Effect of pedogenic processes and formation factors on organic matter stabilization in alpine forest soils

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ABSTRACT

Understanding the mechanisms involved in the building up of organic matter pools with long residence time in soils is fundamental for the comprehension of carbon dynamics. As organic matter persistence depends on environmental conditions and soil properties, both pedogenic processes and factors should be key elements in identifying the link between organic pools and stabilization mechanisms.

In the Ligurian Alps, an area where pedodiversity is large, we evaluated the importance of two soil formation factors, vegetation and parent material, and consequently pedogenic processes and soil features, on organic matter stabilization in forest soils. We thus selected 20 profiles, developed on different parent materials and forest stands, which ranged from Regosols, to Cambisols, to Chernozems/Kastanozems, to Podzols and Luvisols/Alisols. In the mineral horizons, we determined the soil physico-chemical properties and fractionated organic matter into labile and stabilized (recalcitrant and mineral-bound) pools using NaClO followed by HF treatment.

Soil and organic matter characteristics were primarily explained by the parent material and soil type, while vegetation affected organic matter quality but not the total amounts. The labile and recalcitrant organic pool proportions were linked to parent material likely through its effect on pH and other microenvironment characteristics. The mineral-associated organic matter instead followed a pedogenic pathway, with higher percentages of stable organic carbon in illuvial B horizons from Podzols and Luvisols/Alisols. In the study area, therefore, the most developed soils were relatively more resilient for organic matter conservation than less developed soils, which are more prone to C losses.

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1. Introduction

Soil organic matter (OM) represents one of the most important carbon (C) reservoirs in the global C cycle (Lal, 2008) also thanks to the slow turnover of some protected OM fractions. Indeed, if a portion of OM, called labile OM pool, is quickly decomposed and its structural C released, a stable OM pool may persist in the soils from decades to millennia (Schmidt et al., 2011). Soil OM stabilization principally consists in the intrinsic recalcitrance of organic compounds to degradation and in the interaction with mineral phases, such as the inclusion of organic components into aggregates and the formation of chemical bonds between OM and mineral surfaces (Sollins et al., 1996; von Lützow et al., 2006; Jastrow et al., 2007). The complexity of the chemical structure of organic molecules has been used to explain OM persistence for long times (Stevenson, 1994), but the importance of recalcitrance as a fundamental mechanism of OM stabilization has been recently questioned (e.g., Marschner et al., 2008). The stabilization of OM by association with minerals is instead acknowledged by many authors as the main reason of OM persistence (e.g., Torn et al., 1997), and this

mechanism accounts for the long residence time of even chemically labile and quickly decomposable organic compounds, such as sugars (Schmidt et al., 2011). All these mechanisms operate simultaneously, although their relative importance may differ depending on specific environmental conditions and soil features, which in turn are related to the factors of soil formation and to pedogenic processes (Jenny, 1994; Schmidt et al., 2011).

Vegetation is among the pedogenic factors that primarily influence soil OM in terms of both quantity and quality. Leaf and root litter from different forest species largely differs in the amount of lignin, tannins, waxes and other recalcitrant compounds; therefore, the molecular structure and chemical composition of organic materials predominate in driving the first steps of decomposition and contribute in controlling the long-term persistence of OM (Schmidt et al., 2011). Besides, biochemical recalcitrance may also arise because of unsuitable conditions for decomposers, such as low N contents in fresh litter (Melillo et al., 1982) or the lack of macronutrients and necessary co-metabolites (Schmidt et al., 2011), which limit OM decomposition rate. On the other hand, parent material sharply affects the characteristics of the soil mineral phase, thus it is expected to influence the extent of OM stabilization by organo-mineral associations. The association between OM and mineral occurs because of the formation of chemical bonds through

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ligand exchange, cation bridges or weaker Van der Waals interactions, depending on soil mineralogical composition. In the last years, several adsorption experiments performed under controlled conditions (e.g., Gu et al., 1994) showed that ligand exchange between hydroxyl(—OH) groups on mineral surfaces and carboxyl groups (—COOH) or phenolic —OH groups of OM is the preferential mechanism for the formation of stable organo-mineral associations. Hence, this mechanism is expected to act mainly in well-developed soils or where Fe and Al (hydr)oxides form a considerable part of the soil inorganic phase (e.g., Kleber et al., 2005). Conversely, in the presence of low CEC minerals, such as lithogenic micas, Van der Waals interactions may account for about 50% of bound-OM (Mikutta et al., 2007). The role of parent material on OM stabilization may also be less specific and related to the effect it has directly on soil properties, such as pH and texture, or indirectly on microfauna activity and microbial biomass (e.g., Anderson, 1988; Heckman et al., 2009; Littke et al., 2011).

Mountain forest soils are often poorly developed due to slope steepness, erosion and other disturbance factors (Legros, 1992). Consequently, the influence of the parent material on soil properties is often remarkable, affecting soil pH, texture and mineralogical composition (D'Amico et al., 2014a). On the other hand, the presence of elevation belts shapes the occurrence of forest vegetation types and contributes in affecting soil development and differentiating soil properties (D'Amico et al., 2014b). In an alpine context, in fact, plant communities represent a good indication of the climatic conditions, since they are especially sensitive to soil temperatures and well differentiated along elevation (Giordano, 2013). The southernmost part of the alpine arc is characterized by a wide range of forest types, which, depending on elevation, range from broadleaved and pine trees of the montane belt to larches and grasslands of the subalpine area. In this geographic area, lithological variability is also large, and vegetation and parent material seem to represent two among the most variable factors affecting soil development; they are thus possibly linked to the large pedodiversity characterizing the site. In this area, we fractionated soil OM into labile, recalcitrant and mineral-associated pools using an oxidative degradation treatment with NaClO followed by mineral dissolution with HF. We hypothesized that the amount and proportion of the OM pools could be affected by soil development and the above mentioned pedogenic factors. The aims of this work were therefore i) to evaluate the relative importance of forest cover and parent material, and consequently of pedogenic processes, on OM stabilization in alpine forest soils; and ii) to verify if soils belonging to different soil groups, and therefore differing in physico-chemical characteristics, showed specific OM stabilization patterns.

2. Materials and methods

2.1. Study area and soils

The study area is located in the Ligurian Alps at the border between the Piemonte and Liguria regions, North-Western Italy (Fig. 1). Based on a much larger number of observations, twenty sites were selected, which represented the most common combinations of forest cover and lithology of the soil parent material (Table 1). Seven sites were identified under beech stands (FS, *Fagus sylvatica* L.), which cover around 30% of the total forest surface, and are the most represented forest type in the considered area (Regione Liguria, 2012; Regione Piemonte, 2012). Other widespread forest stands in the area are chestnut (CS, *Castanea sativa* Mill.; 5 sites), Scots or bog pines (PS, *Pinus sylvestris* L. or *Pinus montana* Miller; 4 sites), and hornbeam-ash associations (FO, *Fraxinus ornus* L. and *Ostrya carpinifolia* Scop.; 2 sites), covering approximately 10–15% of forest surface each. Larch stands, often associated with grasslands (LD, *Larix decidua* Mill.; 2 sites) occupy around 8% of the area. From the geological point of view, all sites are located on either the Ligurian Briançonnais domain or the Helminthoides Flysch units, and on their colluvial deposits (ISPRA, 2004). Specifically, the soils selected on the Ligurian Briançonnais domain developed on

strata composed by quartzite or metamorphic porphiroids (QTZ; 6 sites) or limestone-dolostone (LIM; 5 sites), while the soil parent material of the sites on the Helminthoides Flysch units (FLY; 9 sites) is formed by both calcareous and non-calcareous weakly metamorphosed siltstones and claystones discontinuously interbedded by sandstones.

The selected sites ranged in elevation from 840 to 1700 m a.s.l. (Table 1), which correspond to the montane and lower subalpine phytoclimatic level. The FO sites were located at the lowest elevation (on average 852 m a.s.l.), the elevation of the sites covered by CS (990 m), FS (1250 m) and PS (1280 m) did not significantly differ and the CS did not differ either from FO. The LD sites were at the highest altitudes (1650 m a.s.l., on average). The area is characterized by two soil temperature regimes depending on elevation: the sites below 1300 m a.s.l. have a mesic regime while those at higher elevation are cryic. The soil moisture regime is udic at all sites (Cagnazzi and Marchisio, 1998).

In each site, a representative soil profile was opened and all the morphological horizons were described. After removing the organic layers, the horizons were sampled from the profile pit walls and the material was collected from the whole depth of the morphological horizons, with a total of seventy-nine samples (Table 1). The selected soils were generally thinner than 1 m and showed a varying degree of evolution. According to the WRB soil classification system (Working Group WRB, 2014), most profiles belonged to the Regosol and Cambisol groups. In addition, some specific diagnostic horizons occurred. On calcareous parent materials with little leaching of basic components, the soils showed humus-rich mollic epipedons and thus were included in the Kastanozem or Chernozem groups (P4 and 6, respectively). Albic and both cemented and non-cemented spodic horizons were instead recognized in soil developed on acid rocks, such as quartzite and/or metaporphiroids, and in the presence of moderate slopes (<50%). Independently from the type of parent material, argic horizons were also identified in the field thanks to the formation of clay cutans on the aggregate faces, although the horizon sequence was sometimes disturbed by natural or anthropogenic soil covers (colluvic, escalic and transportic qualifiers; Table 1).

2.2. Soil physico-chemical analyses

The mineral soil samples were air-dried and sieved to 2 mm before chemical analyses. The pH was determined potentiometrically in a 1:2.5 soil:deionized water suspension (Van Reeuwijk, 2002), the C and N contents were determined through dry combustion (CE Instruments NA2100 elemental analyzer, Rodano, Italy). The content of inorganic C was measured with the TIC-solid module of a TOC analyzer (Vario TOC Elementar, Hanau, Germany) and the amounts were subtracted from the total C to obtain organic C (OC_{UT}). The particle size distribution was evaluated by the pipette method after H_2O_2 treatment and dispersion of the sample with Na-hexametaphosphate (Gee and Bauder, 1986). Iron was extracted using dithionite-citrate-bicarbonate (Fe_D, Mehra and Jackson, 1960) and acid ammonium oxalate (Fe_O, Schwertmann, 1964) solutions, and the concentrations were determined by atomic absorption spectrophotometry (Perkin Elmer Analyst 400, Waltham, MA, USA) in both extracts. All analyses were duplicated.

2.3. Organic matter fractionation

The samples were chemically treated following the procedure described by Mikutta et al. (2006). The samples were oxidized 3 times with 6% NaClO at pH 8, with a ratio soil:solution 1:10. They were then washed with deionized water until the electrical conductivity was below 40 μS cm^{-1}, oven-dried at 40 °C and the OC concentrations were determined as described above. The oxidized samples were treated successively with 10% HF to remove the mineral phase, washed and dried. The C concentrations were again determined and assumed to represent the OM pool which is stabilized by chemically recalcitrance (OC_{rec}). The NaClO-labile pool (OC_{lab}) was calculated as the difference