks of these
 7 functional groups after heating a soil sample, our finding could be additional evidence that fire
 8 frequency at Mt. Etna was historically higher with decreasing elevations.

9 The hydrophobic character of a soil is essentially due to the methyl, methylene and methine
 10 moieties present in aliphatic and aromatic groups (Capriel et al., 1995; Capriel, 1997; McKissock et
 11 al., 2003). Ellerbrock et al. (2005) hence proposed a hydrophobicity index, the A/B ratio, where A
 12 represents the FTIR band of hydrophobic CHs of methyl and methylene groups ($2980 - 2880 \text{ cm}^{-1}$),
 13 and B the bands of hydrophilic C=O functional groups, which in our spectra were at 1725 to 1710
 14 cm^{-1} and at 1660 to 1600 cm^{-1} (Table 3). We did not find any trend of the A/B ratio with altitude
 15 (Fig. 5), neither in the topsoil nor in the subsoil. The A/B ratio for the 2 depths seems to have an
 16 overall opposite behaviour with altitude. The reason for this is however not clear.

17 Aliphatic and phenolic compounds ($1470 - 1440 \text{ cm}^{-1}$ and $1413 - 1333 \text{ cm}^{-1}$, respectively)
 18 decreased with increasing density with the exception of the fraction $<1.0 \text{ g cm}^{-3}$ (Table 7). These
 19 compounds mainly indicate lignin. Phenolic moieties and polysaccharides, in the region $1413 -$
 20 1333 cm^{-1} and $1080 - 1030 \text{ cm}^{-1}$ respectively, showed the largest differences between the light
 21 fractions and the heaviest one. Peptides and proteins appeared to increase with increasing fraction
 22 density. In the topsoil, they were concentrated in the heaviest fraction, probably due to the
 23 association with minerals that tends to protect these labile components from degradation (Table 7).
 24 In the deeper layer, the highest abundance for proteinaceous compounds, however, was found in the
 25 $1.0 - 1.6 \text{ g cm}^{-3}$ fraction, possibly indicating here a larger concentration of fire derived compounds
 26 that include thermally altered N components in their structure (Knicker, 2007).

In contrast to our expectance, the relative intensity of the DRIFT peaks that are indicative for aromatic carbon mostly showed a similar concentration for site 4 and 6, both in the bulk soil and the density fractions. The aromatic components seemed to be more abundant at site 4 in the 1.0 – 1.6 g cm⁻³ fraction. However, as suggested by Knicker (2007), multiple burning does not necessarily lead to an increase in the degree of SOM aromaticity. The absence of this relationship is due to the fact that the new shrub and herb cover developed after a fire provides an available fuel that could burn completely leaving little char. Moreover, also the previously accumulated charcoal could be oxidised during burning.

¹³C CP/MAS NMR spectroscopy

With the aim of highlighting possible effects of fire frequency on SOM, we performed the NMR analysis on the density fractions of samples from the top 10 cm of soils at different elevations: sites 1 and 2 (low fire frequency) vs sites 4 and 6 (high fire frequency). Figure 6 shows the NMR spectra and Table 8 their intensity distribution of all soil fractions except the >2 g cm⁻³ one, which did not produce any significant signal because of its too low C content (less than 1% in weight after the HF treatment). Only four chemical shift regions were considered in Table 8 since aldehydes and ketones, when present, were negligible.

In general, only rather small differences in the NMR spectra between the density fractions was detectable, hence indicating a more or less similar SOM composition (Table 8). Baldock et al. (1992) obtained similar results when comparing NMR spectra from different particle size fractions from an Australian Andosol. They explained this behaviour by a rapid decay of fresh organic residues in Andosols which undergo very slow decomposition once they are protected from microbial attack by the formation of stable organic-aluminium complexes, so minimising differences in SOM chemical structure. Such a process may be hypothesised for the Etna soils.

Clearer differences in chemical structure occur between the soil density fractions of the samples from the lower sites. There were particularly strong signals in the ranges 60 – 90 and 90 – 110 ppm

in the $<1.0 \text{ g cm}^{-3}$ fraction (Table 8). These are typical of carbohydrate-derived structures and the anomeric carbon of carbohydrates and syringyl units of lignin, respectively (Knicker et al., 1996). The $1.0 - 1.6 \text{ g cm}^{-3}$ fraction showed a less intense signal in the O-alkyl C region and a more intense peak in the aromatic C region compared to the other fractions. This fraction seems to contain more PyOC compared to the other fractions, as shown by the occurrence of a major signal at around 130 ppm (Skjemstad et al., 1996). The $1.6 - 2.0 \text{ g cm}^{-3}$ fraction finally showed a pronounced, sharp peak in the alkyl C region, indicating the presence of waxes, cutin, suberin and other lipids (Table 8).

Composite samples from the two highest sites showed a more intense signal in the aromatic region in the $1.0 - 1.6 \text{ g cm}^{-3}$ fraction than samples (Fig. 6, Table 8), suggesting an accumulation of charred material. Moreover, the samples from the highest sites gave a stronger alkyl C signal in the lightest fraction ($<1.0 \text{ g cm}^{-3}$) and a higher contribution of O-substituted aryl C - mainly related to lignin phenols - in all the fractions. These results are related more to the different types of vegetation (coniferous stand versus maquis/oak tree) than to a potential fire influence. However, a reduction of the chain length of alkyl compounds and, hence, a subsequent loss of intensity in the alkyl region is a common occurrence in burned areas (González-Peréz et al., 2004).

SEM observations

Scanning electron microscopy (SEM) showed that the density fractions display different morphologies (Fig. 7). The lightest fraction mostly included undecomposed and slightly decomposed OM whose structure was often still recognisable. Also, a few charcoal fragments were detectable in this fraction. In the fractions $1.0 - 1.6 \text{ g cm}^{-3}$ and $1.6 - 2.0 \text{ g cm}^{-3}$, there were many aggregates having an organo-mineral character that undoubtedly contributes to the protection of the organic component from biogenic decay (Christensen, 1992). Finally, the $> 2.0 \text{ g cm}^{-3}$ fraction was dominated by mineral particles while the organic material was hardly visible.

1 Chemical oxidation resistant carbon (*COREC fraction*)

2 Dichromate oxidation as a method to quantify PyOC in soil was originally proposed by Bird and

3 Gröcke (1997). In literature, this method has been reported to be effective in determining the

4 pyrogenic organic matter pool (e.g., see Song et al., 2002; Rumpel et al., 2006; Hammes et al.,

5 2007; Knicker et al., 2007, 2008; Certini et al., 2011). This method exploits the chemically

6 refractory nature of charred materials, which mostly comprise graphite-like polycondensed aromatic

7 domains (Knicker et al., 2007). However, as Hammes et al. (2007) underlined, this interpretation is

8 based on the (erroneous) assumption that all of the carbon that resists to the treatment (COREC) is

9 PyOC. As demonstrated by Certini et al. (2007) and Knicker et al. (2007, 2008b), one part of PyOC

10 is oxidised (Knicker et al., 2007; Rumpel et al., 2006b), while the residual C maintained a marked

11 lipid nature. In view of these findings, we analysed the dichromate oxidation resistant fraction

12 (COREC) of a composite sample using NMR for assessing its chemical composition. To assess the

13 optimum oxidation time for PyOM isolation, two composite samples obtained by mixing the same

14 amount of HF-treated soil from all sites at the two depths, 0 – 10 cm and 10 – 30 cm, were

15 subjected to different oxidation times (1, 2, 3, 6, and 19 h). In addition, a mix of ground litter layer

16 from all sites and ground charcoal particles hand-picked during the sieving procedure (Fig. 8) were

17 used. We found that within 3 to 6 h the litter was totally oxidised, while the residual carbon of the

18 soil samples amounted to 10 to 14%. Finally, the carbon of the finely ground charcoal that resisted

19 to the treatment was 91% of the original amount after 6 h and 19 h. Following these results, we

20 chose to apply an oxidation time of 6 h.

21 The COREC fraction ranged between 0 and 35% of total OC (Table 9). The total C and N stocks

22 and concentrations of this fraction increased with decreasing altitude (Fig. 9). This would again

23 support the hypothesis of an increasing influence of fire on SOM properties at low elevations. The

24 NMR analyses revealed that the COREC had a prevailing lipidic nature due to the signal being

25 mostly confined to the 0 – 30 chemical shift region (Fig. 10). In addition, the C/N ratio of the

26 COREC was similar to the one of the bulk soil (Tables 4 and 9), hence much lower than that

1 expected for PyOC. In our case, the dichromate oxidation resulted to be non-specific for PyOC,
 2 hence not reliable for PyOC quantification. It seems that part of the charred organic matter was
 3 indeed oxidised using the dichromate procedure. A major effect of fire on soil organic matter is the
 4 formation of particulate C forms highly resistant to oxidation and biological degradation, including
 5 the so-called 'black carbon' (González-Pérez et al., 2004). The fire-affected soil organic matter can
 6 be ascribed rather to the labile and, therefore, more easily degradable fraction (Egli et al., 2012).
 7 The accumulation of this labile fraction at lower altitudes is probably due to fire damage to the soil
 8 biota (and the subsequent lower biodegradation of organic matter, Bárcenas-Moreno and Bååth,
 9 2009) or to the reduced biological activity induced by the aridity of soils during the summer
 10 months. According to Knicker (2007), char is a heterogeneous mixture of heat-altered bio-polymers
 11 having domains of relatively small polyaromatic clusters, but considerable substitution with N, O
 12 and S functional groups. Such a concept implies fast oxidation due to both microbial attack and
 13 dissolution.

14 Knicker et al. (2007) reported that in soil samples with a contribution of aromatic C to total organic
 15 C lower than 20%, the aromatic component of COREC is hardly measurable. Actually, this could be
 16 the case for our samples. The NMR investigation revealed that lipids are resistant to dichromate
 17 oxidation. Knicker et al. (2007) advanced the idea that lipid structures are protected from the acid
 18 treatment due to their hydrophobic nature and that, in general, higher lipid contributions and longer
 19 lipid chains enhance the resistance of lipids to oxidation. Several authors (e.g. Cheshire et al., 2000;
 20 Eusterhues et al. 2005) found oxidation-resistant organic matter enriched in aliphatic compounds
 21 (e.g., fatty acids, waxes). The resistance of these compounds is also caused by strong binding
 22 mechanisms to minerals. Specifically, the alkyl chain interacts with hydrophobic parts of the
 23 mineral matrix via van der Waals forces (Deng and Dixon, 2002). In addition, aliphatic compounds
 24 are believed to penetrate the interlayer space of expandable phyllosilicates at low pH (Theng, 1974).
 25 Particularly in soils where allophanes are present, potentially easily biodegradable substances are
 26 strongly adsorbed or stabilised by complexation processes with amorphous surfaces and,

consequently, protected against degradation and oxidation (see e.g. Hernandez et al., 2012). However, Hernandez et al. (2012) found no significant relationships between the amorphous minerals and aromatic compounds. We consequently hypothesise that the dichromate treatment was not able to oxidise all organic fractions that were strongly bound to mineral surfaces. This procedure is thus probably more problematic when applied to volcanic soils.

Conclusions

In the investigated toposequence on Mt. Etna, there is undoubtedly an effect of fire on SOM. This effect is difficult to quantify. In fact, the factor ‘fire’ is not the only one that determines SOM properties. Furthermore, methodological constraints with respect to the dichromate method limit extended conclusions about the fire effect on SOM. Nonetheless, there are clues that indicate that fire plays an important role. Density fractionation helped to distinguish the influence of different environmental factors– fire included – on SOM characteristics. Climate and vegetation seem to strongly determine the amount and the chemical nature of the very light fraction ($<1.0 \text{ g cm}^{-3}$). The C-OH stretching of aliphatic alcohols distinctly changed at the transition from conifer stands to maquis/oak tree vegetation. Such an effect must be mainly attributed to a vegetation change. In addition, the C/N ratio of the bulk soil, and particularly of the fraction $< 1 \text{ g cm}^{-3}$, abruptly changed between 1090 and 1515 m asl, which also must be attributed to a change in vegetation (transition from maquis/oak to coniferous forest). PyOM, on the other hand, prevails in the $1.0 - 1.6 \text{ g cm}^{-3}$ fraction. The highest C and N concentrations in this fraction were measured at the lowest sites, particularly at the site affected by annual fire.

The COREC stocks exhibited an increasing trend with lower altitudes where a higher fire frequency is documented. Dichromate oxidation to evaluate the PyOC content in soils proved, however, to be not so straightforward as initially assumed. In fact the NMR analyses of the dichromate oxidation resistant fraction showed that most of the COREC consisted of alkyl components, namely lipids and

only a small part could be attributed to aromatic compounds. The scarce selectivity of the method is perhaps one of the reasons why we did not find distinct differences in SOM characteristics between the two sites having similar altitude and vegetation but different fire frequency. Nonetheless, the site more affected by fire had the highest carbon concentration in the 1.0 – 1.6 g cm⁻³ fraction, where PyOM is preferentially confined.

In spite of the relatively high fire frequency, the content of aromatic compounds was in general modest in the studied sequence on Mt. Etna. Bulk soil and density fractions were instead rich in lipids. Either not much of aromatic compounds, besides macro-charcoal, were produced by fire events (due to the high severity of the fire events) or they were partially oxidised by the high fire frequency that in turns could stimulate the production of fresh labile biomass (fertilising effect of ash) that masks the contribution of PyOC to SOM.

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Table 1
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Table 1. Characteristics of the study sites in the Etna region.

Altitude (m asl)	Site	Coordinates	Aspect	Slope (°)	MAT ¹⁾ (°C)	MAP ¹⁾ (mm)	Soil moisture regime	Soil temperature regime	Parent material	Vegetation	Soil type (IUSS Working Group WRB. 2006; Soil Survey Staff. 2006)
551	5	37.8784° N / 15.0900° E	N	0	15.3	1000	xeric	thermic	Trachy- basaltic lava	Macchia Mediterranea/ <i>Quercion ilicis</i> with <i>Quercus pubescens</i> , <i>Asphodelus microcarpu</i> , <i>Carlina nebrodensis</i> , <i>Artemisia spec.</i> , <i>Genista aetnensis</i> , <i>Rubus spec.</i> , <i>Dryopteris filix-mas</i>	Vitri-Mollic Andosol Humic Haploxerand
866	4	37.8512° N / 15.07025° E	N	4	13.1	1100	udic	mesic	Trachy- basaltic lava	Macchia Mediterranea/ <i>Quercion ilicis</i> with <i>Quercus pubescens</i> Wild, <i>Genista aetnensis</i> , <i>Rubus spec.</i> .	Vitric Andosol Typic Udivitrand
998	6	37.8538° N / 15.0027° E	N	3	12.5	1100	udic	mesic	Trachy- basaltic lava	Macchia Mediterranea/ <i>Quercion ilicis</i> with <i>Castanea sativa</i> , <i>Quercus pubescens</i> Wild, <i>Genista aetnensis</i> , <i>Rubus spec.</i> , <i>Dryopteris filix-mas</i>	Vitric Andosol Typic Udivitrand
1090	3	37.8266° N / 15.0831° E	N	0	11.9	1150	udic	mesic	Trachy- basaltic lava	Macchia Mediterranea / <i>Quercion ilicis</i> with <i>Quercus ilex</i> , <i>Quercus pubescens</i> Wild, <i>Castanea sativa</i> , <i>Genista aetnensis</i> , <i>Daphne laureola</i> L., <i>Orchis commutata</i> , <i>Muscari spec.</i> , <i>Rubus spec.</i> , <i>Dryopteris filix-mas</i>	Vitri-umbric Andosol Humic Udivitrand
1515	2	37.8097° N / 15.0640° E	N	4	9.2	1250	udic	mesic	Trachy- basaltic lava	Coniferous forest (<i>Pinus nigra ssp. laricio</i>) with a few deciduous trees (<i>Fagus silvatica</i> , <i>Castanea sativa</i>)	Vitric Andosol Vitric Hapludand
1772	1	37.7915° N / 15.0428° E	N	12	7.5	1400	udic	frigid	Trachy- basaltic lava	Coniferous forest (<i>Pinus nigra ssp. laricio</i> , <i>Dryopteris filix-mas</i> , <i>Iuniperus</i>	Vitric Andosol Humic Udivitrand

¹⁾MAT = mean annual temperature (°C). MAP = mean annual precipitation

Table 2. Chemical (total content) and mineralogical composition of the BC, B or B(C) horizon and parent material of the investigated sites (cf. Egli et al., 2008, 2012).

Altitude m asl	Soil depth cm	site	Chemistry								
			Na ₂ O g kg ⁻¹	MgO g kg ⁻¹	K ₂ O g kg ⁻¹	CaO g kg ⁻¹	SiO ₂ g kg ⁻¹	Al ₂ O ₃ g kg ⁻¹	Fe ₂ O ₃ g kg ⁻¹	TiO ₂ g kg ⁻¹	MnO g kg ⁻¹
	551 55 - 85	5	31.6	20.5	20.5	71.6	520.3	176.7	89.4	19.1	1.74
	866 40-70	4	13.4	17.7	10.5	58.6	482.2	169.5	86.0	17.7	1.63
	998 40-90	6	25.2	25.2	17.1	83.0	487.1	142.0	101.3	21.3	1.75
	1090 40-70	3	26.3	20.2	14.0	60.7	511.2	181.8	88.0	20.2	1.80
	1515 40-55	2	18.7	17.8	11.6	55.8	487.4	196.6	95.0	20.7	1.68
	1772 70 - 80	1	23.0	34.6	12.9	102.8	504.8	140.0	103.7	18.7	1.75
	Parent material 998 (> 90cm)	6	36.9	45.8	16.3	69.5	468.0	179.6	107.8	32.0	2.10
			Mineralogy								
			Amorphous g kg ⁻¹	Zeolithes g kg ⁻¹	Cristobalite g kg ⁻¹	Clinopyroxene g kg ⁻¹	Olivine g kg ⁻¹	Hematite g kg ⁻¹	Magnetite g kg ⁻¹	Plagioclase g kg ⁻¹	K-feldspar g kg ⁻¹
	Parent material 998 (> 90cm)	6	75	28	11	221	67	45	32	467	53

Table 3. Major IR absorption bands and assignments (Piccolo and Mirabella, 1985; Stevenson, 1994; Senesi et al., 2003; Tan, 2003).

Band	Wave number cm ⁻¹	Assignment
1	2980 - 2880	Aliphatic C-H stretching (aliphatic methyl and methylene groups)
2	1725 - 1710	C=O stretching of COOH, aldehydes and ketones
3	1660 - 1630	C=O stretching of amide groups, quinone C=O and/or C=O of H- bonded conjugated ketones
4	1620 - 1600	Aromatic C=C, strongly H-bonded C=O of conjugated ketones
5	1535 - 1500	Aromatic rings, amide II vibration
6	1495 - 1470	N-H stretching of proteic amides
7	1470 - 1440	Aliphatic C-H bending
8	1413 - 1333	OH deformation and C-O stretching of phenolic groups
9	1280 - 1200	C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers and phenols
10	1190 - 1127	C-OH stretching of aliphatic alcohols
11	1116 - 1050	Secondary alcohols
12	1080 - 1030	C-O stretching of polysaccharides

Table 4. Bulk density and C and N contents of the sampled soils along the toposequence (mean values and standard deviation of n = 4).

Altitude m asl	Soil depth cm	Bulk density g/cm ³	Soil skeleton wt-%	Corg g/kg	Ntot g/kg	C/N
1772 (Site 1)	0 - 10	0.98 (±0.16)	10 (±2)	39.1 (±5.1)	1.69 (±0.38)	23.7 (±3.2)
	10-30	1.13 (±0.12)	8 (±3)	16.9 (±2.9)	0.91 (±0.23)	19.0 (±2.5)
1515 (Site 2)	0 - 10	0.87 (±0.12)	8 (±6)	33.7 (±15.1)	1.48 (±0.32)	21.9 (±6.6)
	10-30	1.02 (±0.09)	6 (±6)	16.3 (±6.9)	0.69 (±0.32)	24.4 (±4.4)
1090 (Site 3)	0 - 10	1.02 (±0.04)	22 (±4)	39.2 (±5.1)	3.19 (±0.73)	12.5 (±1.2)
	10-30	0.93 (±0.10)	24 (±4)	20.2 (±10.0)	2.23 (±0.64)	9.3 (±3.7)
998 (Site 6)	0 - 10	1.06 (±0.13)	43 (±16)	50.6 (±7.0)	3.47 (±0.67)	14.8 (±2.7)
	10-30	1.50 (±0.07)	63 (±17)	25.8 (±12.1)	2.61 (±0.51)	9.9 (±4.0)
866 (Site 4)	0 - 10	1.17 (±0.17)	14 (±3)	54.1 (±3.3)	3.92 (±1.51)	15.5 (±6.5)
	10-30	1.02 (±0.12)	14 (±3)	27.0 (±7.1)	2.70 (±0.44)	9.9 (±1.5)
551 (Site 5)	0 - 10	0.85 (±0.24)	33 (±21)	57.4 (±6.5)	5.08 (±0.39)	11.3 (±0.8)
	10-30	1.31 (±0.09)	40 (±11)	47.0 (±11.5)	4.47 (±1.63)	10.9 (±1.7)

Table 5. C and N concentrations and C/N ratio in density fractions from 0-10 cm and 10-30 cm soil depths along the toposequence.

Soil depth cm / (site) and altitude m asl	C concentration in fractions (g/kg)				N concentration in fractions (g/kg)				C/N			
	< 1 g cm ⁻³	1 - 1.6 g cm ⁻³	1.6 - 2 g cm ⁻³	> 2 g/ cm ⁻³	< 1 g cm ⁻³	1 - 1.6 g cm ⁻³	1.6 - 2 g cm ⁻³	> 2 g cm ⁻³	< 1 g cm ⁻³	1 - 1.6 g cm ⁻³	1.6 - 2 g cm ⁻³	> 2 g cm ⁻³
0 - 10 cm												
(Site 1) 1772	304.3	215.3	234.7	48.7	11.7	9.4	12.5	3.0	25.9	22.9	18.8	16.3
(Site 2) 1515	254.3	275.6	203.5	21.8	7.2	7.6	8.1	2.0	35.6	36.5	25.1	11.1
(Site 3) 1090	209.4	328.8	178.3	31.4	12.2	15.5	13.0	1.3	17.1	21.2	13.7	24.7
(Site 6) 998	215.4	370.5	183.9	76.4	14.9	18.0	14.2	6.8	14.5	20.6	12.9	11.2
(Site 4) 866	244.3	280.1	193.8	91.4	17.2	19.9	17.4	7.5	14.2	14.1	11.1	12.2
(Site 5) 551	244.1	327.7	186.9	43.2	16.6	21.2	16.0	3.7	14.7	15.5	11.7	11.8
mean	245.3	299.7	196.9	52.1	13.3	15.2	13.5	4.0	20.3	21.8	15.6	14.6
sd	33.9	54.3	20.5	26.7	3.7	5.6	3.2	2.6	8.7	8.0	5.4	5.3
10 - 30 cm												
(Site 1) 1772	292.2	249.9	164.0	33.4	10.8	11.3	8.6	2.9	27.1	22.1	19.2	11.6
(Site 2) 1515	235.6	97.2	199.5	11.9	6.4	2.5	7.2	1.0	36.6	38.4	27.6	12.5
(Site 3) 1090	267.8	345.5	103.2	28.7	10.9	14.4	8.4	2.4	24.5	24.0	12.3	11.9
(Site 6) 998	200.1	403.4	162.0	73.3	13.9	18.0	13.1	6.1	14.4	22.5	12.4	12.1
(Site 4) 866	229.6	237.0	156.7	71.2	16.1	17.2	14.3	6.4	14.3	13.8	10.9	11.1
(Site 5) 551	244.1	330.3	162.0	43.9	15.7	20.9	14.0	1.4	15.6	15.8	11.6	31.8
mean	244.9	277.2	157.9	43.8	12.3	14.0	10.9	3.3	22.1	22.8	15.7	15.2
sd	31.9	107.9	31.0	24.4	3.7	6.5	3.2	2.3	9.0	8.7	6.6	8.2

Table 6. Distribution (relative proportion) of IR bands with the corresponding absorption bands of bulk soil from either depth (0 – 10 cm and 10 – 30 cm) (see also Table 3).

Soil depth cm / (site) and altitude m asl		Relative distribution in %											
		Absorption bands											
		1	2	3	4	5	6	7	8	9	10	11	12
0 - 10 cm													
	(Site 1) 1772	37.7	0.2	0.8	0.1	1.3	0.2	1.1	2.1	37.1	17.0	1.6	0.7
	(Site 2) 1515	34.0	0.0	0.7	0.0	0.7	0.2	0.7	1.8	42.1	17.0	2.2	0.5
	(Site 3) 1090	32.8	0.2	1.7	0.2	0.4	0.2	1.7	3.5	23.0	32.8	1.6	1.9
	(Site 6) 998	34.0	0.1	1.9	0.4	1.0	0.1	1.7	4.2	17.6	35.0	1.5	2.5
	(Site 4) 866	28.3	0.3	0.2	0.4	0.4	0.5	1.4	2.8	34.5	27.8	2.7	0.5
	(Site 5) 551	25.5	0.0	0.8	0.1	0.6	0.4	1.3	3.3	40.2	24.2	3.2	0.3
10 - 30 cm													
	(Site 1) 1772	25.0	0.1	0.3	0.1	0.4	0.3	0.6	0.7	52.6	17.7	2.0	0.3
	(Site 2) 1515	25.3	0.4	2.7	0.2	0.2	0.8	0.6	7.8	33.7	24.0	2.0	2.3
	(Site 3) 1090	21.9	0.2	0.6	0.1	0.1	0.1	1.2	2.2	44.1	26.0	2.8	0.7
	(Site 6) 998	27.9	0.1	1.7	0.3	1.2	0.4	1.8	4.2	24.9	32.4	3.5	1.6
	(Site 4) 866	26.5	0.4	1.1	0.1	0.6	0.3	1.5	3.5	34.0	30.5	0.9	0.5
	(Site 5) 551	26.7	0.0	0.1	0.5	0.5	0.3	1.5	4.2	35.1	27.3	3.3	0.5

Table 7. Relative distribution (mean and the standard deviation) of the functional groups of organic matter, with the corresponding absorption bands, for the soil fractions from either depth (0 – 10 cm and 10 – 30 cm).

Soil depth cm / (absorption band)	Relative distribution in %			
	< 1.0 g cm ⁻³	1.0 - 1.6 g cm ⁻³	1.6 – 2.0 g cm ⁻³	> 2.0 g cm ⁻³
0 – 10 cm				
Aromatic components (4)	0.4 (±0.2)	0.4 (±0.5)	0.2 (±0.1)	0.4 (±0.3)
Proteins and peptides (6)	0.3 (±0.2)	0.4 (±0.3)	0.4 (±0.1)	0.9 (±0.6)
Aliphatic component (7)	4.8 (±1.4)	6.3 (±1.0)	5.4 (±0.9)	2.9 (±1.4)
Phenolic groups (8)	9.5 (±2.3)	11.6 (±1.0)	11.0 (±2.2)	2.3 (±0.8)
Aliphatic alcohols (10)	70.8 (±6.1)	65.7 (±4.3)	73.2 (±4.1)	80.7 (±2.5)
Polysaccharides (12)	5.6 (±2.6)	7.1 (±2.0)	5.0 (±1.1)	2.3 (±1.1)
10 – 30 cm				
Aromatic components (4)	0.6 (±0.3)	0.1 (±0.1)	0.2 (±0.2)	0.4 (±0.4)
Proteins and peptides (6)	0.3 (±0.2)	0.7 (±0.2)	0.3 (±0.1)	0.6 (±0.3)
Aliphatic component (7)	3.5 (±0.9)	5.2 (±0.9)	4.6 (±0.7)	2.3 (±1.5)
Phenolic groups (8)	9.2 (±2.8)	11.4 (±1.4)	12.2 (±1.4)	2.5 (±1.3)
Aliphatic alcohols (10)	70.5 (±5.8)	67.6 (±5.7)	75.2 (±3.7)	79.1 (±2.2)
Polysaccharides (12)	4.2 (±1.6)	6.2 (±3.4)	3.2 (±1.6)	2.2 (±0.6)

Table 8
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Table 8. Relative distribution (%)^a of the chemical shift regions of ¹³C CPMAS NMR spectra of the topsoil (0 – 10 cm). The contribution of aldehydes and ketones (chemical shift region 185-220) is not reported because negligible.

Site/ density fraction	Relative distribution (%) of chemical shift region (ppm)						
	Alkyl C	O-Alkyl C			Aryl C		Carboxyl C carboxyl C/amide/ester
		Methoxyl/N-alkyl	O-alkyl	Di-O-alkyl	C substituted (aromatic C-H and C-C)	O substituted	
0 – 45	45-60	60-90	90-110	110-140	140-165	165-185	
Highest sites (1+2)							
< 1 g cm ⁻³	34	7	28	5	6	9	11
1 – 1.6 g cm ⁻³	30	6	26	4	7	14	13
1.6 – 2 g cm ⁻³	36	5	26	4	6	9	14
Lower sites (4+6)							
< 1 g cm ⁻³	24	7	35	8	10	6	10
1 – 1.6 g cm ⁻³	25	5	26	4	15	10	15
1.6 – 2 g cm ⁻³	32	7	25	5	9	3	19

^a Maximum error ± 4.

Table 9. Organic C recovered after the HF treatment, content of COREC (chemical oxidation resistant carbon) and C/N of the material left after dichromate oxidation

Altitude m asl	Soil depth cm	OC recover after HF % of initial C	COREC % of initial C	C/N
1772	0 - 10	68	9	20
(Site 1)	10 - 30	55	13	37
1515	0 - 10	49	0	n.d.
(Site 2)	10 - 30	86	35	n.d.
1090	0 - 10	49	2	19
(Site 3)	10 - 30	58	17	16
998	0 - 10	57	17	17
(Site 6)	10 - 30	87	4	19
866	0 - 10	62	14	13
(Site 4)	10 - 30	58	27	15
551	0 - 10	63	17	14
(Site 5)	10 - 30	86	14	14

Figure captions

Fig. 1. Location of the investigated sites in Mt. Etna region, Sicily, southern Italy.

Fig. 2. Soil C and N stocks along the toposequence (mean values and standard deviation; $n = 4$).

Fig. 3. C and N content distribution among soil density fractions (0 – 30 cm).

Fig. 4. Relationship between the altitude and the relative proportion of methyl and methylene groups. The regression curve is given for the depth 0 – 10 cm.

Fig. 5. Relation between altitude and the A/B ratio (hydrophobic groups/hydrophilic groups) in the DRIFT spectra of bulk soils for soil depths 0-10 cm and 10-30 cm.

Fig. 6. ^{13}C CPMAS spectra of density fractions from composite samples from the topsoil (0–10 cm) of the two highest sites (1+2; below; sites having a low fire frequency) and the two lower ones (4+6; above; sites having a high fire frequency).

Fig. 7. SEM images of the four separated fractions and, in white on the low side, EDX spectrograms of the areas marked off by squares. **A)** charcoal from the $< 1 \text{ g cm}^{-3}$ fraction, in which structure cells are clearly visible, **B)** particles of the $1.0\text{-}1.6 \text{ g cm}^{-3}$ fraction; inset 1 shows an organo-mineral aggregate, **C)** the $1.6\text{--}2.0 \text{ g cm}^{-3}$ fraction; inset 2 shows a glass particle, **D)** the $>2 \text{ g cm}^{-3}$ fraction: mineral particles are clearly dominant; inset 3 shows a possible iron (hydr)oxide.

Fig. 8. Percentage of the initial OC recovered after dichromate chemical oxidation treatment of soil samples from two depths, litter material and ground charcoal particles.

Fig. 9. Concentrations of C (A) and N (B) in the organic matter resistant to dichromate oxidation and C and N stocks (C and D) along the toposequence.

Fig. 10. ^{13}C CPMAS spectrum of COREC in the top 10 cm of bulk soil of site 5. Numbers represent relative distribution of the three major chemical shift regions (from the left: Carboxylic C; Aromatic C; Alkyl C).

Figure 1
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