Features of skeleton water-extractable fines from different acidic soils

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ABSTRACT

The skeleton water-extractable fines (SWEF) is a soil fraction smaller than 2 mm located at the interface between rock fragments (RF) and fine earth (FE). It is made of illuvial and/or RF weathering products comprising neoformed clay-size particles and organic substances. Contrary to FE and even to soil RF, SWEF represents a poorly documented soil fraction despite its unique ion exchange properties. To fill this knowledge gap, we compared mineralogy, effective cation exchange capacity (ECEC), and exchangeable cation composition of SWEF with those of FE and RF from three acidic soils derived from either mica schist (Mottarone, Italy), granite (Aubure, France) or glacial till of varied lithology (Gårdsjön, Sweden), and subjected to distinct climatic conditions. Further, we provided a general hypothesis on the formation of SWEF. The SWEF had a different acidity level, a significantly higher accumulation of organic C, a higher Al_p and/or Fe_p content (in two over three soils), was enriched in neoformed minerals, and had a larger concentration of exchangeable cations than both FE and RF. A key role in the development of the SWEF properties was attributed to mineralogy, weathering and pedogenesis. The interactions between mineralogical composition, pH, and organic C content not only determined the extent of ECEC in SWEF but also the source of exchangeable cations originating either from organic complexes (Mottarone soil) or from the dissolution of the mineral phases (Aubure and Gårdsjön soils). However, the abundance of SWEF appeared to be independent from the actual abundance of RF. Its formation was rather controlled by the combination of mineralogy of the parent material, weathering intensity, pathway of mineral dissolution (congruent and/or incongruent dissolution), and to the duration of pedogenesis.

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1. Introduction

The chemical composition and the cation exchange capacity of the soil have been extensively investigated in the whole range of soil orders (e.g., Peinemann et al., 2000; Costa et al., 2004; Hepper et al., 2006; Tomašić et al., 2013). The vast majority of these investigations were conducted on fine earth, while comparatively few studies dealt with the skeleton, also named rock fragments or clasts (Ugolini et al., 1996; Martín-García et al., 1999; Kohler et al., 2000; Cuniglio et al., 2009; Zabowski et al., 2011). As reported by Dambrine et al. (1997), Jongmans et al. (1997), van Breemen et al. (2000), Bailey et al. (2004) and Cuniglio et al. (2009), soil rock fragments can acquire a significant cation exchange capacity when clast-forming minerals weather. However, some contribution to cation exchange capacity is also due to the presence of organic matter carried into the clasts by the soil solution (Agnelli et al., 2002a, 2008; Cuniglio et al., 2009). Corti et al. (1998a) further showed that the weathering degree of the soil rock fragments was positively correlated with their cation exchange capacity. These

studies point to the fact that cation exchange capacity may occur in both fine earth and rock fragments, and that, in the latter case, the magnitude of the cation exchange capacity depends on the degree of clast weathering. Located at the interface between fine earth and rock fragments, there is a poorly-documented smaller than 2-mm fraction obtained by dry and wet sieving of the skeleton (Corti et al., 1998a; Fernández Sanjurjo et al., 2011). In sandstone-derived Inceptisols under *Abies alba* Mill. forest, Agnelli et al. (2002b) found that this fraction was a by-product of the alteration of rock fragments into fine earth (weathering rim) in the upper horizons, whereas it was mostly made of coatings accumulated by illuviation in the sub-surface horizons. In contrast, Fernández Sanjurjo et al. (2011) found that these fines derived from both illuviation and weathering rim, whatever the depth, in Entisols developed from pyroclastic deposits. Given its dual origin, Fernández Sanjurjo et al. (2011) attributed to this fraction the operationally defined term "skeleton water-extractable fines" (SWEF). Over the long term, both illuviation and weathering are capable of producing the accumulation of a fine material, the SWEF, which contains illuvial and/or neoformed clay minerals and illuvial organic substances. Moreover, tree roots tend to grow around rock fragments and other localized soil areas of large density and coherence (e.g., Bengough et al., 2001; Gilman, 2006; Di Iorio et al., 2008), thus favouring the accumulation of

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organic matter in SWEF following the in-place decomposition of roots. The latter effect could be exacerbated in soils containing high amounts of coarse fragments such as those developed in stony glacial tills, pebbly fluvial sediments, or unconsolidated materials over fragmented bedrock.

These and other findings (Agnelli et al., 2000, 2002a; Corti et al., 2005) indicate that composition and properties of SWEF depend on soil texture and mineralogy, and differ from those of fine earth and rock fragments. In particular, because SWEF has the potential to accumulate organic matter and clay minerals, it could be hypothesized that: i) the cation exchange capacity of SWEF would be higher than that of other proximal soil fractions such as fine earth and rock fragments, and ii) the cationic population of SWEF would be more acidic than in fine earth and rock fragments. Yet, the cation exchange capacity and the cationic population of the exchange sites of SWEF have never been thoroughly investigated. To fill this gap, we compared analytical results of fine earth, SWEF, and rock fragments from three acidic soils developed from different parent materials, and submitted to distinct climatic conditions.

Therefore, the aims of this work were: 1) to compare the features, mineralogy, cation exchange capacity, and exchangeable cation composition of SWEF with those of fine earth and rock fragments, and 2) to provide a hypothesis on the formation of SWEF.

2. Materials and methods

2.1. Study sites

The field approach was to study acidic forest soils that vary with respect to the abundance of rock fragments, nature of the parent material, duration of pedogenesis, climate, and dominant vegetation in order to obtain SWEF fractions that differ in terms of their volumetric abundance, mineral composition and origin. To meet these needs, the soils selected for this study originated from the following three sites:

1) *Mottarone* (60 km N of Novara, Italy). The site is located in the pre-alpine fringe, at about 800 m above sea level, on a 5 to 7% slope and a W exposure on the flanks of Mount Mottarone, under a 100 to 140 years old *Fagus sylvatica* L. plantation. The climate of the area is temperate and humid with a mean annual air temperature (MAAT) of 11.5 °C and a mean annual precipitation (MAP) of 2060 mm. The soil developed from a Pre-Permian mica schist and was classified as a Typic Humudept, coarse-loamy, mixed, mesic according to the Soil Survey Staff (2014), and as a Cambic Umbrisol (Colluvic) according to the IUSS Working Group WRB (2014).

2) *Aubure* (120 km SE of Nancy, France). The site is part of the Vosges mountains, at 1070 m above sea level, on a 20% slope and NE exposure, and hosts a plantation of *Picea abies* (L.) Karsten from 100 to 140 years old. The climate is temperate oceanic mountainous with a MAAT of 5.5 °C and an evenly distributed MAP of about 1300 mm, with 15% falling as snow from November to April. The soil developed from granite, and was classified as a Humic Dystrudept, loamy-skeletal, mixed, isofrigid according to the Soil Survey Staff (2014), and as a Skeletic Cambisol (Colluvic) according to the IUSS Working Group WRB (2014).

3) *Gårdsjön* (50 km N of Gothenburg, Sweden). The site is at 124 m above sea level, on a 5% slope with NW exposure, in a forest of *Picea abies* (L.) Karsten (90 to 110 years old) with few *Pinus sylvestris* L. The climate is maritime, with a MAAT of 5.0 °C and a MAP of about 1150 mm. The soil parent material is a glacial till mostly composed of gneiss and diorite that was deposited at the end of the last glaciation (Würm), approximately 14,000 YBP (Olsson et al., 1985). The soil was classified as an Aquic Haplocryod, coarse-loamy, mixed, isofrigid according to the Soil Survey Staff (2014), and as a Histic Podzol (Gelic) according to the IUSS Working Group WRB (2014).

While at Gårdsjön glacial retreat started about 14,000 YBP, on the Alps it occurred about 17,000 YBP (Hinderer, 2001) and on the Vosges in happened 18,000–20,000 YBP (Seret et al., 1990). As a consequence, the duration of pedogenesis was shorter at Gårdsjön than at the two other sites.

2.2. Field procedures and sample preparation

At each site, a trench 1.5 m in width was opened in a representative area of the forest to assess the soil morphology. Then, three profiles were sampled, one is the trench and other two were opened about 10 m away one from the other. Hence, for the three sites a total of nine profiles were considered. The morphological description of one soil profile for each site is given in Appendix I. Soil samples were collected from all horizons of each profile on a volume basis according to Corti et al. (1998a). Briefly, a soil sample that increased in volume as a function of the size of the largest rock fragment found in the horizon of interest was collected, and its volume measured by the irregular hole method of Blake and Hartge (1986). In general, at least 6 L of sample were collected in the A horizons, and up to 15 L in the BC horizons. At Mottarone and Aubure, samples of fresh rocks (mica schist and granite, respectively) were collected from bedrock outcrops located close to the soil sampling sites. At Gårdsjön, gneiss and diorite blocks were gathered from a morainic exposure at 40 m from the soil trench.

Each soil sample was separated into fine earth (FE), rock fragments (RF) and SWEF. The SWEF was obtained by dry and wet sieving of the RF (Fernández Sanjurjo et al., 2011). According to Corti et al. (1998a), the RF were subdivided into three classes based on their degree of alteration, which corresponded to the size of the clasts: as size decreased, weathering increased. The size limit of the classes was obtained by merging five features: colour intensity, roughness and irregularities of the surfaces, cracks, and surface aspect of the exposed minerals. The classes formed were called highly altered RF (HARF), moderately altered RF (MARF) and slightly altered RF (SARF). The size range for the three classes differed with soil horizons (Table S1 of the Supplementary data). In the Mottarone and Gårdsjön soils, in addition to the RF weathering classes, we identified a separate class of quartzite RF, which was independent of weathering stage. The percentage distribution of FE, SWEF, and RF classes, and of all the measured variables, except for pH and mineralogy, were expressed on a volume basis (Ugolini et al., 1996), by using the bulk density of all fractions (Appendix II) as determined by Corti et al. (1998a).

2.3. Analytical methods

The pH was determined potentiometrically in H_2O and in 1 M KCl solutions (both at pH 6.2), using a combined glass-calomel electrode immersed into the suspension (1:2.5 solid:liquid ratio). For RF classes, amounts of intact clasts accounting to at least 50 g were used, while for the fresh rocks we used aliquots of 50 g made of fragments having the same size as the SARF of the deepest horizon. On specimens ground to less than 0.5 mm, organic C was estimated by the Walkley-Black method without the application of heat (McLeod, 1973). Aliquots of FE, SWEF, and RF classes were submitted to a Na-pyrophosphate extraction, which is considered able to solubilise Al and Fe associated with soil organic matter (Bascomb, 1968). Aliquots of 1 g for FE and SWEF, and amounts of intact clasts accounting to 10 g for HARF, and 20 g for MARF and SARF were shaken for 16 h in a 0.1 M $Na_4P_2O_7$ solution (1:100 solid:liquid ratio). On the extracts, Al and Fe were determined by Varian SpectrAA 220Z atomic absorption spectrophotometer equipped with graphite furnace.

The mineralogical composition was determined on powdered specimens of the bulk materials of FE, SWEF, RF classes and fresh rocks to identify primary minerals, and on the clay separates obtained from each of these fractions to identify clay minerals. The clay of FE and SWEF was recovered by sedimentation after removal of organic matter