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Abstract

In podzolic B horizons illuviated Al, Fe and organic matter (OM) increase with the ongoing of the pedogenic process. Depending on OM load on mineral surfaces, modifications of the soil surface properties are expected and may influence OM stabilisation. The proportion of labile organic pools should thus vary depending on the type of podzolic horizon. In this work we selected B horizons at increasing intensity of podzolisation, evaluated the labile OM pools through oxidation with 2% NaClO and characterised surface properties with N_2 and phosphate sorption. Before and after oxidation, we assessed the NaOH-extractable OM fractions. Oxidation was more effective on the least polar organic compounds and lead to an increase in the fulvic to humic acid ratio. Specific surface area (SSA) increased after oxidation only in the least podzolised horizons, while selectively preserved OM induced a decrease in SSA in the more developed Bs, Bsm and Bhs. Phosphate sorption induced a release of OM and always decreased after oxidation, although variations in P affinity for the surfaces were observed. The effect of oxidation on surface parameters pointed to a specific association between organics and minerals that changed during soil development. At the very beginning of podzolisation, the dominant forms seemed related to organo-metallic complexes with little interaction with surfaces. When a Bs has developed, weak interactions between mineral surfaces and OM appeared, while at a later stage OM differentiated into bulky structures and tightly bound, rigid ones, with extremely low N_2 accessibility. The latter were not sensitive to low concentration NaClO while the former were easily oxidised.

Introduction

Podzolisation is a widespread process of soil formation and occurs extensively in boreal and mountain areas (Sauer et al. 2007). Podzolisation induces a clear differentiation in the soil profile with organic matter (OM), Fe and Al enriched B horizons, overlaid by grey to whitish eluvial layers. Several theories have been proposed to explain podzolisation, but in most cases the co-migration of OM, either as fulvic or as low-molecular weight organic acids, and metals (Me) is acknowledged (Lundström et al. 2000). In addition to illuviated organic complexes, B horizons may also contain OM as remnants of root decomposition (Buurman and Jongmans 2005). The illuviated OM pool increases with podzolisation: for example, Buurmann et al. (2008) observed that most OM in a Spodic Udipsamment was root- and char-derived, while both illuviation and root decomposition contributed to the accumulation of OM in the B horizon of a Typic Haplorthod. Bhs horizons have higher organic carbon (OC) contents and typically narrower metal/OC ratios than Bs, thus indicating that OM may accumulate as a result of both organo-mineral and organo-organo interactions. The migration of OM into illuvial horizons favours the presence of large OC pools in deep horizons of podzolic soils (Grand and Lavkulich 2011), where the interaction with the mineral phases and metals (Sollins et al. 1996; von Lützow et al. 2006; Jastrow et al. 2007) may be responsible for the long residence times of OM (Spielvogel et al. 2008). At the beginning of the process, podzolisation may be visible only through bleaching of quartz grains in the upper soil horizons, with little accumulation of illuviated organo-metallic compounds. Subsequently, with the accumulation of illuviated materials a Bs horizon develops. At a more advanced stage, as the eluvial part of the soil becomes depleted in weatherable minerals, the B horizon may differentiate a top part (Bhs) which is enriched in OM with respect to the lower Fe and Al-richer zone (McKeague et al. 1983). Upon changes in drainage or active cementation, indurated materials such as the placic horizon or the ortstein (Bsm or Bhsm) may develop (Bockheim 2011). It can be hypothesized that the interactions between OM and mineral phases change during the different steps of podzolisation both because of the increasing illuviation and because of the ageing of mineral components when inputs of fresh organic material has stopped and cemented horizons have formed.

Several methods have been proposed to evaluate OM stability, and the use of oxidising agents has been widely adopted (Mikutta et al. 2005). OM resistant to NaClO oxidation is assumed to be stabilised either by interaction with the mineral soil components or due to its intrinsic resistance to biochemical degradation (Mikutta et al. 2006). Intrinsic recalcitrance has a minor effect in mineral soil horizons with respect to other stabilisation mechanisms (Marschner et al. 2008), while the interaction of OM with metal ions and/or mineral surfaces is more important and has been related to the amounts of organo-metallic complexes and poorly crystalline Al and Fe (oxy)hydroxides (e.g. Kleber et al. 2005; Kögel-Knabner et al. 2008; Heckman et al. 2009). Since chemical oxidation with NaClO removes the most labile OM fraction with little or no effect on the mineral phases (Siregar et al. 2005), coupling it with the assessment of surface properties may provide a useful tool to evaluate the extent and strength of organo-mineral interactions at different podzolisation steps.

Gas adsorption is one of the most widely used techniques for the evaluation of specific surface area (SSA) and of meso- and microporosity (Kaneko 1994). When analysed using N_2 as the probe molecule, OM typically returns low values of both SSA, even <1 m^2 g^{-1} (Sasaki et al. 2007), and porosity due to the extremely slow diffusion of N_2 into very small-sized pores (<0.5 nm) at the temperature conditions used for the analysis (De Jonge and Mittelmeijer-Hazeleger 1996). Primary silicate minerals also have a low SSA (Brantley and Mellott 2000), but soils show a wider range, from less than 10 to above 25 m^2 g^{-1} (Skopp 2000), depending on texture and amounts and types of pedogenic minerals. The presence of Al and Fe (hydr)oxides greatly influences surface properties because of the large SSA of poorly crystalline phases, up to 400 m^2 g^{-1} for ferrihydrite, while more crystalline oxyhydroxides always show lower values (e.g. 9 m^2 g^{-1} for goethite) (Cornell and Schwertmann 1996). Organic matter removal typically induces an increase in surface area (e.g. Kaiser and Guggenberger 2003) due to (i) the elimination of the low-SSA component, (ii) changes in the accessibility of N_2 into pores previously filled by OM (Echeverrìa et al. 1999), and (iii) exposure of new mineral surfaces due to the removal of OM from aggregates (Feller et al. 1992). In addition, the elimination of patchy distributed OM on mineral surfaces increases accessible surfaces and results in a greater affinity between the adsorbent and the adsorbate (Mayer 1999).

The effects of OM-Me complexes and OM-mineral association on surface properties may be evaluated also by following the sorption of anions, such as phosphate. It is well known that phosphate sorption decreases when Fe and Al (hydr)oxides are mixed with humic substances (Gerke and Hermann 1992) or other simpler organic compounds (Violante et al. 1991; De Cristofaro et al. 2000; Liu and Huang 2000), as a result of the competition between negatively charged OM functional groups and phosphate species for the same hydroxyl groups in a wide pH range. In soils, the effect of OM on P sorption is more complex due to the simultaneous presence of several mechanisms in addition to competition, such as the inhibition of oxide crystallization and the formation of ternary complexes between the Fe, organic compounds and phosphate. According to Gerke and Hermann (1992), Fe-humic compounds were six to seven times more active than amorphous Fe oxides on P sorption, as Me in Me-humic substances is more finely distributed on the organic surface and not present as Me polymers, hence creating a larger number of sites for P retention. When OM is removed from soils the results are not always straightforward. In some cases P sorption capacity is reduced, while in others it increased (Hiradate and Uchida 2004). The increase in P sorption is expected because of the removal of organic coatings from mineral surfaces, but on the other hand the removal of labile organo-Me association may reduce total P sorption (Wada and Gunjigake 1979; Giesler et al. 2005) .

Based on these considerations, the aim of this work was to evaluate the variations in organo-mineral interactions at different steps of podzolisation. Our working hypothesis was that the arrangement of organic compounds on mineral surfaces changes because of different OM and metal loads in B horizons, thus affecting OM stabilisation. To test the hypothesis we evaluated surfaces properties through N_2 and P sorption before and after weak chemical oxidation of the most labile organic fraction in B horizons collected from incipient to well-developed podzols.

Materials and methods

After preliminary soil surveys five B horizons were selected for this study representing different types of B horizons that develop during podzolisation (Table 1). Two of them sampled in Gressoney (Valle d'Aosta region, North-western Italy) from soils showing different intensity of podzolisation according to soil classification (Soil Survey Staff 2010), were located on the same mountain slope at backslope position, and differed for approximately 100 m in elevation. The first one was a Bw from a Spodic Dystrudept (thereafter called Bw, 45°4'29''N, 7°49'40''E, 1700 m a.s.l.) in which the beginning of podzolisation was visible from bleaching of quartz grains below the organic horizons (Scalenghe et al. 2002). The other one was a Bs horizon taken from a Typic Haplorthod (Bs-1). Typic and Lithic Haplorthods and Haplocryods are the most common Spodosols in the area (Costantini et al. 2004). Gneiss was the dominant lithology in the soil parent material. At the Bw site vegetation was a spruce forest, while larches with abundant herbaceous vegetation and blueberry shrubs dominated at the Haplorthod site. The other three B horizons were sampled in Bohemia (Krkonose National Park, North-western Czech Republic) where, thanks to wetter climatic conditions, podzolisation was always well expressed: a Bs horizon was sampled from a Typic Haplocryod (Bs-2, 50°47'53''N, 15°27'50''E), while the other B horizons were a Bhs from a Humic Haplocryod (Bhs) and a Bsm from a Placic Cryaquod (Bsm). Spodosols are the climax soils and Placic Cryaquods are the most developed ones in that area. They typically form upon changes in water translocation through the profile due to the presence of OM rich-horizons and ultimately converge on Histosol development (Bonifacio et al. 2006). These soils develop on granite under a highly degraded spruce forest locally replaced by abundant herbaceous and shrub vegetation (Bonifacio et al. 2008), and were located on a gently undulating mountain top at approximately 1100 m a.s.l., some tens of meters apart from each other.

The soil samples were air-dried and sieved to 2 mm. The < 2 mm samples were chemically oxidised three times with NaClO (pH 8) as described by Mikutta et al. (2006). Briefly, this method involves treatment with 6% NaClO that leads to the removal of significant amounts of OM (Kaiser et al. 2002). To better study the arrangement of organic compounds on the mineral surfaces in podzolic B horizons, we used 2% instead of 6% NaClO to limit the removal to the most labile organic fraction. In addition, we used diluted HCl (1:10) to bring the NaClO solution to pH 8 and we did not freeze-dry the samples after oxidation, but allowed them to dry.

Total C was determined by dry combustion (NA2100, Carlo Erba Instruments, Rodano, Italy) while total extractable C (TEC) was extracted in NaOH as described by Schnitzer (1982). Humic (HA) and fulvic acids (FA) were separated from the alkaline extract by acidifying to pH 1 with HCl followed by centrifugation (1300g). The flocculated HA were redissolved in alkali while the FA in the supernatant were purified by eluting through PVP resins to separate the extracted non-humic material. Carbon contents of TEC, HA and FA fractions were determined by Pt-catalysed, high-temperature combustion (680°C) followed by infrared detection of CO_2 (Vario TOC, Elementar, Hanau, Germany). Acid ammonium oxalate extractable-Fe and Al (Fe_O and Al_O; Schwertmann 1964) and the pyrophosphate extractable Fe (Fe_P;

Bascomb 1968) were determined by atomic absorption spectroscopy (Perkin Elmer, 3030). Fe_O and Al_O were also used to calculate the Spodic Index (IS: $0.5Fe_O+Al_O$; Soil Survey Staff 2010) to quantitatively assess the illuviation processes, in addition to the podzolisation intensity depicted by soil classification. All analyses were performed in duplicate on soil samples before (UT, untreated samples) and after NaClO oxidation (T, treated samples), and data for the latter were corrected for weight loss during treatment. The surface properties were evaluated by P and N_2 adsorption on finely ground samples (<0.5 mm) both before and after oxidation.

The specific surface area (SSA) of the samples was determined by N_2 adsorption at 77 K at a relative pressure (p/p^0) range 0.05–0.30 (Gregg and Sing 1982) with a surface area analyser (Sorptomatic 1900,Carlo Erba, Rodano, Italy) by applying the Brunauer-Emmett-Teller (BET) equation:

$$\frac{p}{n(1-p/p^0)} = \frac{1}{n_m C_{BET}} + \frac{C_{BET}-1}{n_m C_{BET}}(p/p^0)$$

where n is the amount of adsorbent at every p/p^0, n_m is the monolayer capacity and C_{BET} value, according to the BET theory, gives an indication of enthalpy of adsorption of the first adsorbed layer that is the magnitude of the adsorbent-adsorbate interaction. From the graphic solution of the equation of $(p/p^0)/[n(1-p/p^0)]$ versus p/p^0 in the range 0.05-0.30, the so called BET-plot is obtained which has slope equal to $(C_{BET}-1)/(n_m C_{BET})$ and intercept $1/(n_m C_{BET})$ (Gregg and Sing 1982). By solving these two simultaneous equations the C_{BET} constant and n_m are obtained and the SSA calculated. Enough sample was used for measurement to ensure a total surface area of >10 m^2. All samples were initially degassed for 16 hours at 50°C. Total <50 nm pore volume was calculated from the adsorption isotherm and expressed on a mass basis ($mm^3\ g^{-1}$) from the amount of N_2 adsorbed at the relative pressure close to unity (Sing et al. 1985), the micropores (< 2 nm) volume and their surface area were calculated using the t-plot method (de Boer et al. 1966), while mesopores (2–50 nm) were derived from the adsorption isotherm using the Pierce's (1953) model. All analyses were at least duplicated.

To determine phosphate sorption, 10 mL of 0 to $6\cdot10^{-3}$ M P-containing solutions (KH_2PO_4) in 0.01 M KCl were added to 200 mg of untreated or treated soil. The suspensions were shaken continuously for 24 h at 25°C, centrifuged (1600g for 15 min), and the supernatants filtered through a 0.45 µm membrane filter. The amount of P at equilibrium was determined spectrophotometrically (U-2000, Hitachi, Tokio, Japan) by the molybdate blue method (Murphy and Riley 1962), as reported by Olsen and Sommers (1982). Blank samples were run for each experiment to assure that no adsorption to the containers had occurred. The amount of sorbed P was calculated from the difference between initial and equilibrium concentrations. Both Langmuir and Freundlich models were used to describe sorption data. The Langmuir adsorption isotherm is:

$$Q = \frac{x_{max} K_L C_e}{1 + K_L C_e}$$

where Q (µmolP g^{-1}) is the amount of P sorbed on the soil, C_e (µmolP mL^{-1}) is the solution P concentration at the equilibrium, x_{max} is the maximum amount of P (µmol P g^{-1}) adsorbed by the soil, and K_L (L $mmol^{-1}$) is the

Langmuir affinity constant. These parameters were found by regression after linear transformation. The Freundlich adsorption isotherm is:

$$Q = K_F C_e^n$$

where, K_F (μmol g^{-1}) is the amount of P that is sorbed at a C_e of 1 μmol mL^{-1}, and n is a coefficient related to the affinity of phosphate for the surface. K_F and n were found by linear regression after log transformation of the equation.

The dissolved organic C (DOC) and total dissolved N (TDN) concentrations at equilibrium were also determined by liquid elemental analysis (Vario TOC) to follow phosphate-induced dissolution and desorption of organic compounds from the surfaces. The concentrations of DOC and TDN desorbed were corrected for the concentration released at 0 P addition. The pH at 0 P addition was also measured to ensure that UT and T samples were comparable in terms of the effects of pH on phosphate sorption. All analyses were duplicated.

Results

The OC contents of untreated (UT) samples ranged from 12 g kg^{-1} in the Bw and Bsm horizons to 51 g kg^{-1} in the Bhs (Table 2); Bs-2 was richer in OC than Bs-1. On the average 52% of C in Bw and Bs horizons was NaOH-extractable (TEC), while the proportions were higher in the Bsm (62%) and Bhs (79%). FA always prevailed over HA although their amounts were comparable in the Bw resulting in the lowest FA/HA ratio (close to 1). The highest FA/HA ratio was detected in the Bsm horizon with a value of 7.6, while the other B horizons had intermediate ratios ranging between 1.4 (Bhs) and 2.1. The amounts of FA were significantly correlated with the concentration of Al_O ($r=0.981$, $p<0.01$), while no relation was found with Fe forms. The concentration of Fe_P ranged from 3.9 g kg^{-1} in the Bw to a maximum of around 8 g kg^{-1} in the Bsm, but also in the Bs-1, while the oxalate extractable Fe showed a wider range, from 5.0 to 18.5 g kg^{-1} in Bw and Bsm, respectively (Table 2). As a consequence, high values of the spodic index (IS, Table 2) were found in the Bhs and Bsm, while as expected, the IS was the lowest in the Bw with a value slightly below the threshold for spodic materials (i.e. IS<0.5).

The chemical oxidation with 2% NaClO removed only between 36 (in the Bsm) to 61% (in the Bhs) of the initial C content (Table 2), while a greater proportion of TEC was removed. The remaining extractable C after treatment was as low as 17% of the initial contents in the Bhs. In all other soil horizons it varied between 36 to 56%. The decrease in TEC after treatment was mainly attributed to a loss in HA and consequently resulted in a sharp increase in the FA/HA ratio (Table 2). After oxidation the amount of Fe_O showed little variations with respect to the UT samples, except for Bs-2 and Bhs that showed an increase in Fe_O after treatment. In contrast, significant amounts of initial Fe_P were generally lost during treatment, with Bw and Bs-1 showing the greatest loss (35 and 56%, respectively). Al_O was more sensitive to treatment than Fe_O and the amounts found after oxidation were never above 80% of the initial contents (Table 2).

The isotherms obtained by gas adsorption analysis on UT samples (Figure 1) showed different amounts of total adsorbed N_2 and different ratios between adsorbed and desorbed N_2, although they shared

similarities in shape. They did not perfectly correspond to any IUPAC classification type (Sing et al. 1985), thus indicating that the samples had a complex surface. The initial part of the isotherm from the Bw horizon (Figure 1a) indicated low microporosity, while mesoporosity was well identified by a marked increase in N_2 adsorption below $p/p^0=1$, caused by the formation of a liquid layer on the multilayer adsorbed film on the mesoporous surface (Kaneko 1994). Moreover, the hysteresis loop in the multilayer range ($p/p^0>0.30$), that is the non-overlapping of the adsorption and desorption isotherms associated with capillary condensation in mesopores (e.g. Groen et al. 2003), was well pronounced. In addition, at the lowest $p/p^0(<0.30)$ the desorption did not overlap the adsorption branch suggesting either the swelling of a non-rigid porous structure or the irreversible uptake of molecules in pores or at pore entrances (Sing et al. 1985). The characteristics of the initial portion of the isotherm therefore indicated an intermediate form between type II according to the IUPAC classification (Sing et al. 1985), which is indicative of multilayer adsorption process in a nonporous or macroporous system, and type I, which is instead typical of microporous solids. At higher p/p^0 values the shape was typical of type IV representing mesoporous systems. The plateau in the hysteresis loop at high p/p_0 was not observed, and the shape was therefore recognized as halfway between a H3 and H4 type of the IUPAC classification. When the Bw was oxidised the amounts of adsorbed N_2 increased slightly, particularly at p/p^0 higher than 0.3, and the adsorption and desorption isotherms overlapped at low p/p^0 (Figure 1b) indicating variations in pore shape. From the calculation of surface parameters a 20% increase in SSA with oxidation was visible (from 6.3 to 7.7 m^2 g^{-1}, Table 3), mainly due to an increase in mesopores. The C_{BET} also increased indicating an increase in surface affinity. The isotherms obtained for two Bs horizons differed in the amounts of adsorbed N_2 and hysteresis loop at $p/p^0>0.3$, and consequently varied in mesoporosity. The characteristics of type I isotherm were in both cases more expressed than in the Bw, while at higher p/p^0 the shape was still well represented by a type IV of the IUPAC classification system (Figure 1c). The contribution of mesopores and micropores to SSA was almost equal in both samples (Table 3). The C_{BET} in these samples was higher than in the Bw (226 and 303 in Bs-1 and Bs-2, respectively). Upon oxidation the behaviour of the two Bs samples differed (Figure 1c and 1d): the SSA increased in Bs-1, but decreased slightly in Bs-2. As for Bw, the variations in Bs-1 were mainly linked to mesopores (Table 3). On the other hand, Bs-2 mesoporosity did not change and the variations in SSA were caused by a 30% decrease in micropore area after oxidation. The adsorption isotherm of the Bhs (Figure 1e) was indicative of macro and mesopororous materials with low microporosity, therefore corresponding to an intermediate form between type II and type IV (Figure 1e). After oxidation, the characteristics of the Bhs pore system changed sharply. The hysteresis loop in the 0.3-1 p/p^0 range almost disappeared shifting the isotherm classification to a more expressed II type (Figure 1f). The calculated surface parameters changed accordingly (Table 3): together with a decrease in SSA, both mesopores and micropores decreased. The C_{BET} however increased after oxidation. The isotherm of the UT Bsm more closely corresponded to a type I isotherm in the initial part, therefore indicating a more microporous material (Figure 1g). Micropore surface was indeed the largest of all samples (i.e. 4.9 m^2 g^{-1}, Table 3), while the amount of mesopores was more similar to the other B horizons. The SSA was 8.43 m^2 g^{-1} and the C_{BET} had a remarkably higher value with respect to all other

samples. After oxidation micropore surfaces decreased sharply by about 40%, affecting the total SSA that diminished consequently. With treatment C_{BET} decreased from 424 to <300, although it still remained the highest among all T-samples (Table 3). The T-sample isotherm was still similar to a type I of the IUPAC classification, although it tended to diverge from that of the UT sample at p/p^0 close to 1 (Figure 1h).

Phosphate sorption was used to follow the changes in the surface properties as a consequence of OM oxidation, while assessing the displacement of organic compounds retained by mineral surfaces through competitive ligand exchange mechanisms. The amount of P sorbed increased sharply without reaching a true plateau in the UT B horizons (Figure 2). Thus the data were consistent with the Langmuir model only at the lowest C_e concentrations, i.e. in the 0-1.0 mmol L^{-1} range, while the whole data range was better described by the Freundlich model (Table 4). The untreated samples showed K_F values ranging from 20 in the Bw to 34-38 μmol g^{-1} in the other B horizons. When the sample surface area was taken into account K_F increased in the order Bw<Bs-1<Bs-2≈Bhs, then decreased to lower values in the Bsm, following the increasing trend of both fulvic acids and Al_O. The release of C-containing compounds in solution increased with increasing P addition, showing values greater than sorbed P for Bw (Figure 2a), whereas lower values for all other samples. In the Bhs (Figure 2e) the amounts of C in the solution were similar to those released from Bw. Moreover, the characteristics of the desorbed organic matter changed with increasing P sorption. This was evidenced by an increasing trend in the C to N ratio (Table 4). At low P addition the C to N ratio of the released organic matter was the lowest in the Bw and Bsm horizon (7.4 and 7.2, respectively) but in the latter a very pronounced increasing trend was visible (up to 13.0). The oxidation reduced P sorption in all soils and the isotherms of T samples always fell below those of the UT ones (Figure 2b, d, f, h). The parameters of the Freundlich equation varied consequently: the decrease in K_F (ΔK_F) ranged from 5 μmol g^{-1} in the Bw to 10-14 μmol g^{-1} in the spodic B horizons (Table 4). Because of the variations in SSA caused by oxidation, K_F expressed per unit area ranged from 1.9 μmol m^{-2} in the T-Bw to 8.5 μmol m^{-2} in the T-Bhs, whereas in the T-Bsm it was 3.2 μmol m^{-2}. While the Freundlich n parameter showed slight differences between UT and T samples, the Langmuir constant at low C_e concentrations more adequately represented the effects of oxidation. No differences in the affinity of P were found in the case of Bw-1, affinity decreased after oxidation in the Bhs, while it increased in the other horizons and the differences between T and UT samples were greater in the order Bs-1<Bs-2≈Bsm. Upon P addition OM was released in similar amounts as in the UT samples in the Bs-2, Bhs and Bsm (Figures 2d, f, h), while in the Bw and Bs-1 (Figures b, d) lower amounts were recovered in solution.

Discussion

Our hypothesis was that the different amounts of illuviated OM and metals in podzolic B horizons influenced the interaction between organic and mineral components, thus that podzolisation intensity ultimately affected OM stabilisation. The OC concentrations in the B horizons were in line with those generally observed in deep horizons of NW Italy forest soils (Bonifacio et al. 2011) and in B horizons of Podzols from the Krkonose (Dlouhá et al. 2009). The selected B horizons represented different stages of podzolisation, from Bw to Bs to Bhs and finally to Bsm. As such, illuviated organic components should represent a different

proportion of OC (Wilson and Righi 2010) and the amounts of extractable Fe and Al should vary accordingly. Although the separation of FA and HA fractions does not allow for the evaluation of OM turnover and stability as a functional link to ecosystem properties (Schmidt et al. 2011), the capability of humic substances to exhibit amphiphilic properties with both hydrophilic and hydrophobic regions (Sutton and Sposito 2005) may nonetheless provide useful information regarding OM translocation in Spodosols. In fact, the more hydrophilic, polar, acid-soluble compounds, i.e. FA, can be adequately used to follow Podzol formation, as evidenced by recent studies that have used this fraction to evaluate podzolisation and weathering in Alpine soils (Egli et al. 2010), as well as the effects of clear-cutting on OM illuviation in podzolic soils (Falsone et al. 2012). The FA contents increased nearly 10-fold on going from the Bw to the Bhs, in agreement with most podzolisation Theories (Sauer et al. 2007; Lundström et al. 2000). In Bsm, the contents of FA decreased probably due to the interruption of the inputs to this cemented horizon (Bonifacio et al. 2006), but the high FA/HA ratio nonetheless evidenced the extent of the podzolisation process. The spodic index (IS) however showed that the accumulation of Al and Fe associated with organic compounds respected only partially the increase in soil evolution depicted by the classification, i.e. the podzolisation steps. Al_O was more adequate than Fe_O in following the podzolisation process and the significant correlation found between the Al_O and FA concentrations pointed towards a co-migration of humic substances and metals in agreement with the results obtained by Egli et al. (2010) on a wide range of Alpine soils. These Authors however found a good correlation not only between FA and oxalate extractable Al, but also with Fe_O. The lack of correlation between Fe_O and FA in our case, as well as the lack of a clear trend in IS may be related to Fe reduction. This process is often associated to podzolisation not only when Aquods develop (Harris et al. 1995: Rochette and Cleary 2004), but also when water saturation is only occasional (Bonifacio et al. 2009). Iron reduction may account for the high Al_O to Fe_O ratio in the Bhs, while shifting redox conditions may favour Fe precipitation as hydroxide in cemented spodic horizons (Bockheim 2011), possibly explaining the large amounts of Fe_O found in the Bsm.

Oxidation with 2% NaClO removed from 40 to 60% of the initial C contents, significantly lower with respect to the 87% losses obtained by the 6% NaClO treatment of acidic forest soils (Kaiser et al. 2002). The low amounts of TEC remaining after treatment suggest that alkali-extractable C was not particularly resistant to oxidation. The greater resistance to oxidation of FA with respect to HA confirmed the scarce influence of chemical recalcitrance as a mechanism for OM stabilisation in mineral soil horizons (Eusterhues et al. 2005), while pointing towards the importance of Me-organic and mineral-organic associations. In fact, the lowest proportion of initial TEC remaining after oxidation (<20%) was observed in Bhs that also had the highest contents of humic substances but a relatively low FA/HA ratio (1.40). On the other hand, this result points to the low importance of molecular composition of litter in determining OM persistence in soils (Schmidt et al. 2011) and thus confirmed that both blueberry (abundant at Bs-1 and Bsm sites) and spruce (dominant at the other sites) have a similar effect on podzolisation (Miles 1985).

An increase in SSA is typically reported upon oxidation of OM in soil samples by NaClO (Kaiser and Guggenberger 2003), H_2O_2 (Theng et al. 1999) or 350°C muffling (Mayer and Xing 2001), due to the

removal of the low-SSA component, the unclogging of soil pores and the breakdown of aggregates. Using a lower NaClO concentration we observed an increase in SSA only in the Bw horizon and in the Bs with the lowest amounts of OC (Bs-1). This was mainly linked to an increase in mesoporosity thus suggesting that oxidation of OM uncovered pore entrances and cleaned the mesopore space resulting in an increase in N_2 adsorption. Larger variations in mesopores than in micropores may be explained by the resistance to desorption and oxidation of OM associated with micropores by multiple bonds at small OC loads (Kaiser and Guggenberger 2003). The weak binding between the removed OM and the uncovered surfaces is confirmed by P sorption isotherms that clearly show that increase in SSA after treatment did not result in a consequent increase in P sorption capacity neither when expressed on a weight nor area basis. Moreover, in the Bw horizon a scarce affinity of P for the newly uncovered surfaces was well supported by lack of changes after oxidation in the K_L constant obtained at low C_e concentrations (C_e = 0-1.0 μmol L^{-1}), where adsorption on mineral surfaces should prevail (Celi et al. 2003). However, the lack of a true plateau in P sorption isotherms indicated that besides adsorption, other mechanisms such as formation of P-Me-OM bridges and/or the precipitation with Al and Fe ions, occurred simultaneously and accounted for the progressive increase in P sorption (Celi et al. 2000; Giesler et al. 2005). Thus, the reduced P sorption after treatment of Bw was probably due to a lower formation of P-Me-OM bridges following the removal of pyrophosphate-extractable Fe after the oxidation of the original metal-complexes. The high specificity of P for Me and/or mineral surfaces led to the displacement of C-containing compounds from soil, liberating additional sorption sites at increasing P loads. The amounts of C released into solution were generally relatively low since competitive desorption involves only low molecular weight organic compounds (Giesler et al. 2005); however, for Bw the molar ratio of desorbed C to sorbed P was >1 even after oxidation, and still increased with P addition. This indicates that part of OM resistant to NaClO treatment in this soil was retained by the solid phase through weak bonds as expected at an incipient stage of podzolisation. In the Bs-1 horizon NaClO treatment influenced the shape of the P sorption isotherm and the treated sample clearly showed the presence of more reactive surfaces where adsorption processes prevailed up to ~ 2 μmol P m^{-2}. The formation of P-Me-OM bridges became instead less important as confirmed by the lower release of C upon P additions and the large decrease of pyrophosphate-extractable Fe after oxidation. In Bs-1 OM seemed to have a patchy distribution and once removed exposed mineral surfaces to P sorption.

In the OM-richer Bs horizon (Bs-2), as well as in Bhs and Bsm, SSA after oxidation was lower than in the untreated samples. While this result is not typical, it is important to remember that we used a lower NaClO concentration than the one normally reported to operate a more pronounced differentiation between NaClO-labile and more resistant OM. The SSA of OM determined by N_2 adsorption is around 1 m^2 g^{-1} (De Jonge and Mittelmeijer-Hazeleger 1996) because 95-99% of OM surface is constituted of very small pores (<0.5 nm) that limit the detection of N_2 diffusion under normal laboratory conditions. Although the removal of OM during oxidation is expected to reveal mineral surfaces, the decrease in SSA observed after treatment of these soils with high OM loadings may be interpreted as a selective removal of superficial organic constituents having a reduced structural density and rigidity with respect to the NaClO-resistant OM. In fact,

as evidenced by the increase in FA/HA ratio, oxidation of these soils also resulted in a relative enrichment in the more rigid and aromatic FA with respect to HA (Table 5), possibly responsible for the changes in surface properties. Kaiser and Guggenberger (2003) have previously reported that OM removed by NaClO had a less dense and more open conformation than the resistant fraction, and that the changes in density after treatment were mainly observed at high OM loadings. Similarly, the samples showing a decrease in SSA with oxidation were those that showed the highest molar ratio between humic substances and Al (4.8–5.1). The different behaviour of surface properties between less and more developed podzolic B horizons may therefore be favoured both by the larger concentration of illuviated C as well as by a more pronounced differentiation between a Me-rich adsorbed FA layer and less tightly retained organic compounds. The higher molecular rigidity and the selective retention of more charged FA over HA may reduce the number of reactive sites, decreasing the formation of Me-P-OM bridges and justifying the significant differences in P sorption between UT and T samples (ΔK_F = 10-14 μmol P g^{-1}). A large decrease in P sorption upon removal of OM is indeed typical of Podzols and other soils with low P-fixing capacity (Serrasolses et al. 2008). This result further confirmed the presence of a tightly bound film of illuviated, hence polar OM resistant to NaClO oxidation as a result of the strong interactions with mineral surfaces. In addition to this general trend, some specific characteristics were visible. In the Bhs having the highest OM contents the decrease in SSA was the greatest, but C_{BET} increased and became similar to those of the other B horizons. The large decrease in OM with oxidation coupled with the high humic C to Al_O ratio suggests that in the Bhs additional OM has accumulated either due to organo-organic interactions or thanks to weak Al or Fe bridges, giving rise to bulky OM accumulations similar to those described by Kaiser and Guggenberger (2007). The increase in C_{BET} could therefore be mainly linked to the change in the proportion between low-affinity components (i.e. OM) and mineral surfaces suitable to N_2 adsorption. However, in this sample the amounts of Fe_O recovered after oxidation were above the contents of the UT sample. This situation was also found by Marzadori et al. (1991), who attributed it to the exposure of poorly crystalline components that were unavailable for oxalate dissolution due to OM covering, in agreement with the high Fe_P concentration we found in the UT-Bhs sample. In our case, the uncovering of mineral surfaces was however not large enough to counteract the effect the high amounts of OM have on SSA, albeit probably sufficient to increase the C_{BET} and the affinity for phosphate adsorption as indicated by the K_L. Oxidation induced specific variations in surface properties also in the Bsm. Cementation in orstein and placic horizons is typically caused by organic compounds that have migrated in the Me-rich Bsm and precipitated in voids and around mineral grains upon dehydration (Wilson and Righi 2010). Part of the OM in this horizon may therefore have weak chemical bonds with the other soil components, therefore showing a lower resistance to oxidation. Microporosity of the UT-Bsm was particularly high but decreased to the same values of the other samples after oxidation suggesting that micropores have developed because of horizon cementation by NaClO-labile OM. The amounts of removed OM in this horizon were the lowest of all samples, in agreement with the fact that even low OM contents may cause cementation (Wilson and Righi, 2010). The removal of the labile component exposed highly stabilised OM and led to surface features similar to those of the other well developed spodic B horizons.

Conclusions

Podzolisation affects both OM stabilisation and surface properties in B horizons. The variations in surface properties upon weak oxidation of OM seem to be linked to the close associations between OM and metals ions and/or mineral phases that develop in podzolic B horizons. The spatial arrangement of OM in B horizons changed with the ongoing of podzolisation. At the beginning of the process the dominant forms seemed related to Me-organic complexes with little interaction with the mineral surfaces and therefore easily removed by oxidation. At the first stage in the formation of spodic materials some interaction between mineral surfaces and OM began to appear: the bonds were however presumably rather weak and oxidation uncovered mesopores and high affinity surfaces for P sorption. At a later stage of podzolisation OM seemed to differentiate into bulky structures and more hydrophilic, rigid ones having extremely low N_2 accessibility. The latter are most likely tightly bound to the mineral surfaces and thus not sensitive to low concentration NaClO, while the former are easily oxidised as they are probably associated to other organic molecules by weak chemical bonds.

Podzolisation occurs in many environments, from tropical to boreal areas, and although typical of sandy substrates, it may take place even in finer textured materials such as the eluvial horizons of Alfisols. Although our results suggest that the interaction between OM and mineral phases evolves during podzolisation in all cases, the intensity at each step should vary depending on the presence of specific mineral surfaces. A full comprehension of these processes however necessitates further understanding on the key factors controlling the evolution in the spatial arrangement of OM on mineral surfaces in podzolic soils.

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Table 1 – Morphological characteristics of the studied B horizons

Sample	Depth (cm)	Munsell Colour (crushed, dry)	Structure[1]	Horizon sequence of the profile[2]	Soil classification
Bw	3-30	10YR 5/5	w, m, sbk	O-E-**Bw1**-Bw2-Bw3-BC-C	Spodic Dystrudept
Bs-1	50-60	10YR 6/6	vw, m, sbk	O-A-E-EB-Bs1-Bs2-**Bs3**-C	Typic Haplorthod
Bs-2	30-40	10YR 5/4	w, f, sbk	O-E-Bs1-**Bs2**-C	Typic Haplocryod
Bhs	3-9	7.5YR 3/3	w, f, gr	O-E-**Bhs**-Bs-C	Humic Haplocryod
Bsm	47-48	10YR 5/6	massive	O-E1-E2-**Bsm**-Bs-C	Placic Cryaquod

[1] Structure: vw= very weak, w=weak, m=medium; f=fine, m=medium; gr=granular; sbk=subangular blocky

[2] Bold indicates the horizons analysed in this study

Table 2 – Characteristics of untreated (UT) and NaClO-treated (T) soils.

Sample		OC	TEC	FA	HA	FA/HA	Fe_O	Fe_P	Al_O	IS
		g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}		g kg^{-1}	g kg^{-1}	g kg^{-1}	%
Bw	UT	12.4	6.37	1.96	1.73	1.13	4.98	3.88	2.20	0.47
	T	6.9	2.57	0.60	0.41	1.46	4.54	2.53	1.49	
Bs-1	UT	13.5	6.39	3.01	1.51	1.99	9.10	8.13	4.06	0.86
	T	5.5	2.32	0.86	0.12	7.17	8.73	3.58	3.04	
Bs-2	UT	22.6	13.10	7.33	3.52	2.08	6.51	6.30	5.09	0.83
	T	13.3	7.30	3.50	0.60	5.83	6.78	6.10	4.07	
Bhs	UT	51.2	40.50	21.10	15.10	1.40	4.80	5.90	16.10	1.85
	T	20.2	6.99	5.71	1.25	4.58	6.70	6.90	1.90	
Bsm	UT	12.8	7.92	5.36	0.71	7.55	18.53	8.08	2.83	1.21
	T	8.2	4.13	2.33	0.12	19.42	18.19	7.05	2.05	

OC: organic C; TEC: NaOH total extractable C; FA: C in fulvic acids; HA: C in humic acids; Fe_O and Al_O: NH_4-oxalate extractable Fe and Al; Fe_P: Na-pyrophosphate extractable Fe; IS: Spodic Index $0.5Fe_O+Al_O$

Table 3 – Surface properties of untreated (UT) and NaClO-treated (T) B horizons. In parentheses the standard deviation is given.

Sample		C_{BET}	total SSA	Surface area of mesopores (2-50 nm)	Surface area of micropores (<2 nm)	Pore total volume	Volume of mesopores (2-50 nm)	Volume of micropores (< 2 nm)
			$m^2\ g^{-1}$	$m^2\ g^{-1}$	$m^2\ g^{-1}$	$mm^3\ g^{-1}$	$mm^3\ g^{-1}$	$mm^3\ g^{-1}$
Bw	UT	129 (11)	6.30 (0.42)	3.92 (0.21)	2.12 (0.47)	8.73 (1.21)	6.65 (0.99)	0.84 (0.22)
	T	152 (2)	7.68 (0.03)	4.62 (0.09)	2.21 (0.05)	9.81 (0.22)	8.95 (0.18)	0.86 (0.03)
Bs-1	UT	226 (45)	9.34 (0.37)	4.19 (0.42)	4.62 (0.09)	8.12 (0.45)	6.19 (0.49)	1.93 (0.04)
	T	220 (74)	12.72 (1.00)	6.21 (0.12)	5.44 (0.99)	10.15 (0.15)	7.94 (0.60)	2.22 (0.45)
Bs-2	UT	303 (39)	6.30 (0.07)	2.82 (0.03)	3.15 (0.17)	6.01 (0.06)	4.70 (0.14)	1.31 (0.08)
	T	232 (14)	5.39 (0.13)	2.89 (0.28)	2.15 (0.45)	5.55 (0.24)	4.68 (0.45)	0.88 (0.21)
Bhs	UT	188 (22)	5.37 (0.19)	3.27 (0.05)	1.78 (0.21)	6.96 (0.96)	6.26 (0.87)	0.70 (0.09)
	T	246 (17)	2.84 (0.02)	1.41 (0.68)	1.33 (0.08)	3.79 (0.24)	3.26 (0.21)	0.54 (0.03)
Bsm	UT	424 (41)	8.43 (0.06)	3.34 (0.61)	4.87 (0.02)	6.95 (0.01)	4.90 (0.13)	2.05 (0.14)
	T	293 (16)	6.59 (0.12)	3.16 (0.31)	2.84 (0.15)	6.03 (0.24)	4.87 (0.29)	1.16 (0.05)

C_{BET}: constant of BET equation; SSA: specific surface area

Table 4 – P sorption characteristics in untreated (UT) and NaClO treated (T) samples and C/N ratio of released organic compounds

Sample			C/N		Langmuir parameters in the Ce 0-1.0 mmol L^{-1} range			Freundlich parameters			
		pH	min	max	K_L	x_{max}	r^2	n	K_F	K_F	r^2
					L $mmol^{-1}$	P µmol g^{-1}			P µmol g^{-1}	P µmol m^{-2}	
Bw	UT	4.5	7.4	8.5	58.3	17.2	0.980	0.20	19.8	3.1	0.985
	T	4.8			57.8	13.1	0.787	0.21	14.4	1.9	0.971
Bs-1	UT	4.6	14.8	16.9	89.1	29.1	0.908	0.20	34.8	3.7	0.975
	T	4.7			98.8	23.6	0.931	0.15	25.0	2.0	0.957
Bs-2	UT	4.5	8.3	10.4	50.3	31.0	0.903	0.23	38.2	6.1	0.975
	T	5.0			115	19.3	0.946	0.22	24.4	4.5	0.997
Bhs	UT	4.4	9.1	12.9	84.4	29.3	0.930	0.21	34.7	6.5	0.931
	T	3.7			39.9	19.9	0.971	0.27	24.2	8.5	0.982
Bsm	UT	4.8	7.2	13.0	24.1	28.2	0.986	0.25	33.8	4.0	0.988
	T	5.3			81.7	15.0	0.897	0.25	21.0	3.2	0.971

K_F: constant of the Freundlich equation; K_L: constant of the Langmuir equation; x_{max}: Maximum P adsorption from the Langmuir equation

Table 5 – Carbon contents and atomic ratios of fulvic and humic acids

Sample	**Fulvic acids**			**Humic acids**		
	C	H/C	O/C	C	H/C	O/C
Bw[§]	49.4	0.89	0.69	55.1	0.96	**0.48**
Bs-1°	49.0	0.85	0.73	54.2	1.02	**0.51**
Bs-2*	47.0	0.80	0.75	51.0	1.20	**0.58**
Bhs*	46.1	0.80	0.80	53.1	1.14	**0.52**
Bsm°	45.2	0.75	0.83	49.4	1.10	0.63

§ data from Scalenghe et al. 2002

* data from Bonifacio et al. 2006

°unpublished data

Figure 1 – N_2 adsorption and desorption isotherms in untreated (UT) and NaClO-treated (T) samples

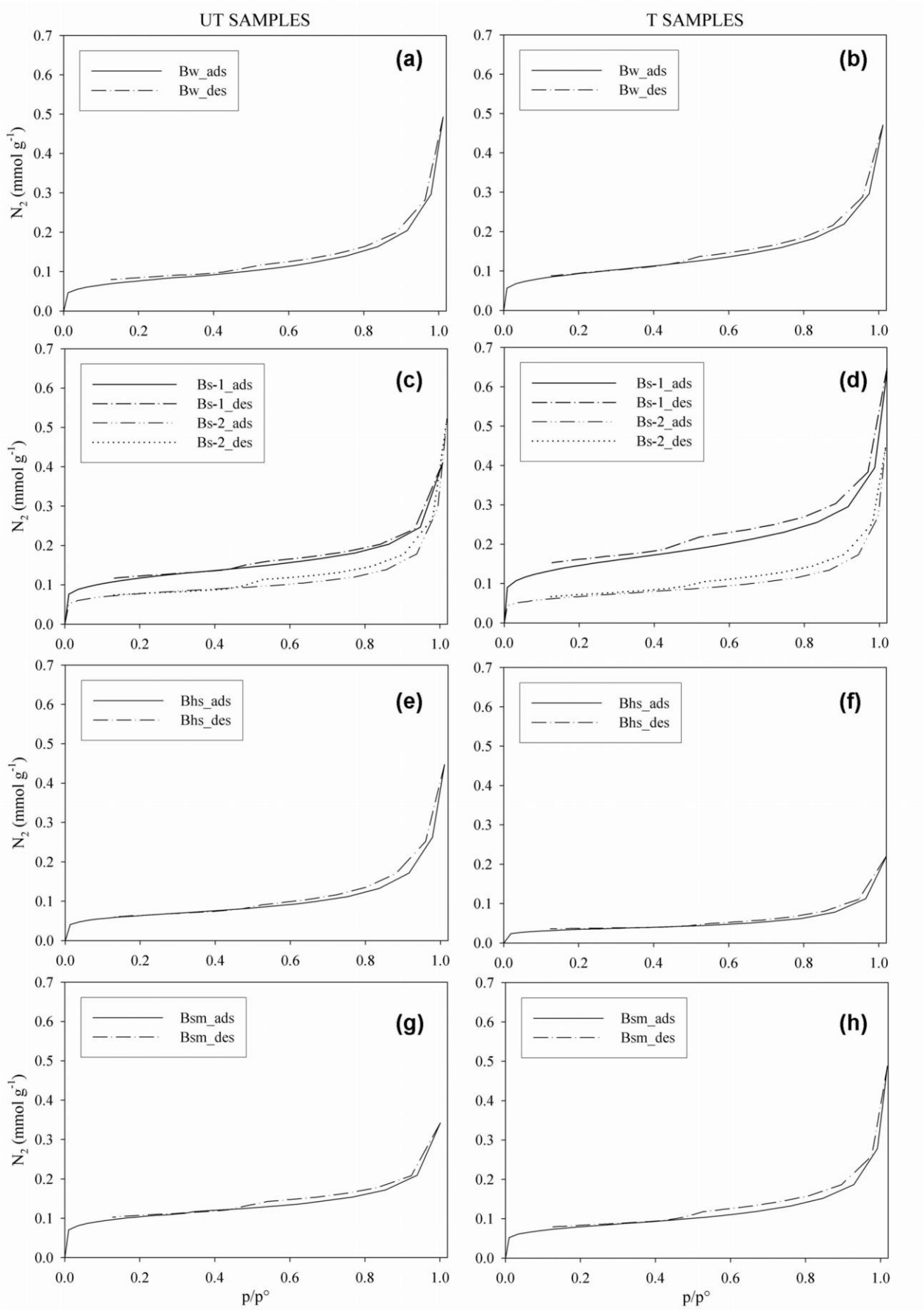

Figure 2 – P sorption isotherms and release of organic C in untreated (UT) and NaClO-treated (T) samples