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Influence of serpentine abundance on the vertical distribution of available elements in soils

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Abstract

Background and Aim: Biotic and abiotic factors contribute in shaping the distribution through the soil profile of elements released by mineral weathering; among them, leaching and biocycling dominate in temperate environments. We evaluated if the intensity of leaching and biocycling of nutrients can be modulated by element deficiencies linked to the abundance of serpentine in the soil parent material, i.e. if the most deficient elements are more efficiently retained.

Methods: We selected twelve poorly developed soils from Northern Italian beech stands, with variable amounts of serpentinites in the parent material, and determined total and exchangeable Ca, Mg and K, as well as an index of abundance of serpentine minerals.

Results: The total element content depended on the abundance of serpentines, while only exchangeable Mg was related to the parent material. The vertical trend of Ca and K indicated the role of biocycling in all soils, but the relative availability of Ca (ratio between exchangeable and total content) was much higher in the top horizons of serpentine-rich soils.

Conclusions: The different element availability among soils suggested that the vertical distribution of available elements was linked to the parent material and that losses were limited in serpentine-rich soils, probably because plants take up the deficient elements as soon as they are released from litter and thus limit their leaching in deeper soil horizons.

Keywords

Soil nutrients, oligotrophic beech stands, Entisols, biocycling, leaching

Introduction

The availability of nutrients drives plant growth and is one of the characteristics taken into account when evaluating soil fertility or assessing soil quality (e.g. Schoenholtz et al. 2000). Limitations in N and P availability are acknowledged as major ecological drivers at different stages of forest ecosystem development (Wardle et al. 2004), but cations such as K, Ca and Mg affect forest productivity as well (Krám et al. 1996). Several plant species are indeed affected by soil cation availability and deficiencies may induce, for example, a reduction in tree vitality, a decrease in wood increment and may alter the foliation pattern (e.g. Jonard et al. 2012, Fromm 2010, Vacek et al 2009). All metal elements derive from the lithosphere, thus need to be released into the soil from the weathering of the parent material before they become plant-available. The parent material defines therefore the potential amounts of elements that are present in the soil and is one of the determinants of soil fertility.

Serpentinities are metamorphic rocks made up almost totally of serpentines, a group of Mg layer silicate minerals; the soils that develop on serpentinites (i.e. serpentinitic soils) are therefore characterized by low contents of all essential nutrients, with the exception of Mg and show poor fertility characteristics. This poor chemical fertility is directly linked to the elemental composition of the parent rock and is well known under the name of serpentine-syndrome (Jenny 1980): serpentinitic soils have low amounts of phosphorus and potassium, an unfavourable Ca to Mg ratio and, in addition, high concentrations of potentially toxic heavy metals, inducing strong limitation in plant growth (e.g. Alexander 1988).

The vertical distribution of available elements through the soil profile arises from the interaction between biotic and abiotic factors. The most important process which is driven by abiotic factors in well drained soils of temperate climates is leaching (e.g. Chesworth 1992): once elements are released in the solution from the weathering of the soil parent material, they move downwards. Leaching acts on the soluble and exchangeable pools of elements, the most available ones, which are poorly retained by soil components in the first stages of soil formation, due to the low cation exchange capacity. In fact, at the beginning of soil development, the genesis of secondary soil minerals has not yet proceeded to such an extent to have a large impact on element mobility, which therefore still mainly depends on element characteristics, i.e. on

ionic charge and radius, and is little affected by the sorption sites along the soil profile. According to the Goldschmidt's sequence (Goldschmidt 1937), leaching of base cations such as Ca, Mg and K is expected, Si is mobilized less easily as hydroxoacid, while Al and Fe(III) tend to accumulate in the form of oxides and hydroxides. The most mobile ions will therefore show an increasing trend in concentration with increasing depth, and both Ca^{2+} and Mg^{2+} are expected to behave in a relatively similar way as they have comparable ionic radii (Krauskopft and Bird 1995).

When plants are present on the soil, the biotic factor deeply influences element distribution through nutrient uptake and inputs of elements back to soil with litter. This process is called biocycling, contrasts leaching (Schaetzl and Anderson 2005), and induces an increase in available element concentration towards the top of the soil profile. The budget between leaching and biocycling will thus determine the vertical distribution of the elements. Several factors control element uptake by plants, hence biocycling. From a general point of view, element mobility and persistence in the soil solution is essential for uptake, as implicit in the concept of nutrient availability. However, biocycling does not occur for all elements that are present in the soil solution, as shown by Jobbagy and Jackson (2004) in a study of a sequence of pine development. The concentration of exchangeable sodium showed an increasing trend with depth, which is typical for leaching dominated systems, while the exchangeable K forms showed high concentration both in the top soil horizons because of biocycling, and in the bottom ones, due to leaching. Biocycling was also demonstrated for Ca, whose recycling between soil organic layers and vegetation dominated annual uptake of the element by sugar maple (Blum et al. 2008). The intensity of element biocycling is also affected by plant species (e.g. Quideau et al. 1999; Jobbagy and Jackson 2004): beech is a highly demanding tree and shows Ca and K concentration in leaves of 7-8 and about 5 mg g^{-1} respectively (Drouet et al. 2005; Berger et al. 2009). Mg concentration is much lower ($\approx 0.5 \text{ mg g}^{-1}$), both in leaves and in roots (Berger et al. 2009; Tyler 2004). Beech stands on serpentinitic soils typically show therefore low productivity, also because of lack of nutrients.

Ca is transported passively and acropetally with the transpiration flux via the xylem and not retranslocated into the branches and stem before litter fall (Marschner 1995; McLaughlin and Wimmer 1999), therefore an

important release of Ca is expected upon litter mineralisation (Palviainen et al. 2004). The release of K is even faster as it can be released from stem and branch residues (Palviainen et al. 2004). In temperate climate, the organic horizons are of utmost importance in replenishing nutrient pools and up to 90% of annual nutrient uptake derives from soil litter (Kelly et al. 1998). Elements released by litter are in available forms, and may therefore either be taken up again by plant roots or leached away.

To the best of our knowledge, among the factors affecting element biocycling, element deficiency has never been taken into account. Our hypothesis was that an efficient system should limit nutrient losses by preventing leaching particularly in case of nutrient scarcity. As the poor fertility of serpentinitic soils is linked among other factors to low K and Ca contents, we tested if the severity of element deficiency could modulate the vertical distribution of soil nutrients. To this aim we evaluated total and available concentrations of Ca, Mg and K in soils developed on parent materials with different serpentine contents, used the abundance of serpentine minerals as an indicator of fertility conditions, and assessed the losses of cations. We selected soils from beech stands because cation input back to the soil with litterfall is much higher in broadleaves than in conifers (Augusto et al., 2002) and the high aboveground productivity of beech trees compared to other broadleaved species (Reich and Bolstad, 2001) should allow us to better assess such effect.

Materials and methods

The study area is located on the south-facing slope of the Susa valley, one of the main Alpine valleys of North-western Italy, which was shaped by the Dora Riparia river flowing from west to east (Figure 1). The preliminary selection of the study sites was made by taking into account the geology of the area and the forest classification provided by the local forest services (Regione Autonoma Valle d'Aosta – Regione Piemonte 2006). From the geological point of view the area belongs to the greenstone belt of the Alps. This metamorphic unit is mainly composed of ophiolites, but variable amounts of micaceous and calcareous schists are also present, giving rise to the so-called complex of "calcschists and greenstones" (Servizio Geologico d'Italia 1999). A large variability in the amount of minerals is therefore expected in soils and,

consequently a large variability in the amounts of Ca and Mg released by the weathering of the parent material. We surveyed the oligotrophic beech stands occurring on the complex of calcschists and greenstones and selected the investigation sites on the basis of topographic position, forest management and soil types. All sites are at elevations ranging from 1100 to 1360 m a.s.l., located on steep slopes (~30–60%), at midslope linear positions, and consist of coppice beech stands, presently minimally managed and on conversion to high forest type. The climatic conditions of all sites are comparable, according to the Atlante Climatologico del Piemonte (Cagnazzi and Marchisio 1998), and the soil temperature and moisture regimes are always mesic and udic. To avoid an effect of varying pedogenic processes on element distribution, we selected only sites where soils are very poorly developed, as evaluated by pit opening and additional augering. Therefore, pedogenic processes are only related to initial weathering of the parent material and incipient accumulation of organic matter in the topsoil horizons, with no formation of diagnostic horizons yet.

Twelve sites were thus selected and pits were dug in the middle of each plot, down to the C horizon. The depth of the pits thus varied between 51 and 92 cm (see electronic supplement). The soil profile was described on the front side of the pit and samples were taken from the whole thickness of all genetic horizons. Organic layers (Oi and Oe types) are present on all soils and Moder humus types were always found. The sequence of genetic horizons was more variable and both A-C and A-AC-C profiles were present (Figure 1). According to the USDA Soil Taxonomy (Soil Survey Staff 1999), all soils are Typic Udorthents, thus they are all very poorly developed. In total, samples were taken from 60 soil horizons: 11 C horizons (at one site it was not sampled), 7 AC horizons, 18 A (A1 and A2 sometimes) and 24 O horizons (electronic supplement). The collected soil samples were air dried and sieved through 2 mm. The organic C (C_{org}) was determined by dry combustion (CE Instruments NA2100 elemental analyser) and soil organic matter (SOM) contents were calculated by multiplying C_{org} by 1.72. The pH was determined potentiometrically in a 1:2.5 or 1:20 soil:deionised water suspension for mineral or organic horizons, respectively (Van Reeuwijk 2002). In all samples with pH above 7, the presence of carbonates was ascertained volumetrically (Loeppert and Suarez, 1996), but no carbonates were found. The total Ca, Mg, K and Fe contents (Ca_T , Mg_T , K_T , Fe_T) were

determined after HCl-HNO₃ and HF digestion (Bernas 1968), by atomic absorption spectroscopy (AAS, Perkin Elmer 3030). On organic horizons the acid digestion was carried out on previously ignited samples (350°C). Organic horizons are dominated by organic matter but they always contain a variable amount of minerals and both phases contribute to element contents. As it is not possible to analyse separately the organic and the mineral components, the element concentration in organic matter ($Met_{T_{SOM}}$) was calculated by assuming that mineral phases in the O horizons are identical to the first mineral horizon as:

$$Met_{T_{SOM}} = \frac{Met_T \times 100 - Met_{T_{MIN}} \times (100 - SOM)}{SOM} \quad (1)$$

where Met_T is the element concentration ($g\ kg^{-1}$) obtained from the analysis of the organic layer, $Met_{T_{MIN}}$ is the element concentration in the first mineral horizon and SOM is the concentration of organic matter in organic layers.

In mineral horizons the exchangeable amounts of elements were also determined (Ca_{ex} , Mg_{ex} , K_{ex}) by AAS after extraction with BaCl₂ at pH 8.1 and the CEC was determined by titration after back-exchange of Ba²⁺ with MgSO₄ (SISS 1985). The saturation of the exchange complex for one element was calculated by dividing the exchangeable amount of that element by the CEC and multiplying by 100 and the base saturation was obtained in the same way by taking into account the sum of the exchangeable basic cations. These ratios are helpful when comparing soils with varying amounts of sites for cation sorption. The ratio between exchangeable and total forms was taken as an indicator of relative element availability; it defines the amounts of elements that are available for plant uptake with respect to the total pool. The particle size distribution was evaluated by the pipette method after dispersion of the sample with Na-hexametaphosphate. The pedogenic iron oxide content (Fe_D) was evaluated by the Na dithionite-citrate-bicarbonate extraction (Mehra and Jackson 1960) at 25°C, as modified by Boero and Schwertmann (1989): 1 g of soil was shaken overnight with 50 mL of a mixture 4:1 of 0.3 M Na-citrate:0.1 M NaHCO₃ and 1 g of solid Na-dithionite).

For mineralogical analyses, the clay fraction dispersed with Na-hexametaphosphate was separated by sedimentation, Mg saturated with MgCl₂, washed until free of Cl⁻, and freeze-dried. The X-ray diffraction

(XRD) analyses were carried out using a Philips PW1710 diffractometer (40kV and 20 mA, Co-K α radiation, graphite monochromator) on air dried oriented mounts. Scans were made from 3 to 35 $^{\circ}2\theta$ at a speed of 1 $^{\circ}2\theta$ min $^{-1}$. The single species of serpentine minerals are differentiated only by morphological observations (White and Dixon 2002), and only the group can be identified by XRD. The presence of serpentine minerals was therefore ascertained by the occurrence of the 0.73 and 0.36 nm peaks, corresponding to the 001 and 002 reflections of all serpentine species. To evaluate the presence of non-serpentine phyllosilicates, we took into account the 1.4 nm peak which on air dried samples corresponds to the most intense reflection of chlorites, vermiculites and smectites, and the 1.0 nm which is only caused by illites. As kaolinite was not present in the samples, the 1.4 and 1.0 nm peaks represent most non-serpentine soil phyllosilicates. For the semiquantitative evaluation of mineral abundance, the background was subtracted from the XRD patterns and the peak intensities and positions were calculated using the second derivative option of the PowderX software (Dong 1999). A semiquantitative index of abundance (IA) of serpentines in the clay fraction was then obtained from the ratio between the intensity of the 0.73 nm peak (serpentine minerals) and the sum of the intensities of the 0.73, 1.4 and 1.0 nm peaks in the sample (all layer silicate minerals, both serpentine and non-serpentine). As the soils are poorly developed, the presence of serpentines in the clay fraction was assumed to reflect the abundance of serpentines in the parent material, but it is important to note that the IA does not represent the mineralogical composition of the whole soil mass. Mineralogical analyses were carried out only on mineral horizons.

Statistical analysis of the data was carried out using SPSS for Windows version 17.0. The correlation between variables was evaluated using the Pearson's coefficient (two-tailed), after a visual inspection of the data to verify that the relationship was linear. The multiple regression analysis was carried out when the dependence was theoretically based (e.g. CEC dependence on clay, organic matter and pH) using a step-wise procedure. The potential multicollinearity was checked and the variables kept in the analysis when the tolerance was above 0.70. The analysis of variance was carried out in mineral horizons using the General Linear Model option that tests the effects of multiple factors on a single variable. The tested factors were the horizon type and the abundance of serpentines and the effects were corrected for sample

size. In organic horizons the effect of abundance of serpentine minerals was evaluated by one-way ANOVA. The homogeneity of variance was checked by the Levene test and the only variable showing significant differences (Mg availability) was \ln transformed for the analysis. The threshold used for significance in all statistical tests was set at 0.05.

Results

A summary of soil chemical properties grouped by genetic horizon are reported in Table 1, while the complete data set is visible in the electronic supplement. The ratio between oxides (Fe_D) and total Fe was similar in all horizon types and the variability of CEC almost exclusively depended on organic matter ($r^2=0.719$, $P<0.001$). The amount of exchangeable elements was extremely variable in both the A and C horizons: Mg_{ex} ranged from 0.19 to 21.59 and Ca_{ex} from 0.44 to 14.45 $cmol_c\ kg^{-1}$. K_{ex} was very low, always below 0.34 $cmol_c\ kg^{-1}$. Na was below the instrumental detection limit. The base saturation of the exchange complex, which can be used as an indicator of site occupancy by acid cations, ranged from 13 to 100% and increased with increasing pH ($r=0.605$, $P<0.001$). The ratio between Ca_{ex} and Mg_{ex} varied between 0.3 to more than 7, both in the A and C horizons. Organic matter was abundant, up to 144 $g\ kg^{-1}$ in the A horizons, although rather variable. The semiquantitative index of abundance of serpentine minerals in the clay fraction was also highly variable and again, no specific trends in relation to soil horizons were found (Table 1). Besides serpentines, the clay fraction contained mainly chlorites, as visible from the peaks at 1.4, 0.71 and 0.471 nm, illites (1.0 nm and 0.499), with sometimes talc (0.93 nm and 0.311) and lower amounts of feldspars, showing several peaks around 0.32-0.31 nm depending on the specific mineral (Figure 2). The total concentration of Mg increased with increasing index of abundance of serpentines in the clay fraction ($r=0.677$, $P<0.001$, Figure 3a), while Ca and K showed an opposite trend ($r=-0.714$, $P<0.001$ and $r=-0.496$, $P<0.01$, Figure 3b and c respectively). Consequently, the ratio between total Ca and Mg was also dependent on IA, with higher values in the most serpentine-poor soils ($r=-0.663$, $P<0.01$). The situation was clearly different for the exchangeable forms (Figure 4). Because of the linear relationship between CEC and organic matter, we computed the cation saturation (i.e. the percentage of CEC occupied by a specific

cation) to eliminate the masking effects of the variability of available sites for cation exchange. The distribution of Mg was still dependent on the semiquantitative index of serpentine abundance ($r = 0.693$, $P < 0.001$, Figure 4a), but those of K and Ca were scattered and no significant trends were visible (Figure 4b and c). The availability of elements (i.e. the ratio between exchangeable and total forms) was also dependent on the presence of serpentines, and it increased with increasing IA for both Ca and Mg ($r = 0.704$ and 0.627 , respectively, $P < 0.001$). A similar trend was also found for K, although the correlation coefficient was lower ($r = 0.436$).

To more deeply investigate element availability, the samples were divided into two groups based on the index of serpentine abundance; the threshold was set at 0.35 as the dataset clearly showed a first group with IA below 0.3 and a second, serpentine-richer one ($IA > 0.4$), as visible in Figures 3 and 4. The availability index showed no trend with depth in the case of Mg (Figure 5), both in the case of serpentine-poor and serpentine-rich soils and indeed no effect of the type of horizon was found ($P = 0.119$). The soils belonging to the serpentine-richest group had a significantly higher proportion of available Mg ($P = 0.000$) than the soils with lower IA, as clearly visible in Figure 5. The availability index of Ca decreased with depth when the IA was above 0.35, while at lower amounts of serpentines a slight increase was found in the bottom C horizons. In this case, both the horizon type and the abundance of serpentines significantly affected the availability of Ca ($P = 0.029$ and 0.003 respectively) but the interaction was not significant ($P = 0.079$). A slight decreasing trend with depth was also found for K availability although sharp differences between the A horizon and the deeper ones were visible mainly in serpentine-poor soils (Figure 5). Because of the large variability, the effect of horizon type was not significant ($P = 0.157$) nor was the effect of serpentine abundance (or very marginally significant, $P = 0.077$). No significant interaction was found either.

The abundance of serpentines also affected the amount of total concentrations of Ca, K and Mg in the organic horizons ($P < 0.01$, Figure 6a), with higher amount of Mg in serpentine-rich soils and a greater abundance in Ca and K in the second group. When the element concentration in organic matter was calculated, Ca and K concentrations were no longer significantly different between the two soil groups

(Figure 6b), thus indicating that differences were mainly caused by the mineral fraction included in the organic horizons. Significant differences in Mg concentration ($P < 0.05$) were instead still visible.

Discussion

Our hypothesis was that an efficient system should limit the losses of nutrients, therefore a more efficient retention of available elements should occur in case of nutrient scarcity, preventing the losses due to leaching. A wide variability in the concentration of Ca and Mg is typical of soils of serpentinite landscapes and depends on the type of parent material and on the presence of Ca-bearing accessory minerals (McGaham et al. 2009). In the serpentinitic landscape of the “calcschists and greenstones” complex of the Susa valley, we considered both sites where ophiolites prevailed and others where micaceous and calcareous schists are more abundant, thus both Ca-poor and Ca-rich situations were expected. The abundance of serpentine minerals in the clay fraction of poorly developed soils should be an index of these varying fertility conditions and indeed, it affected, as expected, the total concentration of Mg, Ca and K. A large variability in the semiquantitative index of serpentine abundance was found, from 0.04 to about 0.8, and Mg_T , Ca_T and K_T varied consequently. In the case of K_T , the relationship, although significant, was poorer probably because of a group of samples with low K contents and low IA. K deficiencies are rather common in Alpine soils and, in addition to those found on serpentinitic soils, could also arise from the scarce presence of K-feldspars or of micas in the parent material (Sparks 1987), and indeed these minerals were virtually absent in the clay fraction of some serpentine-poor soils with low K_T contents (e.g. profile 12, Figure 2 and electronic supplement) Among the factors inducing the serpentine-syndrome, K deficiencies seem therefore the least specific. At the highest IA values, the amounts of total Ca and Mg were in good agreement with the average composition of Alpine serpentinites reported by Legros (1992). Upon mineral weathering these elements are released into the soil solution and can be leached downwards, take part in the formation of secondary minerals, or become sorbed on the soil exchange complex.

The formation of soil minerals was of little importance in the selected soils; the low development typical of Entisols was confirmed by the ratio between iron oxides and total iron, which is often taken as an indicator

of weathering intensity (e.g. Arduino et al. 1984; Bech et al. 1997; Ortiz et al. 2002). This ratio is high when compared to the data reported by Cornell and Schwertmann (1996) for soils developed after the last glaciation, but is rather common in poorly developed serpentinitic soils: Fe_D/Fe_T ratios of 0.3-0.4 have been found in C horizons from a wide range of environments, from Oregon (Burt et al. 2001), to the Vosges Mountains (Chardot et al. 2007), to western Italy (Bonifacio et al. 1997). The similarities in clay mineralogy among horizons further confirm that the formation of secondary minerals is still of little importance. Smectites and low charge vermiculites are among the first soil layer silicates that develop in serpentinitic soils (e.g. Caillaud et al. 2009), but these minerals were not present in this soil set, although they were found in the Inceptisols of the same area (Bonifacio et al. 2010). As a consequence, the sites available for cation exchange were mainly dependent on organic phases, that sharply decreased with depth, and induced therefore high amounts of exchangeable cations in the A horizons. Mg dominated the exchange complex in serpentine-rich soils and was the only element still showing dependence from the parent material. Due to high Mg concentrations, the ratio between exchangeable Ca and Mg may be extremely low, and typical for serpentine dominated soils (e.g. Alexander 1988). In the case of exchangeable Ca and K instead, the lack of dependence from the soil parent material suggested that biota, hence biocycling, may play an important role in affecting the distribution of the available pool.

The effect of biocycling was well depicted by the distribution of element availability with depth. The average availability of Ca and K was higher in the top horizons than in the deeper ones, even when the concentrations were normalised to take into account the variability of CEC with depth, while no depth trend was visible for Mg. Differences in the behaviour of elements during biocycling occur in all soils; Jobbagy and Jackson (2001) found significantly higher proportions of K and Ca in the first twenty centimetres in a data set of over 8000 samples. On the other hand, Mg increased with depth since plant uptake from the soil limited its leaching to a lesser extent. In the case of Ca, our results showed a more marked depth trend in serpentine-rich soils that, in addition, had a much higher availability of Ca with respect to serpentine-poor ones, both in the top and in the middle horizons. Moreover, the relative

availability of Ca in serpentine-poor soils was the lowest in the middle of the profile, providing evidence for the effect of biocycling in the top and of leaching in the bottom horizons.

The higher element availability when serpentines were more abundant could be related to the inputs of elements through litter mineralisation. Oze et al. (2008) found that vegetation growing on serpentinite chaparral had a higher Ca concentration than that growing on chert and that both vegetation had Ca and Mg equally distributed throughout its biomass indicating that Mg was not overwhelming Ca uptake into the plants. Our results agree with their findings as we found here that element concentration in soil organic matter did not depend on the presence of serpentine minerals, suggesting therefore that the uptake of essential elements was only influenced by plant requirements. The decomposition of beech litter seems to be little affected by soil nutrient availability (Trap et al., 2011), but serpentinitic soils are expected to display a lower mineralization rate because of the effect heavy metals have on microbial communities (Kazakou et al., 2008). Microbial and fungal communities may however be adapted in serpentinitic areas (e.g. Amir and Pineau, 1998), thus showing little effect on litter decomposition, in agreement with the home field advantage hypothesis (e.g. Ayres et al., 2009). If litter decay rate does not change significantly with the abundance of serpentines, litter mineralisation should release comparable amounts of Ca and K in both soil types of our study area, thereby increasing the proportion of available forms where the element was more deficient. This result clearly points to a more efficient retention of the most deficient nutrients that modulates the vertical distribution of the elements, and fits rather well in the general concept tested by Jobbagy and Jackson (2001) that the most limiting elements have the shallowest vertical distribution. To provide support for their hypothesis they evaluated a gradient of increasing leaching (from Aridisols to Mollisols to Ultisols) and could demonstrate that abiotic processes were subordinate to plant cycling in shaping the profile distribution of elements. Our results add to their findings as the effect of nutrient limitations, marked by the index of abundance of serpentine minerals, were visible even in poorly developed soils, when leaching has not yet acted to a large extent. As the most effective biocycling occurs when vegetation has a high requirement for that element (Anderson 1988), we cannot transfer our results to other plant species as beech is indeed a highly demanding tree and Ca is preferentially accumulated in

foliage even over Sr (Dasch et al. 2004). In the case of K, the effect linked to the presence of serpentinites was less visible, although the vertical distribution, with higher availability in the top horizons, was undoubtedly shaped by biocycling. This may be caused by the low K_T contents of eight serpentine-poor samples, confounding therefore the limitation in soil fertility associated to the parent material. The effect of biocycling on Ca is still a matter of debate as it was not evinced in some tree species (oak and birch, Pape et al. 1989) and in several cases atmospheric depositions significantly contributed to the shallow element distribution of Ca or K (e.g. Reynolds et al. 2006; Drouet et al. 2007; Bélanger and Holmden 2010). Although we did not investigate specifically this last aspect, the differences between lithologies we found in element availability and in element contents in the whole organic horizons, coupled with the scattered distribution of lithotypes and the relatively small size of the study area point to a marginal effect of exogenous sources. Although no data are available to our knowledge on exogenous inputs of cations in the study area, African dust deposition prevails in the Alps (Goudie and Middleton 2001); the west-east orientation of the Susa valley should therefore prevent important additions of materials from atmospheric sources.

Conclusions

The vertical distribution of Ca and K in the soils of oligotrophic beech stands depends not only on the budget between leaching and biocycling but also on nutrient deficiency which, in these soils, is linked to the presence of serpentine minerals in the parent material. As the concentration of Ca and K in organic matter is independent from the concentration of the elements in the soil mineral fraction, the inputs of elements with litter mineralisation increase the available forms in the top soil horizons more where the deficiencies of the element are greater. The losses of elements from the available pools are limited, probably because plants take up the deficient elements as soon as they are released from litter, restricting therefore their biogeochemical cycle to the upper, root-rich layers.

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Table 1: Selected chemical characteristics and abundance of serpentine minerals in soil horizons from oligotrophic beech stands in the Susa valley (NW Italy)

		N	Mean	Std. Deviation	Minimum	Maximum
pH	O	24	6.1	0.6	4.6	7.3
	A	18	5.7	0.8	4.4	7.6
	AC	7	5.7	0.6	4.9	6.7
	C	11	6.2	0.5	5.2	6.8
Mg _T g kg ⁻¹	O	24	38.9	25.7	5.1	99.9
	A	18	49.7	31.4	13.9	134.0
	AC	7	43.4	18.6	18.0	71.7
	C	11	47.1	20.1	19.0	95.1
Ca _T g kg ⁻¹	O	24	24.5	8.7	3.5	34.5
	A	18	13.4	8.3	4.2	31.8
	AC	7	15.3	10.3	2.9	29.4
	C	10	16.6	9.7	3.6	33.5
K _T g kg ⁻¹	O	24	8.7	5.2	2.8	17.8
	A	18	9.3	7.1	2.6	23.8
	AC	7	5.5	4.3	1.8	14.7
	C	11	10.2	8.8	2.4	27.2
SOM g kg ⁻¹	O	24	499.9	206.1	174.4	811.0
	A	18	65.2	36.9	20.3	143.9
	AC	7	29.3	3.5	25.7	35.0
	C	11	22.0	17.4	5.2	67.3
Clay g kg ⁻¹	A	18	45.3	13.9	25.0	74.0
	AC	7	56.6	5.4	48.0	62.0
	C	11	54.6	16.1	27.0	82.0
CEC cmol _c kg ⁻¹	A	18	14.2	6.9	5.4	34.5
	AC	7	9.4	2.3	6.3	13.8
	C	11	7.7	3.9	2.4	14.7
Ca _{ex} cmol _c kg ⁻¹	A	18	5.48	3.46	1.19	14.45
	AC	7	2.66	1.52	1.09	5.10
	C	11	3.53	3.04	0.44	9.61
Mg _{ex} cmol _c kg ⁻¹	A	18	3.97	5.03	0.45	21.59
	AC	7	1.86	1.45	0.34	4.11
	C	11	1.90	1.52	0.19	4.83
K _{ex} cmol _c kg ⁻¹	A	18	0.11	0.09	0.02	0.34
	AC	7	0.03	0.02	0.01	0.06
	C	11	0.05	0.03	0.01	0.08
Base saturation %	A	18	63	24	21	100
	AC	7	46	17	23	67
	C	11	71	29	13	100
Fe _D /Fe _T	A	18	0.30	0.08	0.18	0.51
	AC	7	0.33	0.07	0.26	0.42
	C	11	0.30	0.11	0.15	0.52
IA	A	18	0.37	0.24	0.07	0.78
	AC	7	0.32	0.22	0.08	0.67
	C	11	0.31	0.24	0.04	0.78

Fig. 1 Sketch of the study area showing part of the Susa valley in North-western Italy, the presence of the complex of calcschists and greenstones, the location of the Entisol profiles and the sequence of horizons found at each site. Oi and Oe horizons are omitted as present at all sites.

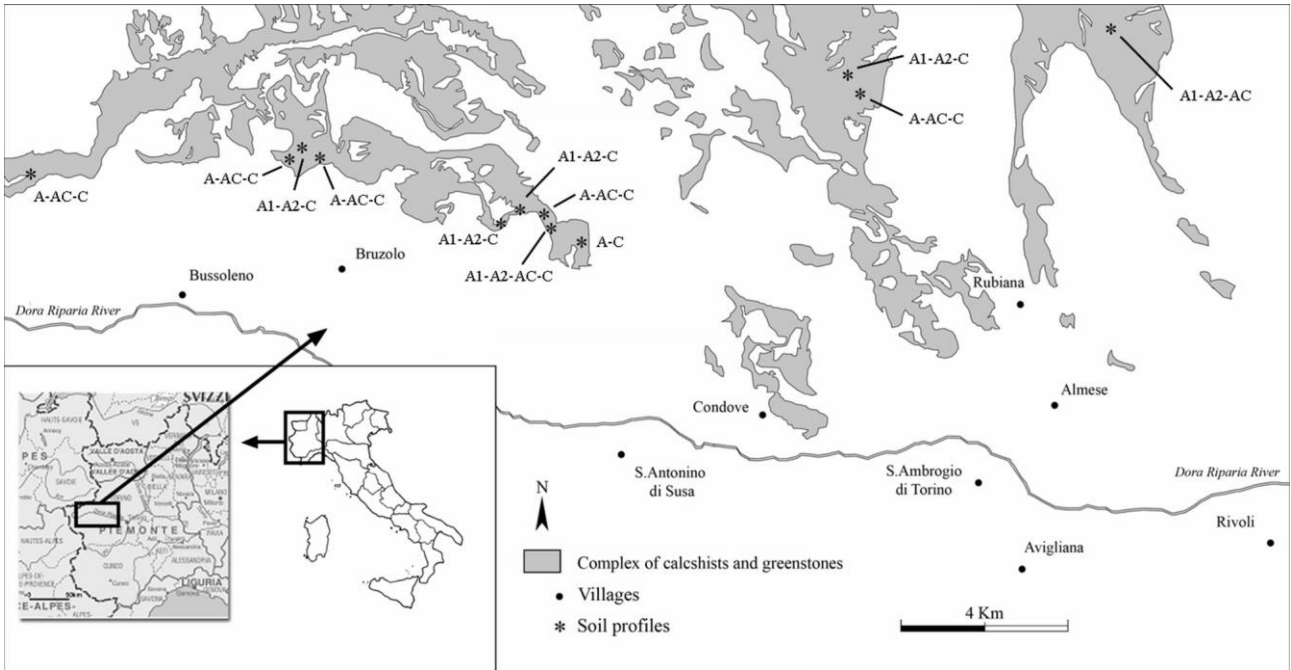


Fig. 2 Examples of XRD patterns of the clay fraction of AC horizons from two serpentine-poor soils (profile 1 and 12) with different accessory minerals and from a serpentine-rich soil (profile 10), sampled in oligotrophic beech stands of the Susa valley (NW Italy). Arrows indicate the most intense peak of serpentine minerals (0.73 nm) and the different height of the peak depicts the variability in sample mineralogy.

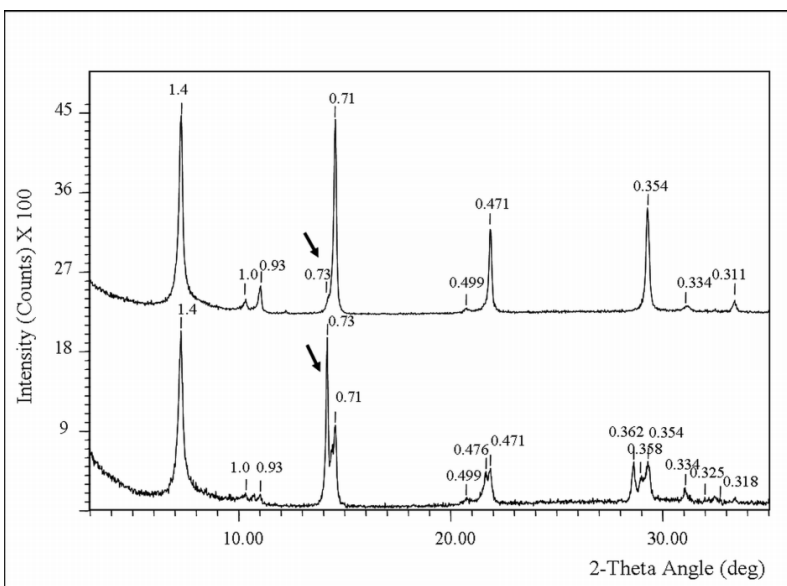


Fig. 3 Relationship between total element concentration and index of serpentine abundance (IA) in soils from oligotrophic beech stands of the Susa valley (NW Italy). a: Total Mg ($r=0.677$, $P<0.001$, $n=34$); b: Total Ca ($r=-0.714$, $P<0.001$, $n=34$); c: Total K ($r=-0.496$, $P<0.01$, $n=34$)

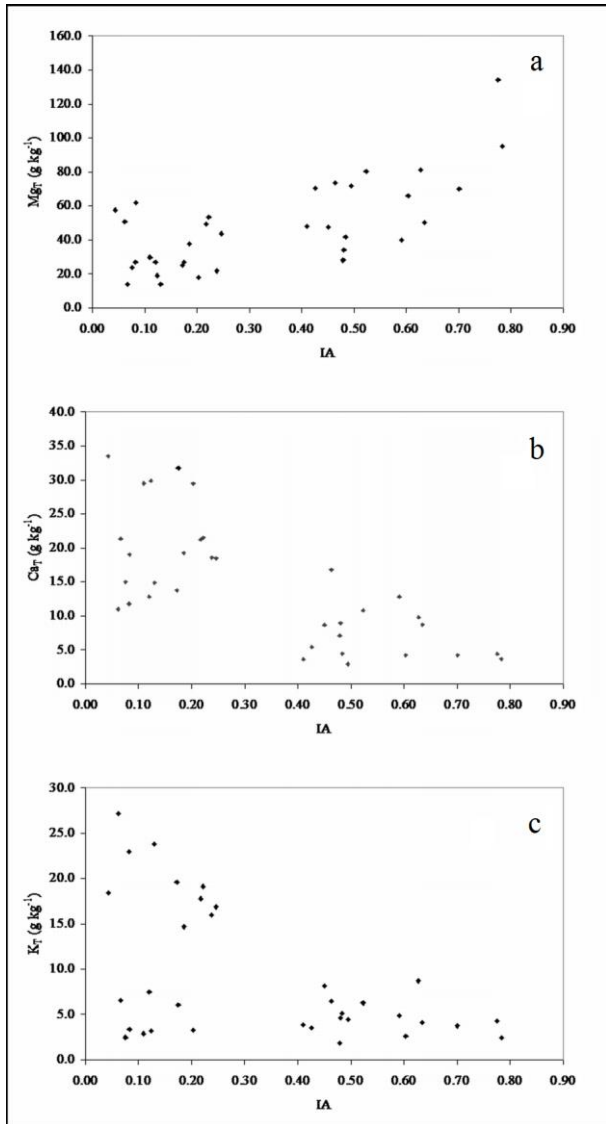


Fig. 4 Relationship between element saturation of the soil exchange complex and index of serpentine abundance (IA) in soils from oligotrophic beech stands of the Susa valley (NW Italy). a: Mg saturation ($r=0.693$, $P<0.001$, $n=34$); b: Ca saturation ($r=0.167$, $P=0.345$, $n=34$); c: K saturation ($r=-0.235$, $P=0.182$, $n=34$)

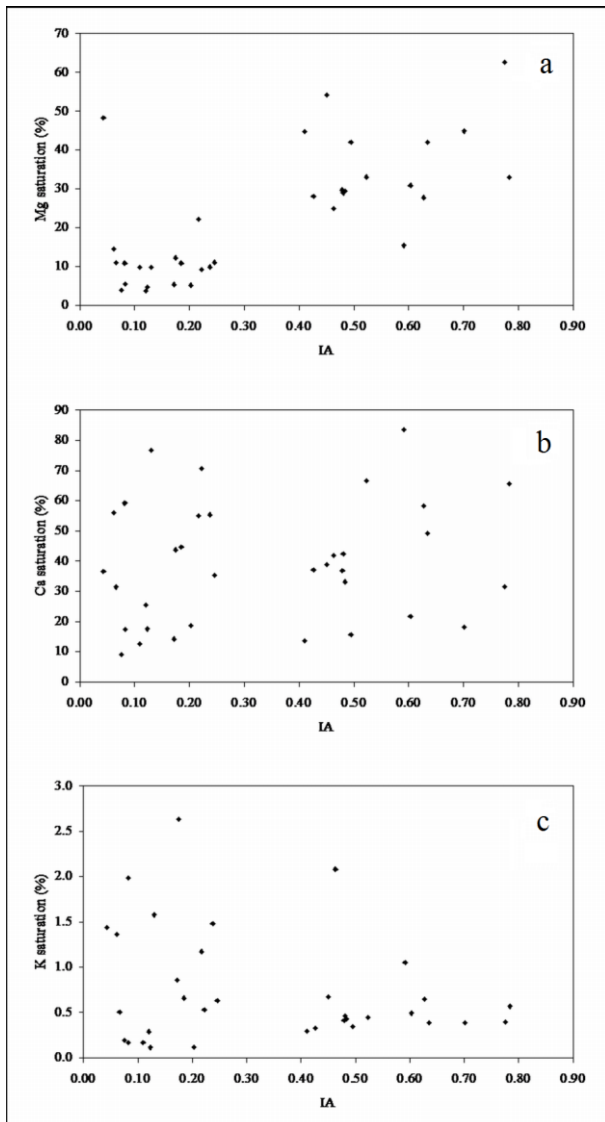


Fig. 5 Index of availability of Mg, Ca and K (ratio between exchangeable and total forms) \pm SE (n=3-9) in soil mineral horizons of serpentine-rich (IA>0.35) and serpentine-poor (IA<0.35) soils of oligotrophic beech stands of the Susa valley (NW Italy)

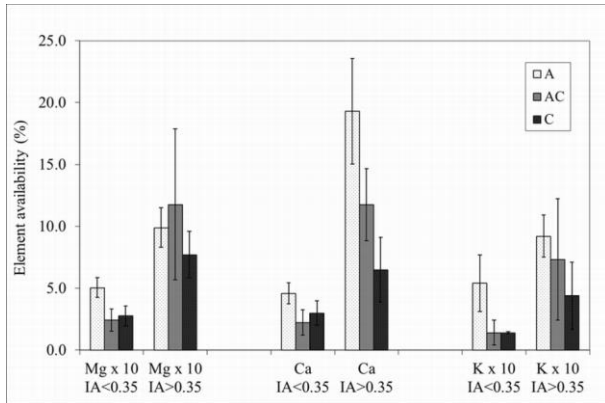


Fig. 6 Total Mg, Ca and K concentration \pm SE (n=3-9) in the bulk O horizons (a) and organic matter of O horizons (b) of serpentine-rich (IA>0.35) and serpentine-poor (IA<0.35) soils of oligotrophic beech stands of the Susa valley (NW Italy). In (b) the element concentration is calculated according to the equation (1)

