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Soil ecology and pedogenesis on ophiolitic materials in the western Alps (Mont Avic Natural Park, North-western Italy): soil properties and their relationships with substrate, vegetation and biological activity.

Università degli Studi di Milano Bicocca
Dottorato di Ricerca in Scienze Ambientali
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Abstract

Soils formed from ultramafic rocks are normally by pH values close to neutrality, a high base status and are usually rich in Mg, Fe and heavy metals. The low Ca/Mg ratio and the high heavy metal content could cause toxic effects in the biological communities. Plant communities, in particular, are usually different from nearby areas with different substrates and rich in endemisms and adapted species and subspecies.

Despite their great environmental and ecological interest, pedological and ecological properties of mountain or boreal soils developed on similar substrates have seldom been studied worldwide. 198 soil pits (associated with phytosociological surveys) have been opened and analyzed in the ophiolitic area of Mont Avic Natural Park (Val d'Aosta, Western Alps, Italy), beween 900 and 2900 m above see level. Soils formed from ultramafic, mafic rocks and calcschists have been observed, in order to recognize the most ecologically important soil factors.

The results show that soil properties are related with altitude and slope aspect in forest habitats, while the effect of substrate becomes important above timberline. Strong leaching in forest soils, related to high acidity and to the podzolization process, decrease the total and bioavailable heavy metal contents, above the treeline pedogenic and geomorphic processes release and accumulate large quantities of potentially hazardous trace elements. The plant communities strictly depend on the edaphic properties above the treeline, while in the forest habitats the differences caused by substrate are less discernible.

Microbial and microarthropodal communities suffer stress caused by heavy metals in forest soils, while at the alpine level non significant statistical or ecological correlation are visible.

Heavy metals (Ni, in particular) are the most important edaphic properties in differentiating plant communities on different substrata, while the Ca/Mg ratio (usually considered the most influencing soil properties on ultramafic soils) has no particular ecological effect.

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1 – Introduction

1.1 Why studying soils on ophiolites: the "serpentine factor"

Ophiolites include associations of ultramafic, mafic and sedimentary rocks, originally formed in the oceanic crust at different depths and brought to the surface by tectonic movements. From the bottom to the top of the original sequence, there are ultramafic rocks, a mafic (plutonic or volcanic) complex, overlaid by a sedimentary, mainly carbonatic, cover. The metamorphism associated with tectonic movements alters the original lithology: ultramafic peridotites and pyroxenites become serpentinites, mafic gabbros and basalts become meta-gabbros and amphibolites, the carbonatic sediments and the shales become marbles or calc-schists (Coleman 1977). The soils formed from these rocks deeply differ from each other, thus supporting different plant communities.

Soils derived from ultramafic rocks (usually called "serpentine soils" by ecologists) have attracted the interest of soils scientists and ecologists for many generations, because they usually host a stunted vegetation, characterized by poor growth and low cover, rich in endemic species and usually distinct from neighbouring areas (Whittaker 1954). Plant species adapted to "serpentine soils" often are characterized by distinct morphologies from the ones closely related but colonizing "different" substrata. They often have xeromorphic appearance (leaves reduced in size, hairiness), smaller dimensions, more developed root system (Brady et al. 2005), also in wet environments. Sometimes, the limit between serpentine and non-serpentine habitats is strikingly sharp (fig. 1.1), evidencing a sharp ecological boundary (Brady et al. 2005, Brooks 1987).

This happens because of the so-called "serpentine factor" (Brooks 1987, Proctor and Nagy 1992). These soils usually contain very high Mg (18–24%), Fe (6–9%) and heavy metals (particularly Ni, Co, Cr and Mn), but very low Ca (1–4%) and Al (1–2%) (Alexander 2004). Many edaphic properties, causing the distinctive vegetation of different ophiolitic areas, have been considered: low Ca^{2+}/Mg^{2+} ratio (later on, Ca/Mg), causing inhibition of Ca^{2+} uptake; toxic effect of high Mg; low Ca^{2+} (Dearden 1979); toxic effects of large concentrations of heavy metals, particularly Ni (Chardot et al. 2007); low available Fe, because of high pH values and competition with Ni and Co (Kataeva et al. 2004); low levels of available macronutrients N, K, P (Nagy and Proctor 1997, Chiarucci et al. 2003); drought due to soil shallowness, sandy texture, erodibility (Oberhuber et al. 1997); dark colour and consequent high temperature and drought (Brooks 1987, and Verger 1987). The relative strength of each factors differs from site to site (Proctor and Nagy 1991).

Fig. 1.1: sharp boundary between serpentine habitats (on the left, with low plant cover and endemic species) and gabbro (with a rich alpine prairie, dominated by Poa alpina and Carex curvula), in Mont Avic Natural Park.

1.2 Plant-soil relationships: the ecology of soils formed on serpentinite

Because of edaphic constraints, the plant communities inhabiting serpentine areas are often stunted and strikingly different from the ones growing in adjacent soils (Brooks, 1987).

Heavy metals (particularly Ni) are perhaps the most discussed factor, because of their toxicity and environmental increase due to human activity. However, their ecological effects in ophiolitic habitats are not clear: some authors claim that Ni negatively affects vegetation, because of toxicity on non-adapted species (Lee 1992, Chardot et al., 2007, Robinson et al. 1996), but according to many others its effect is negligible, particularly if nutrients are sufficiently available (e.g., Chiarucci et al. 2001). Some authors claim that excessive Mg is the most important contributor to the serpentine factor, also in cold and wet environments that should cause a strong base leaching (Proctor and Woodell 1971). This element, when present in large quantities, inhibits the uptake of nutrients because of an antagonistic behaviour with Ca (Proctor 1971).

The importance of metals in serpentine plant ecology, however, is shown by the presence of species which hyperaccumulate them (i.e., containing more than 1,000 mg*kg^{-1} of Ni on the dry weight (Jaffrè et al. 1976)), normally endemic to ophiolitic habitats. These unique plants are potentially important tools for the phytoremediation of soils contaminated with metals from anthropogenic sources (Baker et al. 1994).

Despite the importance of serpentine environments, very few studies deal with the relationship between soil and vegetation cover in boreal or high mountain regions.

In temperate mountain areas, biodiversity decrease with altitude on ultramafic substrates, because of the interaction between the stresses caused by altitude and edaphic properties (Wilson et al. 1990). On ultramafic substrates in humid mountain areas in the Klamath Mountains in northern California, forest productivity and density on mountain slopes on ultramafic material are low compared to nearby terrains (Burt et al. 2001), but it becomes higher on ancient and well developed soils than in young and disturbed ones, because of the progressive leaching of Mg, leading to an increase in the Ca/Mg ratio, and of toxic and mobile Ni and Co (Alexander 1988).

On a serpentinite outcrop in Newfoundland, around the tree-line, the vegetation is sharply different from the one found on nearby substrates; it is similar only where the available Ca^{2+} approaches the values typical on nearby substrates (Dearden 1979).

In subalpine areas in northern Japan, on serpentinite, the presence of spruce (*Picea abies*) is lower than on other substrata, and laboratory experiments show that the growth of this species is inhibited on "serpentine soils" because of the combined toxicity of excessive Ni and Mg (Kayama et al. 2005). Similarly, Kràm et al. (1997) show how spruce grows with a stunted shape in a serpentinite-dominated basin: it is not clear if this feature is due to Ni or Mg toxicity, or insufficient K content.

Chemical relationships between soils and vegetation in an arctic area in Russia is described by Kataeva et al. (2004), but the relationships between vegetation communities and soils are not shown. Alpine soils on serpentinite are described in detail by Roberts (1980), while high altitude soils formed from serpentinite and mafic rocks enriched in sialic colluvium are shown by Sanchez-Marañon et al. (1999).

In the Western Italian Alps (Val d'Ayas), Vergnano Gambi and Gabbrielli (1981, 1987) showed the mineral composition of some plants growing at high altitudes on ophiolitic soils, in relation with the metal content in soils. However, the ecological effect of heavy metals, as well as the "serpentine effect" was not studied.

In other studies concerning ophiolitic habitats in Val d'Aosta, the weak edaphic acidity was considered the most important factor in the differentiation of plant communities on ultramafic rocks: the dry, base-rich and "eutrophic" soils on serpentinite did not permit the development of the typical subalpine spruce and *Pinus cembra* forest (Verger 1990) which grew on Podzolic soils developed on mafic and acid rocks. On serpentinite, the soils were either too dry for spruce and *Pinus cembra*, or too wet for *Pinus uncinata*. The understory vegetation was mostly neutrophilous (Verger et al. 1993). At the alpine level, on serpentinite, neutrophilous or basophilous communities grew on neutral soils. Possible effects of heavy metals were not mentioned (Verger et al., 1993).

Recent studies (D'Amico 2006a and 2006b, D'Amico et al. 2008) in the ophiolitic area of Mont Avic Natural Park (Valle d'Aosta, Western Italian Alps), showed a different situation, both from a pedological and a botanical point of view.

Buffa et al. (1998) describe alpine vegetation on serpentinite in Mont Avic Natural Park from a phytosociological and from an ecological point of view, but soils are not studied.

In temperate of boreal habitats, soils and vegetation covers on mafic rocks (gabbros, meta-gabbros, prasinites and amphibolites) are usually similar to the ones developed on acid rocks (Verger et al. 1993); only in dry climates, and where pyroxenites bodies are associated with the mafic outcrops, community composition is somewhat intermediate between the one typical on acid and on ultramafic substrates (Alexander et al. 2007).

1.3 Soil forming processes on ultramafic materials

Worldwide, "serpentine soils" are often considered as shallow, primitive and eroded soils. This idea probably depends on the fact that usually recently exposed ultramafic outcrops support the most peculiar vegetation cover, and the chemistry of these soils is the most similar to the parent material and the most stressing for vegetation. A large number of studies were performed in this "primitive" habitats, while well developed soils under well-developed plant cover were often neglected on mafic and ultramafic substrates. Another reason often cited for the explanation of the shallow thickness of serpentine soils is the lack of alumina, which inhibits the formation of clay minerals and enhances erosion (Cleaves et al. 1974).

In temperate or cold, humid climates, three main pedogenic processes are commonly active on ultramafic materials: fast Ca leaching, formation of a mull humus type, biologically active because of near-neutral pH values, illuviation of clay minerals and formation of an argillic Bt horizon (Duvignaud 1996, Rabenhorst et al. 1982). In a recent review of serpentine geoecology of Western North America (Alexander et al. 2007), it emerges that most kinds of soils and pedogenic processes can be found on ultramafic substrata. Only Podzols/Spodosols are not found on pure serpentine: the surface horizons must be developed from volcanic ash or sialic alluvium in order to permit the development of a strongly acidic E horizon and the leaching of Fe and Al complexed with organic matter. Only in the coldest and most humid sites in Alaska spodic horizons can form, overlaid by A horizons. In subalpine habitats, in Western North America the most common soil formed on serpentinite in stable sites is the Cambisol, with Bw horizons strongly enriched in Fe oxi-hydroxides.

Serpentine minerals (antigorite, chrysotile and lizardite) are unstable in surface environment, and are easily transformed into other layer silicates by weathering processes: in relation to drainage properties, Mg and Si leaching, some clay minerals can form: in well aerated sites, vermiculitic minerals are common, while in low drainage situations smectites are dominant (Bonifacio et al. 1997, Bulmer et al. 1992, Lee et al. 2003, Rabenhorst et al. 1982). Secondary Fe-oxy-hydroxydes are also normally accumulated, particularly in the most weathered B horizons (Alexander 2004, Bonifacio et al. 1997). Goethite and hematite are formed after the release of Fe from the structure of primary minerals. Because of high pH values, metal leaching is inhibited. These oxides are often an important sink for heavy metals (Becquer et al. 2006, Schwertmann and Latham 1986).

Podzolization (formation and illuviation of organic acids complexed with Al and Fe, and downward transportation of Al and Si in colloidal form) is the typical pedogenic process acting on acidic and silicate rocks under subalpine or boreal coniferous forests or ericaceous shrubs in cold, humid climates. However, this process is somewhat inhibited over easily weatherable mafic and ultramafic parent materials (Lundström et al. 2000) because of the high base status, high siderophile element content (Souchier 1984) and near-neutral pH. In general, these chemical factors slow down podzolization considerably, even when climate and vegetation favour the process.

Sasaki et al. (1968), Sticher et al. (1975), Verger (1990), Bulmer et al. (1992), Verger et al. (1993), Alexander et al. (1994), Bulmer and Lavkulich (1994), Gasser et al. (1994)), deal with pedogenesis on ultramafic substrates in boreal or mountain habitats. Many more have focused on “serpentine soils” in tropical areas.

In addition to the above cited processes, there are a few reports of podzolic soils developed from serpentinite; however, according to the most widespread taxonomic systems, such as the World Reference Base for Soil Resources (IUSS Working Group WRB 2006) (hereafter WRB) and Soil Taxonomy (Soil Survey Staff 2006) (hereafter ST), none of these soils can be classified as Podzols or Spodosols. Alexander et al. (1994a and 1994b) describe soils on ultramafic till in Alaska as having an E horizon but a pH=6 in the Bs horizons, which is inconsistent with that of Spodosols. Bulmer and Lavkulich (1994) report that a soil developed from ultramafic materials in Canada has a spodic Bf horizon (Expert Committee on Soil Science. Agriculture Canada Research Branch, 1987), but lacks the E horizon and has a rather high pH (5.7). A similar soil profile was observed by Ragg and Ball (1964) on the Scottish island of Rhum. Soils with a podzol-like morphology (a bleached E horizon overlying a reddish-brown Bs) described by Gasser et al. (1994) in Switzerland show lithological discontinuity between the wind-driven material from which the E horizon formed and the Bs derived from serpentinite debris. The same profile was previously described by Sticher et al. (1975). The high quartz content (15%) in the eluvial horizon was interpreted as presence of aeolian material. Sasaki et al. (1968) found a podzol-like soil on serpentinite in Northern Japan: they conclude that podzolization is active, but the pH value (6.5) is higher than the one typical of podzolic soils. Verger (1990) and Verger et al. (1993) compared soils developed on serpentinite and on mafic and acid rocks in the western Italian Alps. They concluded that podzolization is impossible on ultramafic parent materials, which usually give rise to Eutric or Dystric Cambisols in the most humid sites under subalpine vegetation.

On other substrates common in the study area (calcschists, at high altitude), the main soil forming processes are decarbonatation and acidification, leading to the formation of strongly acidic soils dominated by sand (mainly composed by mica). Nutrients are abundant, thanks to the easy weatherability of the parent material and to the favorable Ca/Mg ratio in the rock-forming minerals (Legros et al. 1980).

1.4 The study area

The Mont Avic Natural Park is located in the Chalamy and the Champorcher valleys (Valle d'Aosta, Western Italian Alps, fig. 1). The substrate is composed of ultramafic, mafic rocks and calcschists, part of the Piedmontese Ophiolitic Complex (Occhipinti 1997). The most common lithology is serpentinite (mainly of antigoritic type), associated with lenses of chlorite-schists, followed by meta-gabbros and amphibolites (rich in tremolite and actinolite). Calcschist outcrops are extensive in the southernmost part, above 2400 m a.s.l..

Pleistocene glaciers completely covered the area until 12000-15000 years BP. Since then, erosion-deposition processes deeply affected the slopes. Thus, the soil parent material is usually made of loose till and debris composed of ophiolitic rocks in different amounts; only seldom the soils formed *in situ* directly from the weathering of the hard substrate.

Cryoturbation heavily affects large surfaces above the treeline, with extensive flat areas covered by active earth hummocks (usually large between 20 and 100 cm, and 10-40 cm high) and slopes by solifluction lobes. Above 2600 m, on north-face slopes, there are active rock glaciers and rock streams which indicate the presence of permafrost (Guglielmin 1997). Surface concentration of rocks (rock fields) is common on easily fragmented rocks, normally above 2500 m. Patterned ground (rock circles and stripes) is also common above the same altitude.

The forest vegetation can be resumed as follows (Bovio and Broglio 2007):

- Beech (*Fagus sylvatica*) forests at the montane level (1000-1400 m) on humid, north-facing slopes (*Luzulo-Fagion*);
- Dry, south-facing slopes at the montane level (1300-1700 m) dominated by xerophilous Scotch pine (*Pinus sylvestris*) forests (*Deschampsio-Pinetum sylvestris,* Verger et al. 1993);
- *Pinus uncinata* dominates the lower subalpine forests (1400/1700-2000/2100 m), association *Rhodoreto-Vaccinietum* (Montacchini 1968),
- Larches (*Larix decidua*) and shrubs dominate the higher subalpine level (2000–2300 m).

Some serpentiniculous species (*Thlaspi sylvium*, *Biscutella laevigata, Carex fimbriata*) are common in open forests where the substrate is dominated by serpentinite (D'Amico 2006b).

Soils are always deeply acidified, and podzolization is the dominant soil-forming process on north-facing slopes (D'Amico 2006b, D'Amico et al. 2008).

Alpine plant communities can be resumed (Bovio and Broglio 2007, Buffa et al. 1998, D'Amico 2006a) as the typical *Curvuletum* on metagabbros and on calcschists; on the latter, there are usually some basophilous species. On serpentinite, *Caricetum fimbriatae* is the most common association.

The climate is endo-alpine with continental influences. The average yearly temperatures decreases with altitude from 5° to -6°C (Mercalli 2003) and precipitation is around 700-1200 mm (the average precipitation at Praz Oursie, located at 1800 m over sea level, is around 850 mm). The precipitation maxima are in autumn and spring. Summers are quite dry (sub-Mediterranean influences), but not enough to cause stress for the vegetation (udic moisture regime according to Soil Survey Staff 2006).

1.5 Aims and structure.

The aim of this study is, therefore, to characterize the pedogenesis and the ecological effect of some properties of the soils formed on different ophiolitic lithologies, and their mutual relationships with the plant communities and with microbial activity and stress symptoms.

This will be achieved by four phases: the first is a general characterization of soils properties and pedogenetic processes, of plant communities and their mutual relationships; the second phase is the chemical and mineralogical characterization of the peculiar pedogenic process of podzolization, unusual on ultramafic substrates; the third is the characterization of metal speciation and bioavailability, in relation with pedogenic processes and environmental properties; the fourth is the recognition of relationships between soil properties and microbial activity and microarthropodal biodiversity and adaptation.

Each chapter in which this dissertation is subdivided consists in the main phases of the investigation, or in parts of them: the main link between the chapters is the search for the main edaphic factor implied in the ecological variability in the study area.

Chapter 1 shows the main objectives and theoretical background: why soils formed from ultramafic materials are important from an environmental and ecological point of view, what are their main peculiarities and why they can be considered toxic to non adapted living organisms. A large number of papers are cited here.

Chapter 2 describes the main results of the first part of the study: the main edaphic and environmental properties have been statistically related to vegetation cover and plant community composition, after having sampled and analyzed a large number (198) of sites.

Chapter 3 deals with one of the most striking features of the subalpine soils formed in the study area: the podzolization process, very unusual on base-rich substrates like serpentinite. This process is described from the chemical and mineralogical (chapter 4) point of view. Podzols are extremely acidic soils, and these low pH values can increase metal mobility and bioavailability.

So, the study of heavy metal speciation and mobility has been studied (Chapter 5), in order to detect differences in metal bioavailability in relation to pedogenesis and environmental properties.

Chapter 6 deals with the effect of metal content, speciation, bioavailability on soil ecology, biological diversity and microbial activity and stress.

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2. Edaphic influences on vegetation of ophiolitic substrates

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Abstract

Edaphic influence on vegetation is particularly strong in ophiolitic areas, because of the typically harsh soil properties on ultramafic substrates, the so-called “serpentine factor” (e.g., high heavy metal content, low available Ca/Mg ratio, low nutrients supply). Plant cover is usually low (the so called “serpentine syndrome”), and many endemic species or sub-species grow over such materials. There is no general agreement about the main factor(s) involved in the “serpentine syndrome”. However, very few studies deal with the relationships between vegetation and soils in alpine or boreal habitats. In particular, in the large ophiolitic areas of the Western Alps, very few comprehensive studies exist.

The aim of the present work is, therefore, to give information about the soil-vegetation relationships in subalpine forests and alpine habitats (Mont Avic Natural Park, Aosta Valley, Western Italian Alps). This is achieved by following a statistical approach: plant communities are recognized and correlated with environmental and soil chemical and physical properties.

In the concerned environments, forest soils are deeply acidified, and the forest vegetation is always acidophilous, and depends mostly on aspect and altitude. Some species endemic to serpentinite grow where Ni is high. Above the tree-line, soils are less developed and soils and plant communities diverge in relation to substrate and slope processes. The different vegetation on serpentinite is related mostly with available Ni.

2.1. Introduction

Ophiolites include associations of ultramafic, mafic and sedimentary rocks, originally formed in the oceanic crust at different depths and brought to the surface by tectonic movements. The soils formed from these rocks deeply differ from each other, thus supporting different plant communities.

Soils developed from ultramafic rocks (usually called “serpentine soils” by ecologists) are very interesting from an ecological and environmental point of view, because of the so-called “serpentine factor” (see chapter 1)

In the Western Italian Alps (Val d’Ayas), Vergnano Gambi and Gabbrielli (1981, 1987) showed the mineral composition of some plants growing at high altitudes on ophiolitic soils, in relation with the metal content in soils. However, the ecological effect of heavy metals, as well as the “serpentine effect” was not studied.

In other studies concerning ophiolitic habitats in Val d’Aosta, the weak edaphic acidity was considered the most important factor in the differentiation of plant communities on ultramafic rocks: the dry, base-rich and “eutrophic” soils on serpentinite did not permit the development of the typical subalpine spruce and *Pinus cembra* forest (Verger, 1990) which grew on Podzolic soils developed on mafic and acid rocks. On serpentinite, the soils were either too dry for spruce and *Pinus cembra*, or too wet for *Pinus uncinata*. The understory vegetation was mostly neutrophilous (Verger et al., 1993). At the alpine level, on serpentinite, neutrophilous or basophilous communities grew on neutral soils. Possible effects of heavy metals were not mentioned (Verger et al., 1993).

Recent studies (D’Amico, 2006a, 2006b, D’Amico et al. 2008) in the ophiolitic area of Mont Avic Natural Park (Valle d’Aosta, Western Italian Alps), showed a different situation, both from a pedological and a botanical point of view.

The aim of the present study is, therefore, to describe an ophiolitic ecosystem on the Alps, and to characterize the ecological effects of some chemical properties of the soils formed on the different lithotypes and their mutual relationships with the vegetation. The high acidity and desaturation found in most soils in the study area have seldom been found on ultramafic substrates worldwide, and could increase metal bioavailability and give rise to toxicity and strong ecological effects.

Available Ni, Ca and the Ca/Mg ratio were the considered components of the "serpentine" factor.

The aim was achieved by following a statistical approach: the first stage was the field recognition of the different plant communities, the second was the verification of the observed differences with statistical classification methods (cluster analysis). The third phase was the constrained ordination of vegetation relevèes in relation with soil and environmental properties in order to understand the fraction of the variability explained by the selected edaphic factors. The fourth was the modelling of the edaphic requirements of some serpentiniculous species, by the use of Generalized Linear Models (GLMs) and Classification Trees (CART).

2.2. Materials and methods

2.2.1. Field data collection and soil sampling

In order to obtain an exploratory overview of the different habitats, 191 sites were chosen subjectively according to the geology and the vegetation cover (from existing cartography and field observation), following many altitudinal and lithological transects. Many plots had already been characterized (D'Amico 2006a, 2006b). Field activities were carried on in July-August 2008. A non-random sampling design was followed in order to obtain data also on some particular, "extreme" habitats which would have been probably missed with a randomized selection of sampling plots, because of the small area they occupy.

A phytosociological survey was completed in homogeneous plots of 16 m^2, visually estimating the cover (%) of each species. The following data were collected: slope (%), aspect, tree cover (%), altitude (m), rockiness (%), herbaceous cover (%). Species were recognized according to Lauber and Wagner (1998) and to Pignatti (1992). The taxonomic names are derived from Pignatti (1992).

The soil pits were excavated in the middle of the plot, to a depth where no sign of pedogenesis was visible (usually no more than 70 cm) or down to the hard rock, in order to characterize the pedogenic factors active in the plot, the development degree of the soil and to make a field classification (IUSS Working Group WRB, 2006).

Field description of soil profiles was performed according to FAO (2006).

Approximately 1 kg of soil material was collected from surface horizons to a depth of 10-15 cm; rock fragments were preserved in order to qualitatively and quantitatively determine their lithology.

2.2.2. Laboratory analysis

All soil samples were air-dried and sieved to separate the fine earth (<2mm) from the coarse fraction. The following properties were determined: pH (H_2O and KCl, soil: solution=1:2.5), total organic carbon (TOC, Walkley and Black), available Ca, Mg, K, Na (Ca_{av}, Mg_{av}, K, Na, extracted with $BaCl_2$–TEA and analyzed with FAAS), total acidity ($BaCl_2$–TEA extraction and titration with 0.1M HCl), Cation Exchange Capacity (CEC) by sum of exchangeable bases and acidity, 5 fraction texture (sand, fine sand, silt, fine silt and clay). Available Ni (Ni_{av}) was extracted with 0.1M EDTA (pH4.5), from the top mineral horizons (to a depth of 10-15 cm). The analyses were performed according to standard methods (Ministero delle Politiche Agricole e Forestali 2000).

The coarse fraction (diameter larger than 5mm) was cleaned with Calgon, observed, divided according to the different lithologies and weighted, in order to semi-quantitatively characterize the parent material of the horizons, which can be different from the substrate because of slope processes.

2.2.3. Data analysis

All statistical elaborations were performed using the R 2.9.1 for Windows software. The complete data set was separated into two groups: forest and alpine habitats. Ni_{av}, Ca_{av} and altitude were log-transformed.

A correlation analysis was performed on the environmental and soil chemical properties, in order to recognize collinearities (R^2 higher than 0.8) and to select a smaller subset of independent variables to be used in the following elaborations. The selected variables were thus pH values (KCl), Ca/Mg ratio, Ca_{av} and Ni_{av}, drainage, aspect, slope, altitude, plant and tree cover; the intensity of cryoturbation was considered for plots above the tree-line.

Trees and shrubs were treated separately from the herb species, in order to better distinguish the different communities (trees and shrubs distribution depends mainly on altitude). Plots were grouped into similar vegetation types using Cluster Analysis: some different clustering agglomeration criteria were tried (single, average (1) and complete linkage, median, centroid, Ward), but only (1) was chosen for later analysis owing to the lower cophenetic correlation value of the other methods (Sneath and Sokal 1973). The best distance algorithm (Bray-Curtis dissimilarity index) was selected according to the function "rankindex" in the "vegan" package, which calculates the correlation between different distance algorithms and a given gradient (in this case, pedo-environmental properties) (Oksanen 2007).

The number of clusters was chosen according to their ecological meaning. Cluster stability was also assessed through the "bootstrap" noise-adding and subsetting method (Hennig 2007). The result of the bootstrap method is the Clusterwise Jaccard mean, whose values indicate stability: if it is below 0.5, the cluster is said to be "dissolved", not significant, while it is "stable", significant, if the value is above 0.75 (Hennig 2007).

An unconstrained ordination of plant communities was performed with the help of the Non Metric Multidimensional Scaling (NMDS, Bray Curtis dissimilarity index) technique ("metaMDS()" function), in order to detect gradients in community distribution. NMDS requires that the dimensionality of the data is specified in advance: as the aim of the NMDS is to show the main gradients in the floristic data, NMDS was used in two dimensions. To facilitate the interpretation of the results, the rock types were plotted as arrows, on the NMDS biplot. The direction of the arrows indicate the direction of the gradient and their length indicate the correlation with the NMDS axes.

Species density was calculated for the understory vegetation and correlated with edaphic and environmental properties.

In order to highlight the important factors correlated with the vegetation gradients, Canonical Correspondence Analysis (CCA, Ter Braak 1986) was used. Biplot scaling focused on inter-species distances, without transforming species or downweighting rare ones, was used. Sites were labelled on the biplot with the number of the cluster they are included in, in order to see the dependence of plant communities on soil and environmental properties. The contribution of each soil and environmental variable to the CCA model was later inspected separately. The statistical significance was verified with Montecarlo permutation tests (function ANOVA()).

Generalized Linear Models (GLM) and Classification Trees were used to detect the relationships between some serpentiniculous species (presence-absence data) and soil and environmental properties. The best distribution (binomial) was verified with the help of the AIC (Akaike Information Criteria; Sakamoto et al. 1986) shown by the ANOVA. It has been demonstrated that GLMs are better than canonical ordinations when considering single common species (Guisan et al. 1999), while CART (De'Ath and Fabricious 2000) shows the optimal distribution ranges (Vayssiéres et al. 2000).

2.3. Results

2.3.1. The vegetation

255 species were recorded, occurring at least once in the sampling plots, 192 in forest habitats and 210 above the tree-line.

2.3.1.1. Forest data sets

The visible lack of a strict dependence of vegetation on rock type was verified: classification (cluster analysis, fig. 2.1, left) and ordination methods (NMDS, fig. 2.2, left) were not able to isolate herbaceous plant communities developed on particular substrates. Only few clusters were statistically meaningful. The clusterwise Jaccard mean of the 11 clusters is not shown.

The highest cluster subdivision separated montane-level, species-poor and low tree-cover plots (clusters 8, 9, 10) from the others. The second division isolated beech woods (clusters 7 and 11), whose species composition was markedly different from other forest types (*Luzulo-Fagion*).

The remaining clusters (1,2,3,4,5) included subalpine and montane communities. Lower subalpine ones (cluster 3, on mainly serpentinite, and 5, on meta-gabbros) were dominated by the acidophilous species of the *Vaccinietum*. Plots belonging to cluster 3 were enriched with the strictly serpentiniculous sedge *Carex fimbriata*.

High-altitude subalpine plots belonged to clusters 1 and 2, which were quite similar to clusters 3 and 5, but were usually characterized by a lower tree cover. Here, the main tree species was larch (*Larix decidua*), while *Juniperus communis* and ericaceous shrubs (*Calluna vulgaris*, *Loiseleuria procumbens* and *Vaccinium uliginosum* subsp. *gaulteriodes*) showed high covering values.

Cluster 4 included xeric plots at altitudes below 1600 m and many rocky sites where serpentiniculous species (*Thlaspi sylvium*, *Cardamine plumieri*, *Asplenium adulterinum*) were common, as well as wet riverbeds and stream banks colonized by the same species.

In short, all the communities were dominated by acidophilous species. At the subalpine level on serpentinite, often but not always, typical and endemic species like *Carex fimbriata*, *Thlaspi sylvium*, *T. caerulescens* (this last species only grows in open montane woods), together with *Cardamine plumieri*, *Asplenium viride* and *Asplenium adulterinum*, were common. These serpentine species colonized crevices in rock outcrops, debris slopes, riverbeds and stream banks.

2.3.1.2. The vegetation: alpine data set

Alpine plots were grouped in 12 ecologically meaningful clusters. The ecological meaning of this subdivision corresponded to a high statistical significance, evidenced by the high cophenetic value with the chosen number of groups (fig. 2.1. right).

The highest cluster subdivision isolated clusters 12, 3, 6, 2, 7 (on the left) from the others. Cluster number 6 included high-altitude acidophilous communities, mostly on meta-gabbros, while the others included few plots on serpentinite, rich in basophilous and endemic species, mostly on debris and on disturbed and eroded slopes. The vegetation cover was low.

Clusters 9,11, 10, 4, 1, 8, 5 were located on the right side of this great subdivision:

- cluster 9 included sites on steep debris with high plant cover, with acidophilous species (typical *Oxyrietum diginae*), on mafic rocks;
- cluster 11, acidophilous communities (*Curvuletum*) enriched by many basophilous species, on stable slopes on calcschists;
- cluster 10 consisted of debris vegetation on serpentinite (*Thlaspietum rotundifolii*)
- cluster 4 included mostly acidophilous communities (*Curvuletum*), on calcschists and gabbros;

- cluster 1 included plots belonging to the most common association on serpentinite, dominated by *Carex fimbriata*, associated with acidophilous herbs and shrubs (*Vaccinium uliginosum, Loiseleuria procumbens, Rhododendron ferrugineum*);
- clusters 8 and 5 were composed of debris and high altitude stands on calcschists and gabbros, dominates by acidophilous species but enriched in basophilous ones.

NMDS ordination (fig. 2.2, right) visually separated the communities belonging to different clusters, and the superimposed substrate confirmed the importance of parent material in vegetation distribution.

2.3.2. The soils

An extremely high variance of chemical properties on similar parent materials was a common feature of all the soils in the study area. For example, the Ca/Mg ratio on serpentinite varied from 0.2 in organic-matter poor E horizons, in subalpine Podzols, up to 16 in disturbed sites. Ni_{av}, which showed a significant decreasing trend from serpentinite to gabbro and calcschists, had an extremely high variance (2-900 mg kg^{-1}) on serpentinite because of leaching that lowered the content in the most stable, developed and acidic pedons (fig. 2.3).

Ca_{av} was normally highest on calcschists; it was sometimes particularly high on serpentinite, in Ni and TOC-rich soils in crevices of steep rocky outcrops, in riverbeds and on stream banks (fig. 2.3).

Humidity and snow cover favour acidification and weathering (Egli et al. 2004): this is why the drier south-facing slopes, where evapotranspiration is higher, and low altitude beech forests, supported less developed soils, with chemical properties more similar to the parent material (weaker acidity, higher metal content on serpentinite).

Texture was finest (loamy or sandy loamy) on serpentinite, because of its strong weatherability.

2.3.2.1: Forest soils

The previously observed strong acidification and desaturation of the forest soils, and the biologically inactive humus types (mor and moder) (D'Amico 2006b, D'Amico et al. 2008) were confirmed. pH values (normally between 3.2 and 4.5) were neutral or subacid only in serpentinic rock crevices, or on stream banks, where water-soluble cations were repeatedly added to the soil materials.

Normally, the value of the Ca/Mg ratio was around 1.5 on serpentinite and 3 on meta-gabbros. It was usually highest in organic matter-rich horizons, because Ca was biocycled and bioaccumulated, while Mg was easily leached away from the profile (Rabenhorst et al. 1982).

K, as a nutrient, was always extremely scarce in the studied soils, and its concentration did not significantly vary on the different parent materials (data not shown).

The correlation matrix (table 2.1) verified the described situation.

2.3.2.2. Alpine soils

The higher number of sampling plots verified what was shown by D'Amico (2006a). The main processes influencing pedogenesis above the treeline were cryoturbation and erosion, while the acidification due to organic matter accumulation related to dense vegetation cover was possible only on stable surfaces. As it happens in Sirois and Grandtner (1992), periglacial movements, the strong erosion and deposition typical on cryoturbated slopes and the (mostly) sparse vegetation cover inhibited soil development. Soils were classified mostly as Regosols or Cambisols, with Cryosols at high altitudes (IUSS Working Group, 2006).There were many differences between the physical and chemical properties in the soils formed on different parent materials (D'Amico 2006a).

On serpentinite, Ni_{av} (1-1000 mg kg^{-1}) was highest in organic matter-rich horizons, owing to their high CEC and the stabilizing effect of organic particles, and in deep horizons, because of the incipient weathering of primary minerals and because of lateral solute transportation from upslope areas. The Ca/Mg ratio changed widely in these soils, particularly in surface horizons, in relation with organic matter: the highest was the organic matter content, the highest the ratio. The pH values were between 4.5 and 6.7.

Soils on mafic rocks (meta-gabbros, prasinite and mixed till) were strongly acidic (pH values always between 4 and 5), the Ca/Mg ratio was above 2, Ni_{av} was between 0.5 and 130 mg kg^{-1} . Podzolic soils can be found at altitudes as high as 2600 m, under ericaceous dwarf shrubs.

On calcschists, carbonates were always completely leached away from the profile, and were absent even in the weathered, fractured parent rock. The pH values of the their soils were usually acidic on the surface and grew fast with depth; only in heavily cryoturbated areas surface they were close to neutrality. Ca/Mg was usually above 15, Ni_{av} could reach high values (between 0.1 and 79 mg kg^{-1}) in deep horizons, probably because of lateral solute transportation from upslope ultramafic areas.

There were no strong collinearities (table 2.2) between soil chemical and environmental properties.

2.3.3. Soil-vegetation relationships

2.3.3.1. Forest data set

Species density was only correlated with tree cover, which seemed negatively influenced only by altitude. The effects of Ni_{av}, Ca_{av} and Ca/Mg seemed negligible.

The CCA analysis (figure 2.4, table 2.4) showed that the combination of the selected environmental and edaphic properties explained only the 18.32% of the variation of the species distribution, while the rest was due to the disorder typical of ecological systems (table 2.5). Despite the low statistical significance of all the axes after the second, according to the ANOVA the model was significant (p-value<0.01, data not shown).

The variables most strongly related with the first axis (which explained the 4.6% of the total variance) were altitude and tree cover. The ones most strongly related with the second axis (which explained the 3.1% of the total variance) were edaphic properties related with substrate (pH values, Ni_{av} and Ca_{av}), followed by drainage and the Ca/Mg ratio. This was shown by the length of the vectors in the biplot (Ter Braak 1987). It is important to remember that Ca_{av} and pH values were the highest in certain serpentinite soils rich in $Ni_{av.}$

When considering only one factor each time, it is immediately possible to see how much of each edaphic and environmental property explained the variance in the vegetation data (table 2.6). The results were similar to the ones shown above.

The low variance-explaining strength of environmental and soil properties have often been found: for example in Mediterranean habitats in central Italy (Chiarucci et al. 2001). It could be related with a weak differentiation between species composition or the omission of more important environmental properties (i.e., rocks outcrops, screes, bare soil, etc.). Edaphic properties alone explained only 11.89% of the total variance of species-environment relationship in the study area (data not shown).

2.3.3.2. Alpine data set

Species density was not significantly correlated with any edaphic properties, and depended negatively on altitude, drainage and cryoturbation. Vegetation cover was negatively, not significantly correlated with serpentinite content in the parent material and with Ni_{av}, and it was better correlated with environmental factors and soil pH.

The combination of the selected environmental and edaphic properties explained the 21% of the variation of the species distribution (CCA analysis, table 2.4) while 79% was due to the disorder typical of ecological systems (table 2.5). The most strongly related variables with the two main ordination axes were Ni_{av}, altitude, slope, drainage, aspect (the first had longer

arrows; Ter Braak 1987). The axes were always statistically significant (P value < 0.001). The same situation was shown when CCA was applied to each factor alone (table 2.6).
The species scores on the ordination axes and their relationships with the environmental factors verified the previously described situation (par. 4.1.2, not shown).

2.3.4. Notes on some species

GLMs and CART, applied to some serpentiniculous, or shrub and tree species showed similar and interesting results:

- *Carex fimbriata* (table 2.8) is a serpentine endemic species. In the forests, it was mostly related with low values of the Ca/Mg ratio; this verified the high tolerance of this species to high Mg. Above the treeline (fig. 2.5a) it seemed well correlated with high levels of heavy metals;
- *Thlaspi sylvium* (fig. 2.5b), *Cardamine plumieri* (both serpentine endemic), and *Biscutella laevigata* were strongly related with Ni_{av} according to both GLM (table 2.8) and tree classifier. *C. plumieri* was also related with high pH values. *B. laevigata* is not a strictly serpentiniculous species (Pignatti, 1992), but in the study area it was present only on serpentinite-dominated parent material (local indicator species, according to Kruckeberg 1992);
- *Thlaspi rotundifolium* subsp. *corymbosum* was similarly related to high Ni_{av}, high pH and low Ca/Mg, reflecting the typical conditions of high altitude serpentine soils;
- *Silene vulgaris* grows on different soils in Mont Avic Natural Park, but on "extreme" serpentine soils it assumes a different form (smaller dimension, thicker and blue-violet coloured leaves). This form seems well correlated with available metals (data not shown);
- *Carex sempervirens* (an euriphilous, mainly basiphilous species) and *Luzula lutea* (acidophilous species associated with *Carex curvula*) were preferentially distributed on serpentinite in the study area and were mainly related with low Ca/Mg values, while Ni_{av} did not influence their distribution;
- *Carex curvula* (fig. 2.5c, table 2.8) and *Luzula spicata*, common alpine species excluded on serpentinite, were negatively related with pH and Ni_{av}.

The two methods gave contrasting results when applied to ericaceous shrubs. For example:

- *Rhododendron ferrugineum,* according to the GLM method seemed favoured by north-facing aspects and high Ca/Mg ratio. According to the tree classifier, the most favourable factor seemed to be low soil Ni.
- *Vaccinium myrtillus* was related mostly with altitude according to the tree classifier (best altitude between 1400 and 1940 m), while, according to the GLM, Ca/Mg ratio, drainage and aspect were the most important.

2.4. Discussion

2.4.1. Forest habitats

Forest soils on serpentinite in temperate and cold areas are usually characterized by a strong Ca leaching, a mull humus type, clay illuviation which creates an argillic Bt horizon (Chardot et al. 2007). In the study area, the processes influencing forest soil evolution are different from the former ones. In fact, Ca is normally concentrated in the most developed soils, while Mg is invariably leached away. Ca is particularly stored in organic matter and root-rich horizons because of biocycling, and it is leached with Mg only in sub-surface horizons of podzolic soils. The humus is of mor or moder types. Metals are not concentrated in B horizons because of weathering, but because of cheluviation by organic acids, otherwise they are leached away from the profile. No clay textured horizons develop. The podzolization process is active on every substrate, also on base-rich serpentinites, particularly under subalpine *Pinus uncinata* and Larch forest, mainly on north-facing slopes, even if ultramafic substrates should inhibit this process worldwide (Alexander et al. 1994, Lundström et al. 2000, Verger et al. 1993). Only seldom podzolic soils have been found on ultramafic parent materials in the world (Bulmer and Lavkulich 1994, Nakata and Kojima 1987, Ragg and Ball 1964, Roberts 1992, Sirois and Grandtner 1992). The soil acidification in Mont Avic Natural Park is stronger and deeper than in the podzolic soils shown elsewhere on serpentinite. Strangely, in nearby valleys, Verger (1987) describes subalpine soils on serpentinite with pH values increasing from 5 to 7 down to the bottom of the profiles, high base status and low total acidity.

The inverse relationship between pH and Ni_{av} is due to increased leaching at decreasing pH values (as shown also by Chardot et al. 2007). An opposite trend has often been observed (Chiarucci et al. 1998, Robinson et al. 1996): this difference can be related with different climates. For instance, the dryer and warmer Mediterranean climate (Chiarucci et al. 1998) inhibits metal leaching.

The extreme concentrations of Ni_{av} were found where the soil development was inhibited by extremely steep slopes (rock crevices) or where water-soluble cations were brought in by floods, on stream banks. An accumulation of labile fraction of Ni due to solute transportation was hypothesized by Lee et al. (2001): solute Ni was fixed by the exchange complex of soils close to riverbanks, or it precipitated during dry periods, when oxidizing conditions were met. The Ni_{av} values observed in these environments were extremely high, and their strong ecological effect on plant life was verified by all the statistical methods applied.

However, the acidophilous forest vegetation depends mostly on altitude, tree cover and aspect, and it is strictly correlated with extremely acid soils (typical *Vaccinietum*). Differently from what usually occurs on similar ultramafic and mafic substrates (Brooks, 1987, Verger, 1987 and Verger et al., 1993), in the study area basophilous species and communities are absent. This is probably due to the podzolization process and to the seasonal waterlogging at snowmelt, which “smooth” the negative properties of serpentine soils by leaching the excessive Mg and Ni. Soil chemistry verifies this situation: available Ni, Mg and Ca inversely depend on the soil development degree, which, in turn, is related with humidity and stable forest cover. A similarly inverse correlation between soil development and “serpentine syndrome” on plant communities was shown by Alexander (1988), on ultramafic substrates in the Klamath Mountains in northern California, under a humid sub-Mediterranean climate (somehow similar to the climate of the studied montane Scotch pine forests). The higher forest productivity on ancient, well-developed soils was due to the progressive leaching of toxic Ni, Co and Mg, which leads to the development of soils similar to nearby ones on different substrates. Similarly, in coniferous forests in the Pacific Northwest, humidity and soil depth smooth the serpentine properties (del Moral 1982).

In the study area, differences in plant community composition are seldom visible. “Serpentine” communities grow only in particular locations, while serpentine endemic or indicator species (*Thlaspi sylvium, Biscutella laevigata, Carex fimbriata*) are often found where Ni_{av} is high (above 5-10 ppm) in the surface horizon, irrespective of other edaphic or environmental properties. The effect of the Ca/Mg ratio is weak, as this value is usually very high also under serpentine vegetation. Comparing similarly “unstable” or “disturbed” plant communities on serpentinite and gabbro, great differences were found, owing to the presence of the serpentiniculous species. However, Ni effect seems positive on these species, and there are no signs of toxicity for the others (no species growing on gabbro are excluded or significantly inhibited on serpentinite). This is different from what happens in New Zealand mountain habitats (Robinson et al. 1996), where acidification leads to enhanced Ni bioavailability and toxicity, with the disappearance of non-adapted tree species.

The dry, south-facing slopes frequently support plant communities clustered together with humid, “extreme” serpentine plots (steep, wet rocky outcrops and riverbeds), rich in endemic and in xerophilous species. In particular, south-facing plots support xerophilous associations because of climatic constraints, as well as some serpentine species because of Mg and Ni abundance in semi-primitive soils. Analogously, wet crevices in rocky outcrops and riverbeds support similar communities, probably because of "serpentine" constraints (i.e., cation excess).

In agreement with Verger (1990), spruce (*Picea abies*) is nearly absent from the study area, even if it is the dominating subalpine tree in nearby valleys on different substrata. This could be due to Ni and/or Mg toxicity on serpentinite (Kayama et al. 2005, Kràm et al. 1997). The absence of spruce from mafic substrata as well could be due to the small surfaces of the gabbroic outcrops: a perturbation leading to the temporary disappearance of this species from such small surfaces could lead to the colonization by *Pinus uncinata*, dominating the forests of the valley.

2.4.2. Alpine habitats

Above the tree-line, the soil chemistry strictly depends on the parent material. pH values, exchangeable bases and metals increase with altitude: cryoturbation and other periglacial processes bring unweathered materials onto the top of the profiles, where weathering releases ions to the soil. On serpentinite, the low pH values and the quite high Ca/Mg ratios were very different from what usually reported in literature (Roberts 1980, Proctor 1992). Low pH values were sometimes found in alpine soils on serpentinite in Canada, where slow drainage caused severe base leaching and Podzol formation (Sirois and Grandtner 1992). Ni_{av} is extremely high in disturbed sites, up to 1000 times larger than in alpine soils in Spanish ophiolitic areas (Sanchez-Marañon et al. 1999), probably because of the more humid climate which helps a faster weathering of surface material.

Like the soils, the alpine vegetation depends on substrate and on micro-climate (average duration of snow cover and altitude). On calcschists, decarbonatation and acidification, together with high Ca_{av}, influence the acidophilous communities enriched with calcophilous species. On gabbro, the low pH values and low available bases and nutrients are the main edaphic properties involved with the *Curvuletum* development. On serpentinite, the basophilous or neutrophilous communities described in nearby valleys (Verger et al., 1993) have seldom been found, only in heavily cryoturbated and eroded areas. Here, base leaching is inhibited by the surface inputs of fresh material caused by periglacial and erosion movements.

The soil-vegetation relationships are only weakly explained by the selected edaphic and environmental variables (21%): this could be due to the presence of other factors which were not considered, such as surface rock cover (outcrops and screes), soil rock content, hydrography, microclimate and winter snow depth, which deeply influence species and community distribution in high altitude ecosystems (Guisan et al., 1998). These factors were omitted, because they don't create distinctions between plant communities on the different substrata.

Among the edaphic properties, high levels of Ni_{av} and a slightly lower than usual Ca/Mg ratio are the most important factors in determining alpine plant communities on serpentinite. Ni effect is particularly strong in cryoturbated soils, where it is probably the most effective ecological constraint (demonstrated by the high Ni_{av} and Ca/Mg values). Many species are likely excluded from high-Ni serpentine soils (for example, *Carex curvula* and *Luzula spicata*) because of metal toxicity.

Ni-adapted species (*Thlaspi sylvium, Biscutella laevigata*) grow where Ni_{av} is above 20-50 $mg*kg^{-1}$ in alpine soils. The lower Ni_{av} values measured where these species were found in subalpine forests can be due to the low pH values of subalpine soils, which efficiently mobilize Ni, so that its concentration in the soil solution is higher than in less acid alpine soils at similar Ni_{av} values. EDTA-extractable Ni (Ni_{av}), in fact, is probably the "easily bioavailable" fraction and not the "immediately bioavailable" one.

In other boreal habitats no ecological effects of metals have been observed. In Scotland, for example, Spence et al. (1987) and Carter et al. (1987) found no ecological effect of exchangeable Ni, despite its extremely high values found in some sampling plots. Proctor (1992) showed that only in one case Ni toxicity was verified in Great Britain.

Despite the quite similar climate, boreal plant communities on serpentinite are different from alpine ones. Serpentine effect on vegetation is normally visible in coarse, eroded and cryoturbated soils (e.g., Proctor 1992), but in Mont Avic Natural Park some serpentine endemic species (*Carex fimbriata, Thlaspi sylvium, Thlaspi caerulescens*) also grow on well developed soils, in closed plant communities. Serpentiniculous species are considered neutrophilous (Richard 1985, Verger 1991), but in the study area they also grow on extremely acid and desaturated soils. This verifies the hypothesis that pH value and base status are not important edaphic actors involved in serpentine species distribution in humid alpine and montane habitats.

Differently from Spence et al. (1987) and Chiarucci et al. (1998), drought is not a key causal factor for alpine plant distribution on serpentinite, nor for enhanced metal toxicity (Chiarucci et al. 2001). Neither does drainage, that is important in Quebec (Sirois and Grandtner 1992), where slow drainage enhances Mg leaching and decreases the serpentine influence on vegetation.

Environmental factors inhibiting soil development (erosion, cryoturbation, alluvial accumulation of materials) are able to maintain high levels and bioavailability of metals. According to Sirois and Grandtner (1992), these periglacial processes maintain high levels of magnesium.

2.5. Conclusions

In Mont Avic Natural Park, pedogenic processes diverge dramatically from forest to alpine habitats, and this causes a different element availability and a different plant ecology. Montane and subalpine acidophilous plant communities on serpentinite are usually similar to the ones on other substrates, but alpine vegetation strikingly differs on the different substrata, and the so-called serpentine factor gains a great ecological influence.

This factor does not seem to be very important in the studied forest habitats, probably because of the extreme acidification (podzolization is active on all substrates) and leaching, but it is very intense above the treeline. The physical factors (coarse texture, excessive drainage, shallowness, dark colour) can altogether be excluded from the list of important ecological soil properties. In fact, texture is finer than in nearby soils on other rocks, because of the higher weatherability of ultramafic minerals. Drainage and soil thickness are related with the topography of the sites, with erosion, aspect and altitude, and not with substrates. The colour is not darker on serpentinite than on mafic rocks.

Some chemical properties can be excluded as well: for example, low nutrients stock (K and P), because their low concentrations, does not significantly change among different substrates. Because of low pH values and frequent redox oscillations related with snow melt, Fe availability should not be a limiting factor for the vegetation. Available Ca (Ca_{av}) is not lower on serpentinite: actually, particularly in forest soils, the concentration of this element is the highest where serpentine-endemic species grow best.

Differently from what is often stated, the high variance of the Ca/Mg ratio under similar plant communities is an evidence of its low impact on plant ecology. In the forests, potentially available Ni is likely the most important ecological factor involved in community differentiation among the different substrates, which consists in the presence of a few metal-adapted species on serpentinite. Above the treeline, Ni is related with the lower plant cover and the different species composition.

The effect of metals is particularly intense where pedogenetic development is inhibited by disturbances (erosion, deposition and cryoturbation), that help the maintenance of possibly toxic concentration of heavy metals in surface horizons.

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Fig. 2.1: average linkage cluster (Bray-Curtis distance) of the forest (left) and alpine vegetation (right).

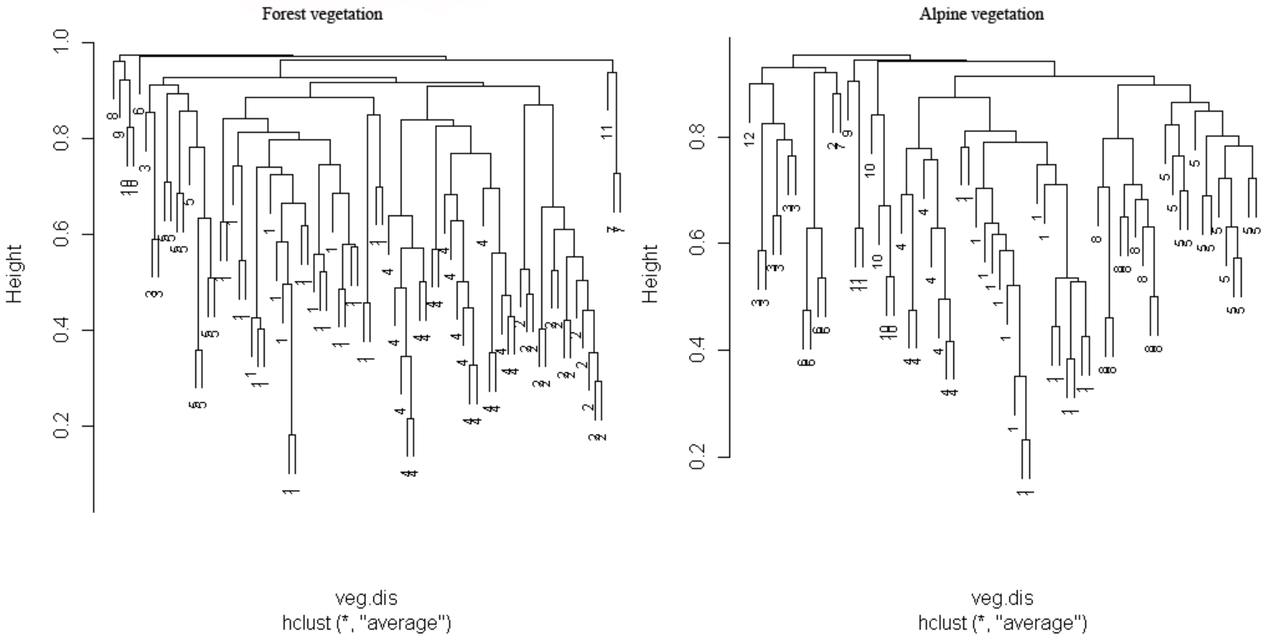


Fig. 2.2: NMDS ordination of forest (left) and alpine plant communities; the numbers represent the clusters.

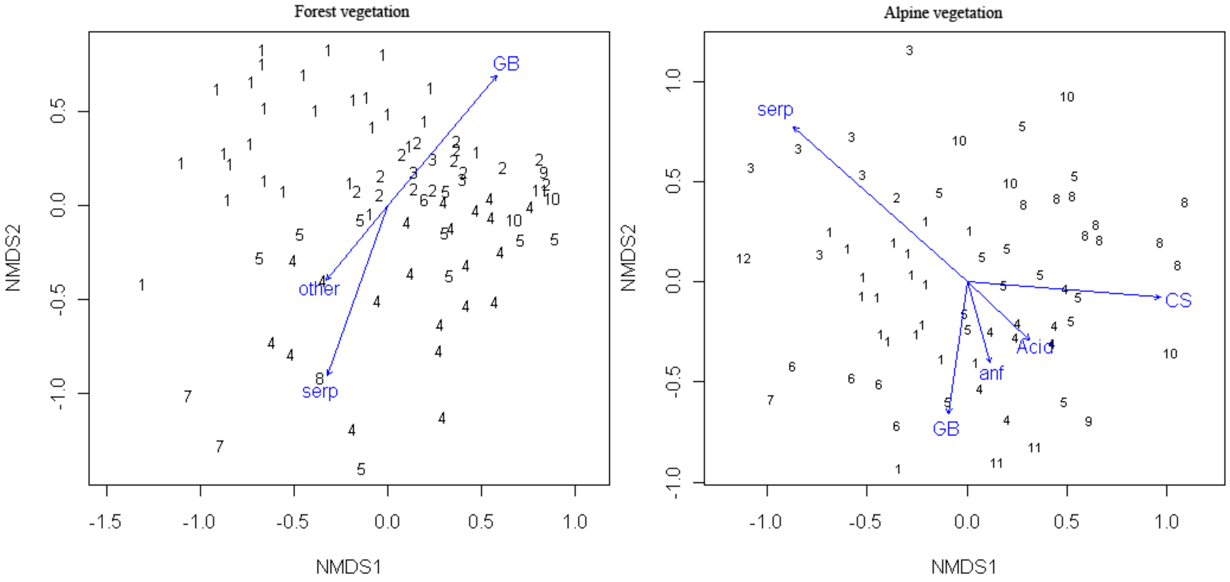


Fig. 2.3: variance of Ni_{av} (left) and Ca_{av} (right) in the alpine soils, formed on substrates with different serpentinite content (%, x axis).

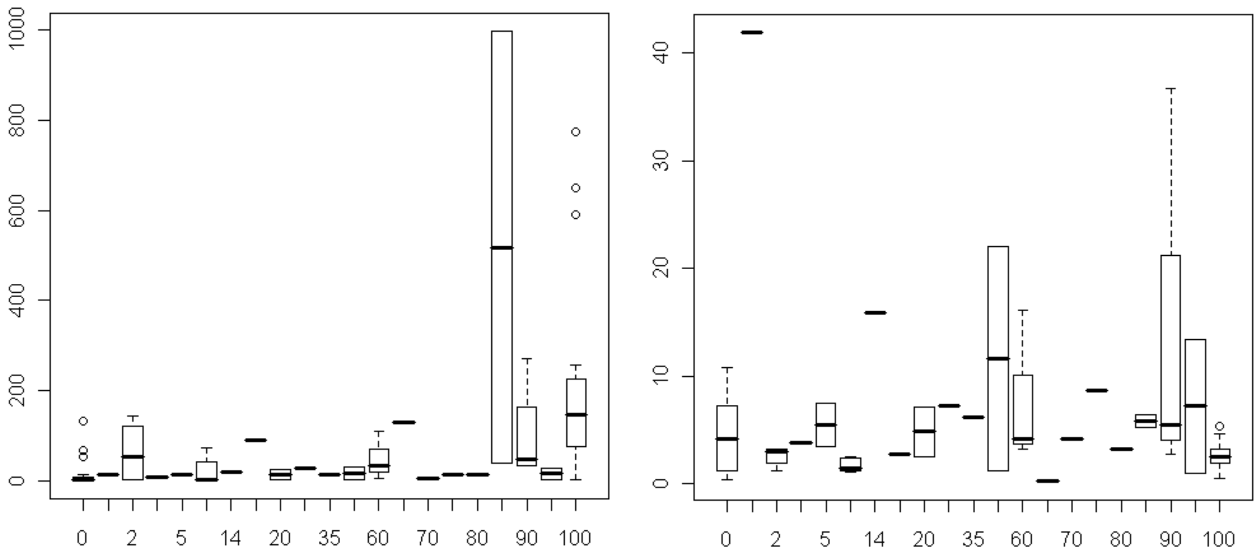


Fig. 2.4: CCA biplot of forest and alpine habitats.

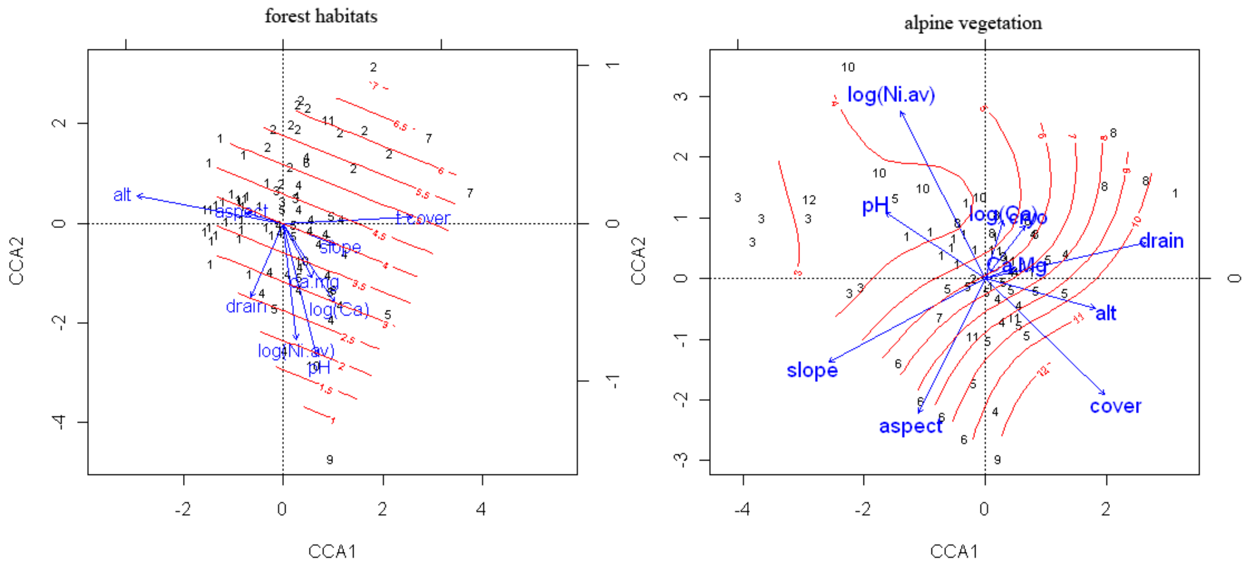
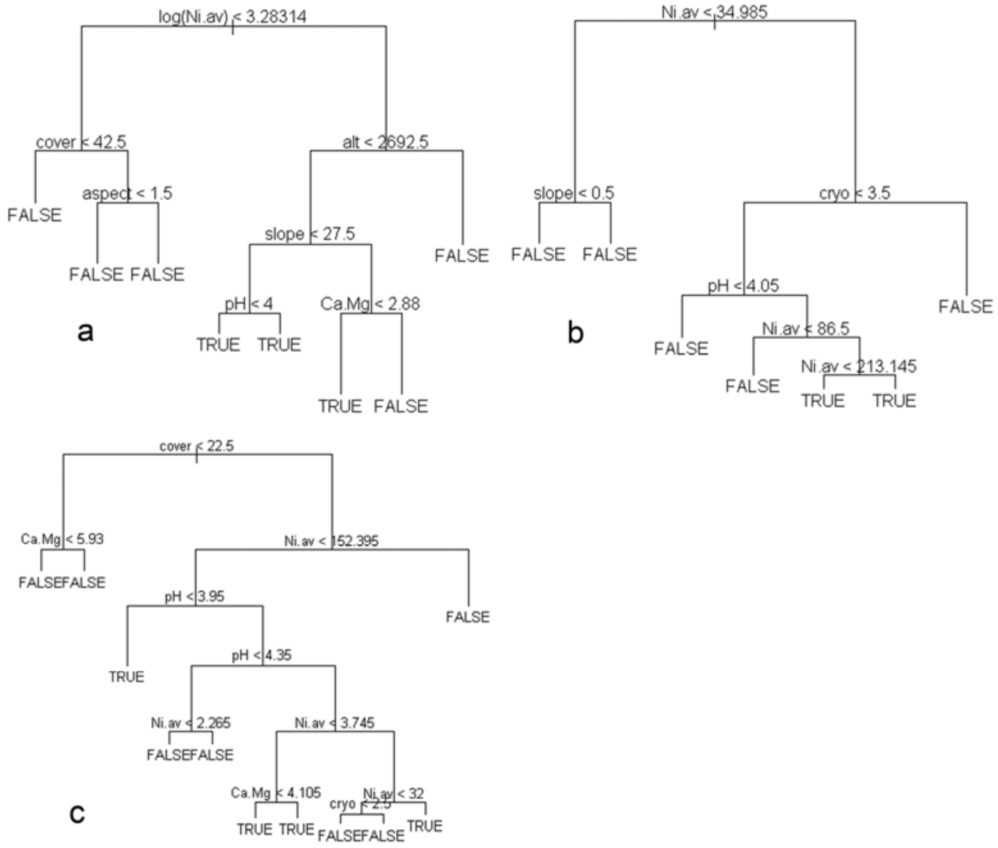


Fig. 2.5: tree classifier graphs explaining the distribution of Carex fimbriata (a), Thlaspi sylvium (b) and Carex curvula (c) in alpine habitats.



Tab. 2.1: correlation matrix between environmental and edaphic properties in the forest soils; significant values are underlined (p-value < 0.05).

	pH	*Alt*	*aspect*	*Ca/Mg*	*Ca*	*Ni_{av}*	*drain*
pH	1.00						
alt	-0.27	1.00					
aspect	0.10	0.23	1.00				
Ca/Mg	0.26	-0.07	0.03	1.00			
Ca	0.49	-0.25	0.04	$\underline{0.60}$	1.00		
Ni_{av}	$\underline{0.59}$	-0.13	-0.07	0.43	$\underline{0.67}$	1.00	
drain	0.16	-0.14	0.02	0.10	-0.03	0.10	1.00
slope	0.20	-0.24	0.08	0.37	0.35	0.34	0.04

Table 2.2: soil and environmental properties correlation table; significant values are underlined (p-value < 0.05).

	pH	*Ca/Mg*	*Ca*	*alt*	*slope*	*cover*	*cryo*	*drain*	*aspect*	*Ni_{av}*
pH	1.00									
Ca/Mg	$\underline{0.43}$	1.00								
Ca	$\underline{0.37}$	$\underline{0.48}$	1.00							
alt	0.06	$\underline{0.32}$	0.09	1.00						
slope	$\underline{0.36}$	0.03	0.07	-0.04	1.00					
cover	$\underline{-0.35}$	-0.05	0.24	-0.02	-0.25	1.00				
cryo	0.24	$\underline{0.28}$	0.10	$\underline{0.52}$	-0.10	$\underline{-0.45}$	1.00			
drain	-0.05	$\underline{0.27}$	0.14	$\underline{0.35}$	$\underline{-0.34}$	0.26	0.24	1.00		
aspect	-0.18	$\underline{-0.35}$	$\underline{-0.29}$	-0.11	0.19	0.07	-0.11	-0.19	1.00	
Ni_{av}	0.13	-0.10	0.02	$\underline{-0.30}$	0.16	-0.17	-0.14	-0.12	0.10	1.00

Table 2.3: correlation table between soil and environmental features and biodiversity indexes; some variables are not shown. Underlined values are significant (p-value<0.05).

Forests	*pH*	*alt*	*aspect*	*Ni.av*	*Tree cover*	*Ca/Mg*	*Ca*	*slope*	*drain*	*Substr.*
Tree cover	-0.01	-0.61	-0.09	-0.09	1.00	-0.05	0.07	0.19	0.03	0.21
Species density	0.09	0.46	0.21	0.05	-0.51	-0.07	0.00	-0.27	-0.15	-0.06

*Table 2.4: the canonical scores of the environmental factors and the eigenvalues of the first 3 canonical axes. *: significant (p value < 0.01)*

Forest habitats		*CCA1*	*CCA2*	*CCA3*
	eigenvalue	0.55	0.37	0.32
	Scores			
	pH*	0.27	-0.81	0.05
	Altitude*	-0.92	0.12	-0.12
	Tree cover*	0.82	0.10	0.06
	Ni	0.14	-0.73	-0.06
	Ca/Mg	0.22	-0.36	0.01
	Drainage*	-0.14	-0.36	0.59
	Aspect	-0.20	0.13	0.37
	Ca	0.28	-0.54	-0.02
	Slope	0.30	-0.06	0.70
Alpine habitats	Eigenvalue	0.18	0.17	0.15
	Scores			
	pH*	-0.40	0.27	0.53
	Alt*	0.44	-0.12	0.81
	Slope*	-0.63	-0.34	0.27
	Ni*	-0.34	0.67	-0.22
	Ca	0.07	0.23	0.29
	Cryo	0.16	0.21	0.48
	Ca.Mg	0.12	0.05	0.42
	Drain*	0.65	0.14	0.03
	Aspect	-0.27	-0.54	-0.08
	Cover	0.48	-0.47	-0.21

Table 2.5: total, constrained and unconstrained inertia in the data.

		Inertia	Proportion
Forest habitats	Total	12.00	1.00
	Constrained	2.20	0.183
	Unconstrained	9.80	0.817
Alpine habitats	Total	12.74	1.00
	Constrained	2.68	0.21
	Unconstrained	10.06	0.79

Table 2.6: the constrained proportion of the canonical axe when applying only one factor each time.

Forest habitats	*Constrained*	*Variance explained (%)*	*Total*
Altitude	0.54	4.00	13.51
Tree cover	0.45	3.33	
pH	0.31	2.29	
Slope	0.29	2.15	
Ni$_{av}$	0.27	2.00	
Ca	0.26	1.93	
Drainage	0.26	1.93	
Aspect	0.23	1.70	
Ca/Mg	0.19	1.40	
Alpine habitats			
Altitude	0.40	3.14	12.74
Plant cover	0.34	2.67	
pH	0.36	2.82	
Slope	0.36	2.82	
Ni$_{av}$	0.34	2.64	
Ca	0.20	1.57	
Drainage	0.38	2.98	
Aspect	0.29	2.28	
Ca/Mg	0.25	1.96	
Cryoturbation	0.25	1.96	

Table 2.7: correlation table between soil and environmental features and biodiversity indexes in alpine habitats. Some variables are not shown. "Spec" is "species density". No significant (p-value<0.05) were found.

	pH	*Ca/Mg*	*Ca*	*Alt*	*Slope*	*Cryo*	*Drain*
cover	-0.35	-0.07	0.22	-0.04	-0.24	-0.46	0.25
Spec	-0.03	0.02	0.32	-0.03	0.02	-0.11	-0.10
	Drain	Aspect	Niav	Serp	GB	Anf	CS
cover	0.25	0.07	-0.20	-0.27	0.15	0.16	0.10
Spec	-0.10	0.26	0.03	0.02	-0.05	0.05	0.00

Tab. 2.8: GLM coefficients between Carex fimbriata and soil and environmental properties, in alpine habitats. Underlined values are significant at p-value < 0.05.

	Carex fimbriata	*Thlaspi sylvium*	*Carex curvula*
Intercept	7.38	96.45	-10.19
pH	0.07	-0.40	$\underline{-3.06}$
Log(Alt).	-0.00	-13.96	0.01
Log(Ni.av)	$\underline{0.27}$	$\underline{1.28}$	$\underline{-1.77}$
Log(Ca)	$\underline{-0.23}$	0.69	-0.02
Plant cover	-0.01	0.01	0.10
Ca/Mg	0.00	-0.10	-0.00
Drain.	-0.70	0.99	0.01
Aspect	0.09	0.42	-2.55
Slope	0.05	0.06	0.01

3. Podzolization over ophiolitic materials

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Abstract

Soil surveys carried out on ophiolitic rocks and till under subalpine forest in the Natural Park of Mont Avic (Aosta Valley, West Italian Alps) revealed the unexpected occurrence of soils showing a horizon set typical of the podzols. Podzolization is uncommon on mafic and ultramafic substrata: the translocation of organometallic compounds in soils developed from such parent materials slows down considerably due to the high Fe and Mg contents, the high base saturation and the close to neutral pH.

In order to determine the real origin and evolution of such soils, 6 pedons, selected among 83 profiles with a similar "podzol" morphology, were sampled and analyzed. Chemical, mineralogical, and petrographic analyses of the sampled soils and parent materials were performed, and correlation analysis of the obtained data was carried out.

Results show that, in favourable environmental conditions (mainly climate and vegetation), even mafic and ultramafic parent materials can undergo different degrees of podzolization. Due to the adopted diagnostic criteria the most common classification systems (particularly the WRB) do not allow satisfactory taxonomic arrangement of such soils.

3.1. Introduction

Two main processes are currently claimed in order to explain the podzolization: the first one is the formation and illuviation of organic acids complexed with Al and Fe; the second one is the weathering of silicates followed by a downward transport of Al and Si as colloidal inorganic solutions (Lundström et al., 2000). Podzolization is a typical pedogenic process mostly acting on acidic and silicate rocks under subalpine coniferous forests or ericaceous shrubs in cold, humid climates. On the contrary, this process is somewhat inhibited over easily weatherable mafic and ultramafic parent materials (Lundström et al., 2000) due to the high base status, high siderophile content (Souchier, 1984) and neutral pH. In general, these chemical factors slow down podzolization considerably, even when climate and vegetation favour the process.

Few studies have been dedicated to soils developed on ultramafic materials under subalpine vegetation at middle and high latitudes (Sasaki et al., 1968; Sticher et al., 1975; Verger, 1990; Bulmer et al., 1992; Verger et al., 1993; Alexander et al., 1994a,b; Bulmer and Lavkulich, 1994; Gasser et al., 1994; Verger, 1995), whereas many works have focused on "serpentine soils" in tropical areas.

There are only a few reports of podzolic soils developed from serpentinite; moreover, according to the most widespread taxonomic systems, such as the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006) (hereafter WRB) and Soil Taxonomy (Soil Survey Staff, 1999, 2006) (hereafter ST), none of these soils can be classified as Podzols or Spodosols. Alexander et al. (1994a,b) describe soils on ultramafic till in Alaska as having an E horizon but a pHN6 in the Bs horizons, which is inconsistent with that of Spodosols. Bulmer and Lavkulich (1994) report that a soil developed from ultramafic materials in Canada has a spodic Bf horizon (Expert Committee on Soil Science. Agriculture Canada Research Branch, 1987), but lacks the E horizon and has a rather high pH (5.7). A similar soil profile was observed by Ragg and Ball (1964) on the Scottish island of Rhum. Soils with a podzol-like morphology (a bleached E horizon overlying a reddish-brown Bs) described by Gasser et al. (1994) in Switzerland show lithological discontinuity between the wind-driven material from which the E horizon formed and the Bs derived from serpentinite debris. The same profile was previously described by Sticher et al. (1975). The high quartz content (15%) in the eluvial horizon was ascribed to the presence of aeolian material. Sasaki et al. (1968) found a podzol-like soil on serpentinite in Northern Japan: they conclude that podzolization is active, but the pH value (6.5) is higher than the one typical of podzolic soils. Verger (1990, 1995) and Verger et al. (1993) compared soils developed on serpentinite and on mafic and acid rocks in the western Italian Alps. They concluded that podzolization is impossible on ultramafic parent materials, which usually give rise to Eutric or Dystric Cambisols in the most humid sites at the subalpine vegetation stage.

Recent surveys (D'Amico, 2003, 2006) carried out in the ophiolitic area of the Mont Avic Natural Park (Aosta Valley, Italy) on soils, vegetation and landscapes found soils showing a podzol-like morphology (Fig. 1) at the subalpine altitudinal level, on stable, northward slopes. The aim of the present work is, therefore, to verify the lithological ultramafic composition of the parent material, and to investigate in depth the pedogenic process going on such substrates. 6 pedons, representing the lithological variability and selected among 94 previously studied profiles, were described, analyzed from a chemical and a mineralogical point of view, and classified according to the most used taxonomic systems.

3.2. Physiographic outlines of the study area

The six selected pedons are located on the north-facing slope of the Chalamy Valley. The description of the study area is in chapter 1.

Glacial till, composed of mafic and ultramafic rocks in different amounts, is the parent material of the examined soils.

The main environmental characteristics of the 6 sites are summarized in Table 3.1.

The forest is dominated by Pinus uncinata and Larix decidua, and the understory vegetation by ericaceous shrubs such as *Rhododendron ferrugineum*, *Vaccinium uliginosum*, *V. myrtillus*, *Loiseleuria procumbens* and *Empetrum nigrum ssp. hermaphroditum*. The strictly serpentinicolous sedge *Carex fimbriata* is common on serpentinite and ultramafic till (pedons 3, 4, 5, 6).

Hygrophilous species such as *Trichophorum caespitosum*, *Pinguicola leptoceras* and *Tofieldia calyculata* grow where drainage is poor or somewhat poor (P3, P6).

3.3. Materials and methods

3.3.1. Soil description and sampling

Field description of soil profiles was done according to FAO (2006). The suffixes applied to the organic horizons are taken from Référentiel Pédologique (hereon RP) (INRA-AFES, 1995; Baize and Girard, 1998).

Approximately 1 kg of soil material was collected from every mineral horizon in the 6 soil pits; rock fragments were preserved in order to qualitatively and quantitatively determine their lithology.

Undisturbed samples are taken from each horizon and later observed with a binocular microscope (40×) in order to verify the existence and the structure of the coatings.

3.3.2. Laboratory analyses: soil chemistry and spodic properties

The textural and chemical laboratory analyses of soils were performed according to the guidelines of the manual of Ministero delle Politiche Agricole e Forestali (2000), unless otherwise indicated.

All the samples were air-dried and sieved to separate the fine earth (b2 mm) from the coarse fraction. The pH in water and in KCl (soil: solution=1:2.5), total organic carbon (Walkley and Black method), CEC by BaCl2 extraction (pH 8.2), available base content and saturation (BaCl2 extraction and analysis by flame atomic absorption spectrometer), 5 fractions particle size distribution, and total acidity ($BaCl_2$ extraction and titration) were determined. In order to determine the spodic properties, the oxalate, pyrophosphate and dithionite-extractable fractions

of Fe, Al and Si were measured. Clarification of the extracts by adding polyacrylamide prior to centrifugation (8000 rpm, 8 min) was used (Schuppli et al., 1983). The optical density of the oxalate extract at 430 nm (ODOE) (Stützer, 1999; Mokma et al., 2004) was also measured.
The following assumptions were made:
- Acid ammonium oxalate readily extracts the active, the short range-order or amorphous Fe, Al and Si oxy-hydroxides (IUSS Working Group WRB, 2006) and some of their organic-bound forms (Jeanroy et al., 1984). Oxalate-extractable Fe, Al and Si (Fe_o, Al_o, and Si_o) are presently considered the best chemical indicators of the podzolization process, and are adopted by some of the main taxonomic systems, such as ST, WRB, and RP.
- Na-pyrophosphate can be used to dissolve amorphous Fe and Al oxyhydroxides bound to organic matter (metallo-organic compounds); this method is presently required by the Canadian System of Soil Classification (Expert Committee on Soil Science, 1987). Pyrophosphate can dissolve some poorly crystalline Fe oxides, such as fine grained goethite and ferrihydrite (Parfitt and Childs, 1988).
- Sodium citrate-dithionite dissolves all the pedogenic “free” oxides, except some organic-bound materials (Jeanroy et al., 1984); there is uncertainty as to whether it can dissolve part of the lithogenic magnetite (Van Oorschot and Dekkers, 1999).

3.3.3. Laboratory analyses: soil mineralogy and parent material

The total elemental composition of bulk soil samples and of some unweathered rock fragments was measured by X-Ray Fluorimetry (XRF). The mineralogy of the different parent rocks was studied in thin section and by X-Ray Diffractometry (XRD) on oriented slides. The bulk mineralogy of the coarse and fine sand fractions was analyzed by powder XRD (using Cu radiation from 2° to 80° 2θ) after dissolution of the pedogenic oxides in dithionite. Magnetite was observed using hand magnets.
All skeletal grains (clasts larger than 0.5 cm) from every horizon: clasts were cleaned (using a hexametaphosphate solution), separated according to their lithology, and weighted. The lithological composition of the skeleton belonging to little weathered C and Bs horizons was assumed to be similar to that of the parent material.

3.4. Results and discussion

3.4.1. Parent material

The parent material of the six pedons can be divided into three main groups (Table 3.2):
- P136, P1 and P65 developed from glacial till composed of serpentinite and metagabbros, amphibolites, prasinites and chlorite schists;
- P135 and P133 are mainly composed of serpentinite with traces of prasinites, amphibolites and chlorite schists;
- P134 mainly consists of serpentinite till lying on a hard, unweathered serpentinite bedrock.

The chemical composition of the investigated rocks (determined by XRF) is summarized in Table 3.
The mineralogical composition of the studied rocks is as follows:
- serpentinite is composed of serpentine minerals (antigorite and traces of chrysotile in fissures) associated with magnetite (up to 4% in volume);
- plagioclase (albite), amphiboles (glaucophane, actinolite and some tremolite), chlorite, and traces of garnet and phlogopite are the components of metagabbros and prasinites;
- amphibolite consists of glaucophane, actinolite and some tremolite, associated with chlorite and small quantities of garnet and plagioclase;
- chlorite schist is almost completely composed of chlorite.

Although talc, quartz and orthoclase were not observed in the parent materials, their presence cannot be excluded. Traces of muscovite can originate from small calc-schist outcrops. Quartz crystals have been observed occasionally in blocks of metagabbros.

The sandy textural fraction shows a similar lithological composition (Table 3.4); only the E horizons are highly enriched in probably residual quartz (up to 25% of the bulk mineralogy). Aeolian inputs in the upper horizons are scarce; in any case their effect on pedogenesis is negligible. Quartz is the only felsic mineral; muscovite and feldspars, which usually coexist with quartz in felsic rocks and are resistant to chemical weathering, are nearly absent.

These data, together with the bulk elemental composition, attest the local origin of the parent glacial till, being the Chalamy hydrographic basin composed only of ophiolitic rocks.

3.4.2. Morphological and physical properties of soil profiles

As can be seen in Table 3.5, the six pedons show some typical features of podzolic soils; i.e. thick, bleached and greyish E horizons sometimes enriched in soluble organic matter (EA or AE horizons).

The texture of these horizons ranges from sandy loam on mafic dominated till to loamy in soils over serpentinite. As expected, the clay content is slightly lower than in the overlying and underlying horizons. Their structure is platy (P136, P135, P133 and P134), absent (P1) or massive, secondarily platy (P65). The platy structure is typical of podzolic soils with fine texture (Dambrine, 1987), a characteristic of soils formed from easily weatherable ultramafic (and, to a lesser extent, mafic) materials (Verger et al., 1993): the high silt content favours the formation of the platy structure under the action of winter frost and snow melt (Dambrine, 1987). The absence of structure in the E horizon of P1 could be due to the loamy–sandy texture.

The high silt content in these horizons is related to the high weathering rate of the coarser particles, which are generally scarce and highly weathered, as the lithorelics completely transformed into silty aggregates testify.

The low stoniness of the surface horizons can only be ascribed to the high degree of weathering, since there are no lithological discontinuities within the profiles and aeolian inputs are negligible.

True A horizons, lacking in structure and showing only an incipient formation of organo-mineral complexes, lie above P65 and P135. They are the so-called “de juxtaposition” horizons according to RP: these are poorly structured horizons with a clear juxtaposition between dark organic matter and clear, pale mineral particles, characterized by a low biological activity, with no significant earthworms activity.

The underlying Bs and BC horizons are less weathered (high stone content, more abundant sandy fractions, coarser texture, weak structure development) and their morphology differs considerably among the examined profiles. In particular:

- P136 and P1 have well developed reddish-brown Bs horizons. Bsm and Cm horizons in P1 are cemented by illuvial silica and iron for a depth of over 20 cm. The structure of Bs horizons in P136 and P1 is subangular.
- The Bsg horizon in P65 has bluish mottles due to waterlogging; it has a strong orange colour and several reddish coatings on the upper faces of the weakly developed peds and rock fragments. The microstructure of the coatings shows crenulation typical of the illuviation of metallo-organic compounds, evidencing podzolization.
- Bs1 in P135 and Bs in P134 are much more reddish than the overlying bleached horizons; however, the colour does not always reach the required limits of WRB and ST, probably owing to the abundance of bluish and greenish sand grains and rock fragments; silty reddish coatings are visible on rock fragments and peds.
- Bs2 in P135 is mainly composed of rock fragments (85%) covered by thick reddish illuvial silt coatings. The structure is absent due to excessive stoniness.

- BC in P133 contains weakly developed morphological features of illuviation of metallo-organic compounds (crenulated brownish coatings); the structure is extremely weak and granular.

3.4.3. Humus forms

According to RP, the OH-E (AE) sequence of horizons found in P136, P1, P133 and P134 is typical of mor humus forms, while the "de juxtaposition" A horizons of P65 and P135 are typical of the moder. The extremely low pH fits these definitions. The mor forms are atypical, as the highly decomposed OH horizons do not show the typical mycogenic matted structure.

3.4.4. Chemical properties

The 6 examined profiles are strongly acidified at all depths (Table 3.6): the pH increases with depth, as expected, but the highest pH (measured in water) is only 5.7 in a weakly weathered C horizon (P136). In contrast to previous findings on podzolic soils developed from ultramafic parent materials (Alexander et al., 1994a; Bulmer and Lavkulich, 1994), the Bs and BC horizons are strongly acidic. The lowest pH values are found in the surface horizons enriched in organic acids released by the decomposition of organic matter (Burt and Alexander, 1996). Despite the serpentintic parent material, extreme acidity values occur in P1 surface mineral horizons and throughout P134. Base saturation is always low, except in the deep horizons of P133,where, in spite of the low pH, it is greater than 50%.
The total exchangeable acidity (H^+, Al^{3+}) is well correlated with iron oxyhydroxides and organic carbon contents (highest values at the surface and in the Bs horizons).
The total organic carbon content is sometimes higher in the root-poor C horizons than in the overlying Bs or BC (P136 and P133): this is unusual in podzolic soils, as the highest values should be found in the illuvial horizons closest to the surface. Similar trends were found by Remaury et al. (2002) under *P. uncinata* in the French Pyrenees. The total organic carbon content (TOC) is higher in some strongly bleached E than in Bs horizons (i.e., P134); this may be due to fine roots accidentally included in the samples.
The Ca/Mg ratio is an ecologically meaningful index, also because a high Mg content is considered to be phytotoxic (Brooks, 1987). This index is around or below 1 on parent materials dominated by serpentinite (P136, P65, P135, P133, and P134), while it is higher on till dominated by metagabbro (P1). Organic matter-rich horizons have higher Ca amounts due to its accumulation through biocycling, while Mg is easily leached away (Lee et al., 2001).

3.4.5. Bulk chemical composition

The six pedons have the typical bulk chemical composition (Table 3.7) of soils developed from mafic and ultramafic materials:
- the silica content is low (N50% only in the most weathered and developed E horizons);
- the Al_2O_3 content and vertical translocation are highest in the soil on gabbros (P1); at all depths the soils on serpentinite are strongly enriched in Al_2O_3 with respect to the parent material, and this
element seems to be slightly mobile within the profile, as it is present in similar amounts within every horizon, probably related with residual chlorite, less weatherable than serpentine minerals;
- Fe_2O_3, MnO, and Ni contents are very high in all horizons, especially on serpentinite (despite the strong variability among soils on similar parent materials); these metals are highly mobile in acidic conditions and easily translocate from the E to the underlying Bs horizons; Cr shows the same trend, evidencing a particularly strong leaching due to podzolization. This behavior is

unusual, since chromium as a rule is residually concentrated in the most weathered pedogenic horizons also in subalpine and alpine soils on ophiolitic substrates, and decreases constantly with depth (Roberts, 1980; Bulmer and Lavkulich, 1994); this happens also as a consequence of the high resistance to weathering of Cr-bearing spinels (chromite and magnetite).
- CaO and MgO are easily leached away from soil horizons (large relative increase from the top to the bottom of the profile);
- Na_2O and K_2O are concentrated in the most weathered horizons, and can probably be ascribed to resistant residual minerals (amphiboles and plagioclases respectively);
- Cu is highly mobile, and its concentration is well correlated with TOC (data not shown): Cu concentrations are highest in Bs horizons and in C horizons enriched in organic carbon (P136 and P133); copper is also concentrated in soils formed from a till rich in mafic clasts.
- the Ti/Zr ratio increases slightly with depth, likely because of the relative mobility of Ti (Evans, 1980; Aide and Smith-Aide, 2003).

The slight change of the Ti/Zr ratio at different depths indicates the lack of lithological discontinuities within pedons P1, P65, P135 and P134; pedons P136 and P133 may have a discontinuity between the AE-E-Bs or BC horizons rich in serpentinite and the C horizons rich in metagabbro (the Ti/Zr ratio in P136 rises from 88 in the Bs horizon up to 200 in the underlying C); these discontinuities should not have affected the pedogenesis in the uniform overlying material.

3.4.6. Extractable forms of Fe, Al and Si and their meaning (Table 3.8)

The poorly crystalline iron oxides (Fe_o) reach their typical minimum values in the E and C horizons, while their highest values occur in the illuvial Bs and in the organic matter-rich A horizons. The P133 profile is an exception, as Fe_o is lower in BC then in AE (probably because of the high organic matter content in the latter). Its contents are greatest in the Bs horizons of pedons P136 and P1, while they are nearly halved in other profiles. Although Fe_o values are similar in all E horizons, they are slightly higher in P135, probably due to lateral podzolization (Sommer et al., 2000) which draws in amorphous materials from higher parts of the slope.

In profiles P136, P1 and P65, Al_o increases from E to Bs horizons. In contrast, P135, P133 and P134 show no trend. Si_o is an index of silica mobilization caused by weathering of primary minerals; it increases in the illuvial Bs and C horizons of pedons P136, P1 and P65, but not in P135, P133 and P134. The high Si_o content in the cemented horizons of pedon P1 (Bsm, Cm) indicates the siliceous composition of the cement, as shown by Moore (1976) and Alexander et al. (1994a). According to the latter, illuvial amorphous silica in podzolic soils is related with the content of easily weathered mafic minerals in the parent material.

In all samples, Fe_p (Fe oxyhydroxides complexed with organic matter) is higher than Fe_o. The highest values are found in the Bs horizons of pedons P136 and P1 and in organic matter-rich A horizon of pedon P135. Its trend is similar to that of Fe_o. Similar levels, though infrequent, have already been reported in literature (Hseu et al., 2004) and can be ascribed to the solubility of finely subdivided, inorganic Fe oxides (Parfitt and Childs, 1988), to their mostly organic-bound form, and to the dispersion of some clay particles.

The Al_p content is always slightly lower than the Al_o content, and the two show similar trends in profiles. The low mobility of Al and/or its enrichment in serpentine soils is also shown by the absence of an increase in Al_p contents between E and Bs horizons in pedons P135, P133 and P134.

The dithionite-extractable fraction of Fe (Fe_d) (free pedogenic oxyhydroxides) is always greater than Fe_o. Fe_d value is oddly lower than the Fe_p content in the Bs horizons of pedons P136 and P1, perhaps due to the dispersion of small Fe oxide particles (Parfitt and Childs, 1988).

According to Remaury et al. (2002), the crystalline Fe oxides (Fe_d–Fe_o) in Bs horizons are the product of in situ weathering of Fe-bearing primary minerals. In the studied profiles, high Fe_d

values in the Bs horizons are related to large amounts of Fe_{tot}, associated with much lower values in the overlying E and in the underlying C horizons; the hypothesis of the above-mentioned authors therefore does not fit the observed situation in the study area. This trend suggests Fe oxide translocation following the extensive dissolution of Fe-bearing minerals in upper horizons due to the presence of organic acids and to the activity of the podzolization process.

The strong Fe depletion of E horizons and enrichment of the underlying Bs are evident everywhere; this contrast is more marked in the soils over mafic–ultramafic till (P136, P1 and P65) than in those ones on serpentinite (P135, P133 and P134).

In every horizon Fe_d content is higher in the soils with a parent material high in Fe oxides rich ultramafic elements, in agreement with Wang et al. (1989).

The Fe_d/Fe_{tot} ratios indicate that a large part of iron in illuvial Bs horizons is of pedogenic origin.

In all the profiles, the Al_d content is higher in the Bs horizons than in the overlying E horizons; this trend is much more evident in pedons P136, P1 and P65, but its meaning is not clear yet.

The high Si_d content in Bsm and Cm horizons of pedon P1 provides further evidence of the illuvial origin and siliceous composition of the cementing material (opal), as reported by Alexander et al. (1994a).

3.4.7. Spodicity indexes

The various taxonomic systems adopt rather similar chemical indexes to attribute a soil to the podzolic soils taxon, which are generally named Spodosols, Podzols or Podzosols. Table 3.9 reports some common spodicity indexes required for identifying Spodosols/Podzols and calculated on the investigated profiles.

To assign a pedon to the taxon of the podzolic soils, ST and WRB require a minimum value of the $(1/2Fe_o+Al_o)\%$ index in the Bs horizon of 0.50 (%). This limit is only reached in the Bs horizons of pedons P136 and P1, because there is a lack of Al in the other horizons.

According to RP, the combined Alo and Fe_o content in the so-called BP "podzolique" horizon of Podzosols must be greater than the one in A or E horizons. Consequently, all the pedons except P133 may be attributed to Podzosols.

The Fe_o/Fe_d "activity ratio", a relative measure of the crystallinity of free (pedogenic) Fe oxides, is also considered an index of the intensity of the podzolization process. When the process is active the ratio is close to 1; when it is not active the value is lower because of the crystallization that follows organic matter decomposition in old spodic horizons (Stützer, 1999). The value of this index in profiles P136 and P1 (N0.50) differs significantly from that one in the other profiles (b0.30). The low activity ratios in the Bs horizons of pedons P65, P135, P133 and P134 are due to high Fe_d levels. These high levels probably do not originate from in situ weathering of primary minerals: the low level of mineral weathering, the brownish illuvial coatings and the Fe_{tot} content (Table 3.7), which has a maximum in these profiles, are evidence of enrichment in Fe oxyhydroxides. The low activity ratio could be due to seasonal reducing conditions during snowmelt followed by drying and oxidation. Low ratios are typical of podzolic soils developed on Fe-rich parent materials (Nicholson and Moore, 1977; Wang et al., 1989), as well as in Ferrods (Soil Survey Staff, 1975).

Although the ratio in podzolic soils should generally increase from E to Bs horizons (Burt and Alexander, 1996), the 6 pedons show no significant trend with depth.

ODOE values increase from E to Bs horizons (or C, as in the organic matter-enriched C horizon in P133), showing translocation of fulvic acids, but the generally required taxonomic limit (0.25) is reached only in P136 and P1. According to WRB, the 0.5% minimum organic carbon content, required as an alternative to a low ODOE, is exceeded everywhere in the concerned horizons.

3.4.8. Soil classification

According to the considered taxonomic systems, pedons P136 and P1 can be fully classified as Podzols and Spodosols or attributed to Podzosols (Table 3.10).

There are strong discrepancies between morphological features and diagnostic requirements (WRB, ST) of pedons P65, P135, P133 and P134. Consequently, their position in the considered taxonomic systems differs greatly.

The P65 profile has a “de juxtaposition” A horizon with no structure or organo-mineral compounds. The same pedon shows waterlogging features, with many redox mottles in Bsg horizon and in Cg horizon in particular and many silty lithorelics in the grey E horizon. The reddish Bsg horizon shows many illuvial and crenulated coatings on the upper faces of rock fragments and structural aggregates. The morphology, the TOC, and the indexes based on Fe_o, Al_o , Fe_p, Al_p , Fe_d and Fe_{tot} indicate that podzolization is active in this soil. Despite this evidence, the “spodicity index” ($1/2Fe_o+Al_o\%$) does not reach the limit required by ST and WRB. The high $Fe_d–Fe_o$ value can be explained by the crystallization of amorphous oxyhydroxides due to alternating reduction and oxidation conditions (Thompson et al., 2006).

The P135 profile is composed of an organic horizon, overlying a “de juxtaposition” A horizon, a bleached E enriched in organic matter and containing strongly weathered rock fragments, and two Bs horizons. Bs1 and Bs2 horizons have greater stoniness than the overlying A and E (40% and 80% respectively), and the stones are nearly unweathered. Only Bs2 meets the color-based taxonomic criterion (WRB, ST). Total metal contents and extractable oxyhydroxides, mainly dithionite extractable Fe, attain maximum values in the Bs1 horizon. The low Al_o content and its redistribution do not fit the requirements of the spodic index according to WRB and ST. The visible depletion in most metals in the E horizon, the ferruginous coatings in the illuvial horizons, and the colour trend within the profile demonstrate the intensity of the podzolization process. The light reddish shades of the E horizon are linked to the high contents of Fe_o, likely translocated from the upper parts of the slope. “Lateral” podzolization (Sommer et al., 2000) is suggested by the different thicknesses of the E horizons along a soil catena extending from 1800 to 2000 m a.s.l.: profile P135, located in a mid-slope position (Table 3.1), has an E horizon with a thickness of about 15 cm, while the E horizons on the summit are 28 cm thick. Soils on the footslope lack well developed bleached horizons (D'Amico, 2006).

The P133 profile shows a bleached AE horizon that is weakly enriched in dissolved organic matter (insolubilization AE horizon). The weakly structured and yellowish underlying BC shows crenulated reddish coatings on rock fragments that testify the illuviation of Fe related to a weakly active podzolization process. P134 shows a well developed podzol-like morphology (Table 3.5). Stones are almost completely weathered in the AE and E horizons. Despite its morphology, chemical properties and metal redistribution with depth, due to the lack of Al and the low Fe_o amount indicating high crystallinity, the spodicity index does not reach the 0.50% threshold value required by WRB and ST.

A peculiar aspect of the majority of the investigated pedons is the Ca/Mg ratio of less than 1, with very low base saturation values. Such values are typical of soils developed from parent materials dominated by Mg-rich serpentinite. The high leaching rate of soils drastically lowers base saturation and pH values.

5. Conclusions

The parent material of the 6 studied soils is a till composed of varying amounts of serpentinite, metagabbros and amphibolites: serpentinite represents 60–70% of P136 and P65 substrata, 30% of P1, and over 95% of P135, P133 and P134. The Ca/Mg ratio is lower than 1 in all profiles except P1.

Although mafic and ultramafic substrates should support soils with a neutral pH, where translocation of metallo-organic compounds is normally inhibited (Verger 1990, 1995; Verger et al., 1993; Alexander et al., 1994a,b; Lundström et al., 2000), all the investigated pedons show the typical properties of the podzolization process.

Namely:

- vertical trend of amorphous and crystalline pedogenic Fe oxyhydroxides and, to a lesser extent, of Al and Si oxides (Table 3.8);
- vertical distribution of organic carbon and fulvic acids (ODOE values, in Tables 3.6 and 3.9);
- vertical trend of total metal content (mainly Cu, Cr, Ni, Fe and Co, Table 3.7);
- extremely low surface pH (which is often less than 4) and low pH in deeper horizons (never higher than 5.8), everywhere linked with low base status (Table 3.6);
- high rock weathering rate in surface horizons;
- thick and bleached E horizons, underlain by reddish-brown horizons (Table 3.5);
- scarce visible biological activity.

Most likely owing to the original composition of the serpentine crystals, the B horizons in P65, P135, P133 and P134 (the latter being the richest in serpentinite parent material) have a low Alo content but a higher Fe_o amount. Fe_o values are not high enough to counterbalance the low Al_o content: the spodic index required by many classification systems (WRB, ST) is not reached. Nevertheless, pyrophosphate and citrate dithionite extractable Fe and Al increase considerably in the B horizons with respect to the overlying E ones. The stronger redistribution of Fe than Al is common in soils developed from Fe-rich parent materials, as shown by Nicholson and Moore (1977). The enrichment in total Al in serpentinite derived pedons in respect to the parent material could be due to the fact that chlorite is the unique Al-bearing mineralogical phase, and it is more stable than serpentine minerals: chlorite thus accumulates as residual material in the highly weathered E horizons. Fe_d is particularly high in B horizons on serpentinite, probably as a result of chemical reduction and oxidation cycles, linked with seasonal waterlogging during snowmelt. Anyway, high Fe oxides crystallinity is common on Fe-rich parent material (Soil Survey Staff, 1975).

In conclusion we notice that the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006) and the Soil Taxonomy (Soil Survey Staff,1975,1999, 2006) do not adequately allow to express the process of podzolization going on in ultramafic materials in the study area.

On the contrary, according to the more flexible criteria adopted by RP (Righi, 1998), most of these soils can be designated as Podzosols. Analogously, despite the very low values (b1) of Ca/Mg ratio,

according to RP and WRB, the “magnesic” qualifier cannot be applied to these profiles, because of the extremely low pH values.

Despite the taxonomic obstacles, we would stress that the podzolization process can be active even in soils developed from serpentinite and mafic rocks. Anyway, it appears to act less intensively on base-rich serpentinites than on mafic rocks.

In conclusion, acidic organic matter formed from conifers and ericaceous shrubs (*Rhodoreto–Vaccinietum*) favours strong mineral weathering in the upper horizons; minerals in ultramafic and mafic rocks easily weather and release bases, which are early leached away under the humid and acidic conditions typical of subalpine environments; these bases cannot inhibit the complexation between oxyhydroxides (mainly Fe) and soluble organic molecules.

On the basis of the observations and analyses performed on a large number of soil profiles under subalpine forest of Mont Avic Natural Park (D'Amico, 2006), it seems that in such an environment the podzolization should be more active mainly on stable and moderately steep northward slopes, where snow cover lasts for longer periods, evapotranspiration is lower and erosion is not a limiting factor for the pedogenesis.

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Fig. 3.1: P1, with strong podzol-like morphology.

Table 3.1. Environmental setting of the 6 investigated pedons.

Pedon	Altitude m a.s.l.	Aspect	Slope %	Landform	Soil drainage class
P136	1775	NNW	1	Glacial plateau	Good
P1	1830	NNW	25	Mid-slope	Good
P65	1795	N	2	Glacial plateau	Poor
P135	1975	NNW	21	Mid-slope	Moderately good
P133	2140	NNE	27	Mid-slope	Good
P134	2117	NNE	18	High-slope	Somewhat poor

Table 3.2. Lithological composition of the parent materials of the six pedons.

Pedon	Serpentinite (%)	Metagabbro (%)	Prasinite (%)	Amphibolite (%)	Chlorite schist (%)
P136	75	18	2	5	0
P1	20	70	7	2	1
P65	50	38	4	4	4
P135	90	0.5	1	3	5.5
P133	88	7	0	2	3
P134	95	0	4	0	1

Table 3.3. Major elemental composition of unweathered rock fragments. K and P are not shown because present in trace quantities. In brackets: deviation.

	Serpentinite	Metagabbro	Prasinite	Amphibolite	Chlorite schist	Calcschist
SiO_2 (%)	42.5	46.1	42.4	36.2	31.5	61.21
TiO_2 (%)	0.02	0.23	3 (±2)	0.05	0.02	
Al_2O_3 (%)	0.3	15.7	10.6	11.8	14.0	15.45
Fe_2O_3 (%)	5.9 (±2)	4.3	10.6 (±3)	7.8	6.5	5.4
MnO (%)	0.1	0.06	0.21 (±0.1)	0.09	0.12	0.21
MgO (%)	42.0	15.6	18.2 (±5)	31.0 (±2)	32.1	3.41
CaO (%)	0.05	10.5	7.6 (±2)	7.8 (±4)	2.1 (±2)	14.21
Na_2O (%)	0.03	2.15 (±1)	0.6	0.05	0.04	0.03
Cr (µg g^{-1})	3700 (±2000)	2654	506 (±200)	860	2242 (±1500)	4.85
Ni (µg g^{-1})	1366	310	284	1390	2373 (±300)	27
Cu (µg g^{-1})	10.7 (±7)	11.2 (±7)	12.3	5.6	3.4	
Zr (µg g^{-1})	1.1	7	72	1.8	1.7	

Table 3.4. Semiquantitative mineralogical composition of the sandy fraction of soils. S = serpentine (mainly antigorite), C = chlorite, A = amphiboles (tremolite, actinolite), Q = quartz, P = plagioclase (albite), T = talc, M = micas, IB = hydrobiotite, Px = pyroxenes. Trace minerals are shown in brackets.

Pedon	Horizon	Minerals
P136	**E**	C>A>>>Q>S>(T,M)
	Bs	C>S>>A>P>(T,Q)
	Cs	C>S>>A>P>(T,Q)
P1	**E**	C>P>Q>>(IB=M=T=S))
	Bs	C>>>S>P=A>>(T=M)
	Bsm	P=C>S>A>>(T>M)
	Csm	-
P65	**E**	C>P,A>S>Q>(T,Px)
	Bsg	C>S>>P,A>Q>(T,M)
	Cg	C>S>P>A>Q>(T)
P135	**A**	
	E	S>>>Q>>(C>M>A=IB>T)
	Bs	S>>>(C=Q>>M=T=A)
	BCs	S>>>>(C=Q>M=T=A)
P133	**AE**	S>>C>P,A>(T)
	CBs	S>>>C>P,A>(T)
	Cs	S>P>>C>A>(T)
P134	**AE**	S>>C=A>Q>P>>(T>M=IB=Px)
	E	S>>C=A>Q>P>>(T>M=IB=Px)
	Bs	S>>C=A>>P>>(Q=M>Px)

Table 3.5. Morphological and physical properties of the 6 pedons (According to FAO, 2006 and, for organic horizons, to INRA-AFES, 1995). *Symbols:*

Horizon boundary: As, abrupt and smooth; Aw, abrupt and wavy; Cw, clear and wavy; Ai, abrupt and irregular; Ci, clear and irregular; Gw, gradual and wavy.

Structure: GR granular; PL platy; PS subangular prismatic; MA massive; RS= rock structure. The number indicates the size class of the soil structure: 1=very fine, 2=fine, 3=medium, 4=coarse.

Consistence : LO loose; FR friable; FI firm; VFI very firm; The second number symbolizes the strength of the aggregates: 1=very weak, 2=weak, 3=moderate, 4=strong, 5=very strong.

Textural class: L loam; LS loamy sand; SL sandy loam; SIL silt loam; S sand.

Roots: Abundance: N none; V very few; F few; C common; M many. Diameter: VF very fine; F fine; M medium; C coarse; FF very fine and fine; VFM very fine and medium; FM fine and medium.

		Depth (cm)	**Munsell colour (moist)**	**Horizon boundary**	**Structure (cementation)**	**Consistence (moist)**	**Textural class**	**Root Diameter abundance**
P136	**OLv**	0-1	10YR3/2	Aw	-	-	-	-
	OFm	1-2	7.5YR2/2	Aw	GR 3	FR	-	FF/F
	OHr	2-4.5	7.5YR2/2	Aw	GR 1	LO	-	FF/F
	AE	4.5-7	10YR4/1	Gw	PL 3	FI	SL	C/F; FF/C
	E	7-17	2.5Y6/2.5	Aw	PL 4	FI	SL	C/F; FF/C
	Bs	17-35/38	8YR5/8	Cw	PS 3	FR	SL	C/F
	Cs	35/38-50+	7.5YR3/3	-	RS	-	S	N
P1	**OLv**	0-1	10YR3/2	-	-	-	-	N
	OFm	1-2	10YR3.5/1	Aw	GR 1	LO	-	VFM/C
	OHr	2-5	10YR3.5/1	As	GR 1	LO	-	VFM/C
	AE	5-15	2.5Y4/2	Gw	PL 4; GR 3	FI; FR	SL	VFM/C
	E	15-25/29	2.5Y6/2	Cw	PL 3; GR 1	FI; FR	SL	VFM/C
	Bs	25/29-32/36	7.5YR5/8	Cw	PS 3	FI	SL	FM/F
	Bsm	32/36-42	7.5YR4/6	Cw	(Cemented)	VFI	SL	FF/M
	Csm	42-53+	2.5Y5/4	-	(Cemented)	VFI	LS	N

P65	**Ah**	0-9/11	10YR3/1	Gw	GR 1	LO	SL	FF/M
	Eg	9/11-20	5Y5/2	Cw	MA	-	SL	N
	Bsg	20-30/33	10YR5/8	Ci	MA	-	SL	N
	Csg	30/33-50+	1Y5/8, 2.5Y5/3	-	MA	-	S	N
P135	**OLv**	0-05	-	Ai	-	-	-	N
	OHr	0.5-3	2.5Y3/3	Aw	GR 1	FR	-	FF/C
	A	3-10/13	2.5Y3/3	Cw	PS 2	FI	L	FF/C
	E	10/13-27	2.5Y4.5/3	Aw	PL 3	FI	SIL	FF/V
	Bs	27-35/40	10YR4/6	Cw	PS 2	FR	L	FF/V
	BCs	35/40-53	7.5YR4/4	Cw	-	-	SL	N
P133	**OLn**	0-0.5	-	Aw	-	-	-	N
	OFm	0.5-1.2	10YR3/2	Aw	-	-	-	N
	OHr	1.2-4	10YR3/2	Cw	-	-	-	FF/C
	E	4-13/8	2.5Y6/3	Cw	GR 3; PL 3	FI; LO	L	VFM/C
	CBs	13/8-25/22	2.5Y5/6	Cw	GR 1	LO	SL	VFM/V
	Cs	25/22-40	2.5Y6/6	Cw	RS	-	SL	VFM/V
	Cg	40-44+	2.5Y6/6	-	RS	-	-	N
P134	**OLv**	0-0.5	-	Aw	-	-	-	N
	OFm	0.5-1	10YR3/2	Aw	-	-	-	FF/C
	OHr	1-3	10YR3/2	Cw	-	-	-	FF/C
	AE	3-10	2.5Y5/3	Cw	PL 2	FR	L	VFM/C
	E	10-22	2.5Y6/3	Aw	PL 3	FI	L	F/V
	Bs	22-42	10YR5/6	Aw	GR 2	LO	L	FM/V
	R	42-50+		-	RS		-	N

Table 3.6. Main chemical properties of soil profiles. CEC, Ca, Mg, Na, K and total exchangeable acidity are expressed in cmol kg^{-1}; base saturation (BS) as percent values; TOC (total organic carbon) is in mg kg^{-1}.

Pedon	**Horizon**	**pH H_2O**	**pH KCl**	**TOC**	**CEC**	**Ca**	**Mg**	**Na**	**K**	**BS**	**Ca/Mg**	**Total acidity**
P136	**OHr**	4.2	3.3	114	-	4.36	1.33	0.48	0.37	-	3.28	-
	E	4.9	4.2	15	6.23	0.52	0.54	0.32	0.16	25	0.96	4.69
	Bs	5.1	4.4	12	10.11	0.65	0.77	0.44	0.13	20	0.84	8.12
	Cs	5.7	4.7	15	5.60	0.49	0.48	0.41	0.16	27	1.02	4.06
P1	**OF-OH**	3.7	2.9	191	-	4.36	1.33	0.48	0.37	-	3.28	-
	E	4.4	3.7	14	10.53	0.58	0.36	0.41	0.11	14	1.61	9.07
	Bs	4.7	4.2	52	16.53	0.62	0.38	0.43	0.11	9	1.63	14.99
	Bsm	4.7	4.3	17	20.65	0.42	0.24	0.41	0.20	6	1.75	19.38
	Csm	4.8	4.5	8	9.42	0.41	0.29	0.45	0.16	14	1.41	8.11
P65	**Ah**	4.8	4.2	70	10.25	1.30	1.44	0.50	0.14	33	0.90	6.87
	Eg	5.0	4.2	7	7.25	0.46	0.65	0.37	0.16	23	0.71	5.61
	Bsg	5.4	4.4	9	8.03	0.68	0.92	0.40	0.09	26	0.74	5.94
	Csg	5.3	4.7	4	5.76	0.58	0.48	0.49	0.15	29	1.21	4.06
P135	**A**	4.9	4.0	23	15.48	1.18	1.91	0.32	0.19	23	0.62	11.88
	E	4.6	3.5	23	7.87	1.43	2.21	0.38	0.10	52	0.65	3.75
	Bs	4.9	3.9	9	13.25	1.19	1.86	0.40	0.10	27	0.64	9.70
	BCs	5.3	4.2	4	9.21	0.89	1.25	0.41	0.10	28	0.71	6.56
P133	**OF-OH**	4.6	4.1	148	-	8.60	3.02	0.51	0.33	-	2.85	-
	AE	4.9	3.5	13	11.62	0.86	0.77	0.44	0.18	19	1.12	9.37
	CBs	5.0	3.9	9	4.13	0.76	0.93	0.47	0.09	54	0.82	1.88
	Cs	5.1	4.4	23	3.17	0.52	0.53	0.41	0.15	51	0.98	1.56
P134	**AE**	4.7	3.4	31	12.93	1.24	1.85	0.43	0.35	30	0.67	9.06
	E	4.7	3.3	17	11.42	0.66	1.15	0.39	0.15	21	0.57	9.07
	Bs	4.8	3.7	11	11.13	0.18	1.36	0.44	0.10	19	0.13	9.05

Table 3.7. Correlation analysis (CA) between the main chemical parameters and environmental factors. BS is base saturation; TOC (E/Bs) is the ratio between total organic carbon in the spodic horizon and that in the eluvial horizon; O Hor is the cumulated thickness of OL, OF and OH horizons. Statistical significant values are above 0,5 or below -0,5 (p value <0,05)

	pH (Bs)	**Ca/Mg**	**BS**	**TOC (E/Bs)**	**Sand**	**Silt**	**Clay**	**O Hor.**	**Altitude**	**Slope**	**Serpent.**	**Gabbro**	**Mafic**
pH (Bs)	1.00												
Ca/Mg	0.51	1.00											
BS	-0.13	-0.43	1.00										
TOC (E/Bs)	0.39	0.88	-0.49	1.00									
Sand	0.79	0.35	-0.11	0.44	1.00								
Silt	-0.81	-0.34	0.12	-0.45	-0.99	1.00							
Clay	0.19	0.84	-0.70	0.88	0.06	-0.08	1.00						
O hor.	-0.10	0.44	-0.61	023	-0.04	0.12	0.41	1.00					
Altitude	-0.93	-0.52	0.31	-0.37	-0.55	0.60	-0.33	0.06	1.00				
Slope	-0.74	0.14	-0.02	0.10	-0.59	0.65	0.26	0.52	0.72	1.00			
Serpentinite	-0.63	-0.85	0.48	-0.91	-0.47	0.51	-0.84	-0.04	0.68	0.23	1.00		
Gabbro	0.78	0.79	-0.35	0.84	0.65	-0.69	0.68	-0.08	-0.77	-0.41	-0.97	1.00	
Mafic	0.32	0.84	-0.62	0.89	0.13	-0.17	0.97	0.22	-0.47	0.09	-0.92	0.79	1.00
Drainage	0.00	-0.54	0.35	-0.27	-0.03	-0.06	-0.36	-0.93	-0.04	-0.56	0.06	0.02	-0.18

Table 3.8. Bulk chemical composition of the sampled soil horizons (by XRF analysis). Only major elements are shown.

Profile	**Hor.**	**SiO_2**	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**Cr**	**Ni**	**Cu**	**Co**	**Zr**	**Ti/Zr**
		%	%	%	%	%	%	%	%	µg g-1	µg g^{-1}	µg g-1	µg g-1	µg g-1	
P136	E	43.44	0.15	13.84	5.63	23.70	5.23	0.05	0.20	1400	627	3.60	29	30.20	51
	Bs	39.61	0.11	12.48	7.33	25.55	5.46	0.05	0.11	1800	698	18.70	33	12.60	89
	Cs	43.06	0.08	11.81	6.54	25.36	7.34	0.18	0.04	2300	590	13.40	32	4.20	200
P1	E	50.44	0.26	14.95	4.43	14.54	6.32	0.66	0.55	900	347	2.06	26	81.00	32
	Bs	40.38	0.25	14.55	7.43	15.02	4.79	0.15	0.49	1000	396	5.40	33	65.60	38
	Bsm	38.56	0.20	16.12	7.24	17.31	4.12	0.05	0.57	1100	613	43.40	32	60.70	33
	Csm	41.11	0.13	15.32	5.65	19.44	6.24	0.39	0.25	1000	597	46.10	29	27.80	47
P65	A	40.64	0.17	10.30	5.12	19.17	4.38	0.05	0.37	1900	526	15.70	27	34.80	49
	E	44.19	0.17	12.33	5.63	24.55	5.25	0.05	0.40	1600	590	17.30	29	34.70	48
	Bsg	43.57	0.15	12.29	7.82	22.74	6.02	0.18	0.36	1800	597	45.30	35	33.80	45
	Cg	42.29	0.11	12.31	5.64	22.83	7.06	0.11	0.12	1400	635	47.40	29	18.40	60
P135	A	40.34	0.22	6.43	9.84	25.45	0.77	0.04	0.68	2800	1071	26.70	37	62.30	35
	E	47.08	0.29	7.90	7.81	23.92	1.05	0.04	0.93	2500	612	8.50	34	119.80	24
	Bs	44.04	0.23	6.23	9.94	27.81	1.05	0.04	0.73	2700	838	17.20	38	85.00	27
	CBs	43.36	0.21	5.77	9.85	29.80	1.14	0.04	0.62	2800	879	29.70	38	67.20	31
P133	E	47.27	0.22	10.60	5.68	23.52	5.04	0.05	0.44	1700	510	2.07	29	72.40	30
	CBs	43.12	0.13	8.30	7.42	29.32	4.52	0.05	0.19	2200	718	11.10	33	19.30	67
	Cs	43.76	0.12	8.22	7.33	31.76	5.14	0.05	0.07	2200	815	14.00	33	10.10	114
P134	AE	48.32	0.41	9.76	5.97	17.78	3.26	0.05	0.87	1400	342	5.20	30	152.80	27
	E	51.62	0.41	9.66	5.73	18.96	4.12	0.49	0.82	1400	344	2.08	30	169.70	24
	Bs	45.35	0.30	7.96	8.69	25.27	4.42	0.05	0.32	1900	597	26.50	36	88.00	34

Table 3.9. Oxalate, pyrophosphate and dithionite extractable Fe, Al, and Si.

Profile	**Hor.**	**Fe_o**	**Al_o**	**Si_o**	**Fe_p**	**Al_p**	**Fe_d**	**Al_d**	**Si_d**	**Fe_{tot}**	**Fe_d/Fe_{tot}**
		g kg-1	g kg-1	g kg-1	g kg-1	g kg-1	g kg-1	g kg-1	g kg-1	g kg-1	%
P136	E	2.20	0.80	0.19	7.10	0.67	4.23	1.21	0.79	39.42	11
	Bs	7.70	2.50	0.45	22.70	1.87	14.40	3.39	1.02	51.34	28
	Cs	2.40	1.80	0.50	7.55	1.36	6.09	1.93	0.85	45.77	13
P1	E	2.20	1.20	0.36	6.60	1.14	3.63	1.37	0.84	31.04	12
	Bs	14.60	5.00	0.82	47.20	3.78	27.45	5.41	1.27	52.02	53
	Bsm	6.60	10.60	2.61	16.25	5.64	16.50	10.64	4.57	50.73	32
	Csm	2.10	5.10	1.66	4.15	2.92	6.45	4.66	2.21	39.56	16
P65	Ah	3.80	0.70	0.38	10.05	0.59	7.80	1.00	0.88	35.88	22
	Eg	0.60	0.20	0.42	2.35	0.18	4.71	0.67	0.86	39.4	12
	Bsg	3.90	0.40	0.44	12.35	0.38	26.10	1.51	1.24	54.76	48
	Csg	2.10	1.20	0.70	7.50	0.91	5.94	1.39	1.06	39.49	15
P135	A	4.30	0.60	0.47	26.45	0.92	31.05	1.96	1.34	68.92	45
	E	3.30	0.70	0.43	11.00	0.52	15.45	0.91	1.28	54.67	28
	Bs	4.30	0.50	0.44	15.45	0.41	35.40	1.18	1.33	69.58	51
	BCs	5.30	0.50	0.49	13.05	0.46	29.10	1.29	1.64	69.01	42
P133	AE	2.00	0.60	0.51	7.30	0.54	7.47	1.01	1.21	39.81	19
	CBs	1.30	0.40	0.46	5.05	0.38	12.75	1.18	0.81	51.96	24
	Cs	1.50	0.40	0.57	3.85	0.33	8.10	0.96	0.87	51.32	16
P134	AE	2.90	1.00	0.57	11.00	0.83	10.62	1.06	1.36	41.78	25
	E	1.70	0.70	0.49	4.10	0.53	6.51	0.64	1.00	40.13	16
	Bs	2.80	0.60	0.48	11.70	0.55	21.45	1.15	0.95	60.88	35

Table 3.10. Some common spodicity indexes.

Pedon	Hor.	$\frac{1}{2}Fe_o+Al_o$ %	Fe_p+Al_p %	Fe_o/Fe_d	ODOE
P136	**E**	0.19	0.77	0.52	0.16
	Bs	0.63	2.46	0.54	0.26
	Cs	0.30	0.89	0.40	0.20
P1	**E**	0.23	0.74	0.61	0.16
	Bs	1.23	5.10	0.53	0.36
	Bsm	1.39	2.20	0.40	0.44
	Csm	0.62	0.71	0.33	0.16
P65	**Ah**	0.25	1.06	0.49	0.18
	Eg	0.05	0.25	0.13	0.04
	Bsg	0.23	1.27	0.15	0.18
	Csg	0.23	0.84	0.35	0.15
P135	**A**	0.28	2.74	0.14	0.14
	E	0.23	1.15	0.21	0.13
	Bs	0.26	1.59	0.12	0.21
	BCs	0.32	1.35	0.18	0.20
P133	**AE**	0.16	0.78	0.27	0.15
	CBs	0.10	0.54	0.10	0.13
	Cs	0.12	0.42	0.19	0.15
P134	**AE**	0.24	1.12	0.27	0.16
	E	0.16	0.46	0.26	0.11
	Bs	0.20	1.22	0.13	0.20

Table 3.11: classification of the 6 pedons according to the main taxonomic system

	WRB (FAO/IUSS/ ISRIC, 2006)	**Soil Taxonomy (Soil Survey Staff, 2006)**	**Référentiel Pédologique (INRA-AFES, 1995)**
P136	Albic Podzol (Episkeletic)	Typic Haplocryod, coarse loamy, magnesic	PODZOSOL MEUBLE from ultramafic till, sub-alpine, under *P. uncinata* pinewood
P1	Albic, Ortsteinic Podzol (Skeletic)	Typic Duricryod, coarse loamy, mixed	PODZOSOL DURIQUE from metagabbro and serpentinite till, sub-alpine, under *P. uncinata* pinewood
P65	Epistagnic Cambisol (Dystric)	Oxyaquic Dystrocryept, loamy skeletal, magnesic	PODZOSOL MEUBLE from ultramafic till, sub-alpine, with groundwater, redoxic, under *P.uncinata* pinewood
P135	Haplic Cambisol (Skeletic, Protospodic)	Spodic Dystrocryept, loamy skeletal, magnesic	PODZOSOL MEUBLE from serpentinite, sub-alpine, under *P. Uncinata* and *L. decidua*
P133	Haplic Regosol (Dystric)	Typic Cryorthent, coarse loamy skeletal, magnesic	REGOSOL coarse loamy, stony, from serpentinite debris, sub-alpine, under *L. decidua* and *Vaccinium ssp.*
P134	Epileptic Cambisol (Hyperdystric, Protospodic)	Spodic Dystrocryept, loamy skeletal, magnesic	PODZOSOL MEUBLE lithic, over serpentinite, sub-alpine, under *P. Uncinata* and *Ericaceae*

4: Podzolization over ophiolitic materials: weathering and clay minerals

Abstract

Despite some previously reported cases in other subalpine areas in the world, the process of podzolization on ultramafic substrates remains enigmatic. As shown in the previous chapter, under the subalpine forests of Mont Avic Natural Park, podzolization is active, probably thanks to a particularly acidifying vegetation and to wet microclimatic conditions. Clay minerals, as a product of weathering, are able to show the weathering conditions of the parent material, and, thus, the pedogenic processes active in the particular area. It is here demonstrated that weathering is particularly strong in subalpine soils, because of strong acidification, leading to the dissolution of serpentine minerals and to the transformation of Mg-chlorite into Al and Fe-smectites and vermiculites, via Fe-rich soil chlorites and hydroxy-interlayered minerals. Mass balance calculations verify these processes.

4.1. Introduction

Chemical weathering, clay mineral formation and pedogenesis on ultramafic materials have been characterized in many studies in tropical areas (e.g., Nahon et al. 1988, Garnier et al. 2009), thanks to the economic interest in metal ores in lateritic soils. In temperate environments, however, the number of studies is small, and even smaller in boreal or subalpine habitats. However, the interest in this kind of study is great, as soils formed from ultramafic materials are particularly rich in heavy metals, and are potentially a source of contamination for surface water and crops. The weathering products are more or less susceptible to weathering in different environments, and knowing the weathering paths helps the understanding of metal mobility, potential bioavailability and ecotoxicological risk.

In temperate habitats, a great variety of clay minerals has been detected in soils formed from ophiolitic materials, depending on age and environmental properties. The weathering products of ultramafic rocks are thought to depend on drainage and topography: in well drained sites and in high part of slopes, vermiculite is the dominant phase, otherwise smectites are more common (Bonifacio et al. 1997). In moist soils, smectite is thought to be the only weathering product of serpentine (Rabenhorst et al. 1982, Bonifacio et al. 1997), derived from the interaction of antigorite and Mg and Al rich chlorites, to form soil chlorite and Fe-rich smectites, with the addiction of Fe oxides and the release of Mg^{2+} into solution (Ducloux et al. 1976). Chlorite itself can be an early weathering product of serpentine minerals (Rabenhorst 1982). Wildman et al. (1971) attributed the presence of Fe-rich smectites to the presence of Fe, Al and Si in solution, derived from the dissolution of serpentine minerals; free energy calculations indicated that trivalent Fe-Al hydroxide would be more stable than Mg-hydroxides (in a neutral pH range): nontronite (Fe-rich smectite) is more stable than saponite (Mg-rich smectite). The latter is stable at high pH values and high humidity (Senkayi 1977).

However, because of its high Al content, smectite formation from serpentine weathering remains enigmatic (Bulmer 1992).

Later works (for example, Caillaud et al. 2004) show how chlorite is the only Al-bearing mineral, and the development and the neoformation of clay minerals will depend exclusively on Al derived from it. Fe and Al contents are usually highest in surface horizons (because of residual accumulation caused by Mg and Si leaching), and the clay minerals will be rich in Fe and Al (Fe-rich smectites and kaolinite).

Quite similar weathering products of ultramafic minerals have been observed in boreal or subalpine habitats. Normally, serpentine mineral content increases with soil depth because of its high solubility, showing an opposite trend than the one of quartz (mostly concentrated in surface horizons) (Sasaki et al. 1968). The most weathered horizons include some clay minerals, such as vermiculite (derived from chlorite weathering in E horizons, according to Sasaki et al. 1968), or hydroxy-interlayered smectites (HIS) and vermiculites (HIV), chlorite, talc and serpentine (in the Bs1 horizon of a cemented podzol, Bulmer and Lavkulich 1994). Often, clay mineralogy indicates a low degree of soil development: for example, Bulmer et al. (1992), in ultramafic B horizons covered by sialic tephra, found chlorites, serpentine, talc, and only traces of smectites in the finest fraction. In similar Bw-Bs horizons in Switzerland, serpentine, with minor kaolinite, illites, HI chlorites and quartz were found.

Bulmer (1992), in a review about the weathering of ultramafic rocks, showed how at low pH values serpentine minerals tended to dissolve: these minerals are stable only in a small range of high pH values and high with Mg^{2+} concentration in the soil solution. Hydroxy-interlayered minerals were formed from the weathering of chlorites, while serpentine mostly dissolved.

The aim of the present study is the characterization of the clay minerals developed in three subalpine podzolic soils developed on serpentinite (P135, P134) and metagabbros (P1) in the Italian western Alps. These soil profiles are chosen between the 6 previously analyzed in detail (D'Amico et al. 2008). The results improve the knowledge of weathering and pedogenic processes active in ophiolitic materials in subalpine areas. The interest of soil functioning in subalpine areas on ophiolites is given by the their "extreme" properties, and by the unusual soil-forming process of podzolization, active in the study area.

4.2 Materials and methods

Three soil profiles were analyzed, chosen between 6 previously studied and described podzolic soils. They were located under subalpine *Pinus uncinata* forest. A description and a chemical characterization of pedons P1 (on gabbro dominated till), P135, P134 (on serpentinitic till) is in chapter 3.

Bulk density was measured after sampling 2-3 cylinders (100 cm^3) from each genetic horizons, considering the rock content and volume.

The mineralogy of the clay textural fraction was analyzed by X-Ray Diffraction methods (XRD) on oriented samples, with a Diffrattometer X'Pert PRO, Cu radiation from 2° to 15°2θ (steps of 0.02 °2θ, 1s/step). Clays were separated via centrifugation, after destruction of organic matter with dilute and Na-acetate buffered H_2O_2, at pH 5 and after the Fe-oxides removal with dithionite (DCB). The first step was the saturation with Mg. Samples were later saturated with ethylene-glycol (EG) and analyzed at 25°C, in order to observe the presence of smectites (appearance of a 16-17 Å peak) or Hydroxy-Interlayered smectites (HIS, formation of a 15-16 Å peak) or smectite-illite, evidenced by a 12-13 Å peak.

After K saturation, at 25°C, vermiculites become visible (migration of the 14 Å peak to 10 Å); after heating at 350°C, HIV (Hydroxy-Interlayered Vermiculites) appear (decrease of the 14 Å peak and increase of the intensity of the 10 Å one). At 550°C, kaolinite becomes visible (disappearance of secondary chlorite peaks). Peaks were separated with a software X'Pert PRO. The area underlined by the peak line was used for the semi-quantitative clay analysis.

The presence of kaolinite was checked with FTIR (Fourier Transform Infrared Spectroscopy) measurements. FTIR was also used to detect the relative abundance of different hydroxilic groups in the clays.

Allophanic materials (ITM, consisting of imogolite and proto-imogolite allophane) were estimated if the Al_{ox}-Al_p/Si_{ox} molar ratio was close to 2 (Al_{ox} and Si_{ox} are respectively oxalate extractable Al and Si; Al_p is pyrophosphate extractable Al). If the ratio is out of the 0.75-2.4 interval, the probability of existence of allophanic materials is extremely low (Egli et al. 2006). In case of a value close to 2, ITM has been estimated according to Parfitt and Henmi (1982):

$$ITM = (5+2.1((Al_{ox}-Al_p)/Si_{ox} - 1))*Si_{ox}$$

Another method used for the assessment of the presence of active amorphous and paracrystalline materials was the measurement of pH in NaF 1N, commonly used for the analysis of soils with andic properties. If the pH(NaF) value is above 9.5, the presence of short range ordered materials is verified.

Magnetite was approximately quantified in the different horizons: 8-10 g of dry soil were crushed to a particle size smaller than fine sand and put on large glass plates where magnetite was removed with a hand magnet, cleaned and weighted. The process was performed many times on each sample.

Mass transport calculation were performed according to Egli and Fitze (2000):

$$\tau_{j,w} = (C_{j,w}\, C_{i,p} / C_{j,p} C_{i,w})-1$$

where:

$\tau_{j,w}$: function of mass transport in the open system of *j* element, in the weathered material *w*;

$C_{j,w}$: concentration of the *j* element in the weathered material *w*;

$C_{i,p}$: concentration of the stable element *i* in the parent material *p*;

$C_{j,p}$: concentration of the *j* element in the parent material;

$C_{i,w}$: concentration of the stable *i* element in the weathered materials.

Ti was considered the stable elements in the calculations. Zr was not used because it had extremely small concentrations in the studied soil samples, and this could have led to increased errors. Ti is, however, weakly mobile in acidic soils and in presence of chelating agents (Aide and Smith-Aide 2003); moreover, in the studied soils, a very low Ti mobility was indicated by the slightly increasing Ti/Zr ratio with depth. Another source of error is the lithological composition of the glacial parent material, which is not exactly the same as the substrate. The C horizon is usually considered the parent material (Egli et al. 2006), but in this case a true C horizon was seldom sampled, because of the presence of hard rock (P134, P135) or cementation (P1). The parent material was approximated by the Cm horizon in P1 and the BCs in P135, even if the cementation and the reddish color were a proof of illuviation of some elements from the topsoil, or by the lithological composition of the skeleton of the least weathered horizon (BC), and by the mineralogical composition of the sandy textural fraction (tab. 3.4). Additionally, an absolute homogeneity of the parent material and the lack of aeolian inputs are probably never encountered in mountain soils, but the errors caused by these approximations seem to be of minor importance on the Alps (Egli et al. 2006).

4.3 Results

4.3.1 Parent material

The studied Chalamy Valley is carved into ophiolitic rocks, with serpentinite as the most common lithology. Associated with serpentinite there are many 1-5 m thick chloriteschist inclusions, while metagabbros are usually well separated. Glaciers actively mixed the different rocks, so the parent material of the three soils is composed of ultramafic (serpentinite and chloriteschist) and mafic rocks (gabbros and amphibolites) in different proportions. The parent till of P134 and P135 are composed of serpentinite (>90%), with a large presence of chloriteschist and traces of mafic rocks, while P1 is mainly developed on mafic till (serpentinite + chloriteschist < 30%) (D'Amico et al. 2008).

XRD samples of the sand is visible in tab. 3.4.

4.3.1.1 Serpentinite

Serpentinite was the parent material for P135 and P134 (>90%), and represented a small fraction for P1 (20%). The diffraction patterns (fig 4.1) of some weakly weathered serpentinite samples showed that this rock is composed mostly of serpentine minerals (antigorite), with small quantities (up to 3-4%) of magnetite (extracted with a hand magnet from the pulverized samples).

Omitting trace elements, the resulting chemical formula of serpentine minerals was (derived from data shown in tab. 4.1):

$$(Mg_{2,85}Fe_{0,15})(Si_{1,94}Fe_{0,06})O_5(OH)_4$$

Si content was lower than usual in antigorites (e.g., Bonifacio et al. 1997); Fe was higher than usual, but could be related with inclusion of magnetite crystals in the analyzed samples.

4.3.1.2 Chlorite-schist

Chlorite-schists XRD peaks (fig. 4.2) demonstrated its homogeneous mineralogical composition. The only minerals detected were chlorite and traces of plagioclases.

The difference of the 001, 003, 005 and 002, 004 peaks was not very large, as was the reduction of the intensity of the secondary peaks in the heated samples: primary chlorite was probably Fe-poor. Omitting trace elements (Cr is 0.2%), the proposed formula for this mineral, based on its chemical composition (tab. 4.2), was similar to chlinochlore (Mg-rich chlorite):

$$(Mg_{4,71}Fe^{2+}_{0,48}Al_{0,72})(Si_{3,1}Al_{0,9})O_{10}(OH)_8$$

In this mineral, Fe is usually well inserted in the 2:1 octahedral groups, while Mg is situated in the more labile hydroxylic layer (Herbillon and Makumbi 1975). Al is in stable groups.

In most soil horizons, chlorite had different diffractometric properties: in heated samples (550°C), secondary peaks were reduced and nearly disappeared, while the difference between 001, 003, 005 and 002, 004 peaks increased. This was an evidence of Fe and/or Al enrichment in weathered, or pedogenic, chlorites.

This was in contrast with Barnhisel and Bertsch (1989), who showed how chlorites weather by lost of OH^- ions, followed by Fe oxidation caused by acid attack: organic chelating agents remove Fe, thus beginning the liberation of Mg and Al. These processes are the beginning of chlorite transformation to vermiculite. A slightly different process is shown by Carnicelli et al. (1997) and Herbillon and Makumbi (1975): the main steps in chlorite weathering are Fe oxidation, the partial removal of the brucitic (Mg-rich) sheet, followed by Al deposition in the interlayer (leading to smectite formation).

4.3.1.3 Metagabbros and mafic rocks

Mafic rocks had a silica content below 50%, and in the study area it was lower than average. Also Ca, Al and Fe were below the normal values (tab. 4.3).

According to XRD analysis (fig. 4.3), metagabbros were composed of amphiboles (actinolite and glaucophane), plagioclase, chlorites, with minor biotite, talc and quartz. Chlorite was similar to the one in chlorite-schists (chlinochlore), and it was particularly rich in Cr.

4.3.2 Mass transport calculations

Bulk density (BD in tab. 4.4) was sometimes below 1 in surface or near-surface horizons, because of the high organic matter content or because of porosity caused by roots, bio and cryoturbation.

Despite the approximations due to the assimilation of the parent material with the C or BC horizons (P1, p135) or with the lithological composition of the coarse fraction (P134), some weathering trends were visible (tab 4.4): Mg was one of the most easily leached element (because of serpentine mineral dissolution and, for a lesser extent, chlorite weathering). The strongly negative open system mass transport functions for Si can be related with serpentine dissolution as well.

Al was concentrated in the most weathered horizons on serpentinite, but not on mafic rocks. This residual accumulation was probably due to the lower susceptibility to weathering of chlorite minerals (which was the main Al-bearing mineral) in comparison with serpentine. Al was leached only in soils on mostly mafic parent materials, probably because of the preferential weathering of chlorites compared to other mafic rock-forming minerals (the high weatherability of chlorite in podzols is shown by Bain 1977).

Fe, Cr and Ni were strongly leached, while Cu was even more mobilized because of its strong affinity with organic chelating molecules. Ca was strongly accumulated in surface horizons on serpentinite, probably because of a residual accumulation of plagioclases and amphiboles (originated from the small fractions of mafic rocks included in the parent glacial till), which were more resistant than serpentine minerals, and because of biocycling (Rabenhorst 1982).

4.3.3 Granulometric evolution

The granulometric weathering trend (fig. 4.4), was an evidence of the podzolization process influencing the 3 soils: the E horizon was always slightly poorer in clay fraction than the overlying, less weathered A horizons and than the underlying Bs horizons. An exception was Bs1 horizon in P1. This reduction in clay content was probably related with dissolution.

Fragmentation was evidenced by the higher clay and silt content in upper horizons than in C or CB. This is a typical pedogenic phenomenon in mountain soils (for example, Verger 1989, and Legros 1984), not strictly related with podzolization. Dissolution of the fine particles in eluvial horizons is, however, characteristic of podzolization: this process is demonstrated by the decrease of clay particles content in E horizons also on serpentinite, differently from what found by Verger (1989), who was able to differentiate serpentinic soils dominated by fragmentation and mafic or acidic soils where dissolution and fragmentation were active together.

4.3.4 Clay minerals

The clay mineralogy is given in table 4.6 and fig. 4.5a, b, c. X-ray diffraction patterns for P134 are visible in fig.4.6a (E horizon) and b (Bs horizons).

The least weathered horizons were the deepest BC or C horizons. Only primary minerals and opal were recognized in the Cm horizon of pedon P1. Opal is shown by a broad peak between 0.47 and 0.33 nm (Alexander et al. 1994); amorphous silica was probably the main cementing agent in Bsm and Cm horizons in P1. The clay fraction of the Cm horizon of P1 was composed of Mg-chlorite (14.08 Å), amphiboles (8.36 Å), serpentine and traces of illite/mica and talc. In this horizon, chlorite is similar to the primary one, with only a slight enrichment in Fe (shown by a larger decrease of the secondary peaks in heated samples). The overlying Bsm horizon also has no secondary clay minerals, but chlorite is changed from Mg-rich chlinochlore to Fe-rich (disappearance of the secondary peaks in 550°C heated samples.

The BC horizon of ultramafic P135 was largely dominated by serpentine minerals (7.4Å). small quantities of intergrade minerals between chlorite and smectite (appearance of a peak at 15.5Å in the EG-saturated sample) and HIVs were probably the results of the early weathering of chlorites. Hydroxy-interlayered minerals have often been found in podzolic soils (Egli et al. 2006). Some clay minerals could be illuviated from upper horizons or neoformed from the elements released in solution by the dissolution of primary minerals (Lee et al. 2003, Rabenhorst et al. 1982). Thin reddish films on rock clasts were probably composed of illuviated Fe-oxyhydroxides and small amounts of clays.

In the spodic Bs horizons, primary minerals were still more common than their weathering products. On mafic rocks (P1), Fe-chlorite was the most common, followed by HIV. Also large quantities of plagioclases and amphiboles are detected.

On serpentinite, serpentine minerals were dominant, with smaller quantities of Fe-chlorites (which are the first weathering product of primary chlinochlore). Smectites, vermiculites and hydroxy-interlayered minerals were in traces. In P134 and P135, the 6.2Å peak was probably lepidocrocite, but there were no secondary peaks of this Fe-hydroxide. Minerals with an intermediate character between chlorite and smectites (HIS) were shown by the appearance of a 15.6Å peak in EG-saturated samples.

The E horizons were the most weathered ones, as it is typical in podzolic soils. Pedogenic minerals were more abundant than primary ones, both in soils formed from serpentinite (P134, P135) and from mafic rocks (P1). On the latter, smectites (with a high interlayer charge, as the 14 Å peak moved to 16.70 Å in EG saturation, Meunier 2005) and HIV were more common than soil Fe-chlorite (par. 4.3.1.2) and vermiculite. Serpentine, mica/illite and talc were very scarce. A similar trend was visible for P134, where the main clay minerals were vermiculite, smectite (high charge, 14Å the peak migrated to 16.43Å in EG saturation), chlorite-smectite intergrades and HIV, followed by Fe-chlorite and serpentine. In P135, chlorite is completely substituted by smectite, chlorite-smectite intergrades vermiculite and HIV. Chlorite-smectite interlayers were present in most E horizons, and there were traces of interstratified illite-smectite (reduction and migration to the left of the diffraction band close to 12Å in the heated samples). Illite, quartz and amphiboles were in traces.

In all the analyzed samples from E horizons, interstratified illite-smectite are in traces as well.

The overlying A or AE horizons (developed on serpentinite) were slightly less weathered than the eluvial E ones. In P135, the peaks were not clearly recognizable, probably because of the presence of amorphous materials illuviated from higher parts of the slopes and complexed by organic matter (see chapter 3 for the explanation of the process of lateral podzolization active in this slope). The 6.2Å peak could be lepidocrocite, despite its instability in extremely acidic soils (Fitzpatrick et al. 1985), illuviated from upslope. Smectite and HIS were visible (reduction of the 14 Å peak and increase of the diffraction band at lower angles in EG saturation), vermiculite was scarce (10 Å in the K-saturated samples at 25°C), while HIV were common (visible 12 Å peak in K-saturation, shifting to 10 Å peak at 350°C, Sawney 1989). Primary minerals were less common: serpentine was the most abundant, followed by Fe-chlorite, illite and talc.

The clay mineralogy and weathering trend with depth was another demonstration of the unusual (on serpentinite) pedogenic processes of podzolization.

4.3.4.1 Talc

This mineral was not observed in the parent material (only traces in metagabbros). Nevertheless, it was always found in small quantities in the 3 soils, particularly on serpentinite; its content was highest in the strongly weathered AE and E horizons. This could be due to the higher stability of talc in respect to serpentinite (Bulmer 1992), or to a pedogenic neoformation. This hypothesis has been demonstrated in the serpentinite weathering microsystem due to lichen growth, on serpentinite outcrops in the same ophiolitic area (Mont Avic Natural Park, Favero Longo et al. 2004). Neoformed talc was detected in weathering profiles in ophiolitic materials on the Pyrenees (Fontanaud and Meunier 1983), but it was easily weatherable in surface horizons and transformed into Mg-rich smectites (saponites).

4.3.5 Magnetic minerals

Magnetite is an important component of serpentinites worldwide, often partially substituted by chromites. Spinels (magnetite, chromite and intergrades) are strongly resistant to weathering, also in acidic soils.

Magnetic minerals (magnetite, chromite and/or intermediate spinels) were mostly concentrated in soils developed from serpentinite (tab. 4.7). A strong weathering state of these resistant minerals was shown by the great increase in Bs and C horizons in comparison with E ones. The trend was the same as the one shown by primary minerals in the clay fraction. This was another evidence of a particularly aggressive pedo-environment, able to dissolve also very resistant minerals.

4.3.6 Allophanic materials

ITM (imogolite-type materials, including allophane, imogolite and proto.imogolite) are often found in podzolic soils. According to the Al_o-Al_p/Si_o molar ratio always far from 2 and the pH value usually too low, these materials should not be present in appreciable amounts. In fact, below pH 4.9, ITM become unstable (Dahlgren and Ugolini 1991). However, the cemented Bsm and Cm horizons in P1 had a pH (NaF) above 10.6, which clearly demonstrated the presence of short range, imogolite-type materials, despite the extremely low pH values.

4.3.8: IR measurements

P1

Trioctahedral occupancies were evidenced by the lack of a band at 3680, particularly in the A and Bs horizon: Mg and Fe were strongly depleted in the E horizon. Fe-rich smectitic groups were visible in the A and Bs horizons (absorption peaks around 3550-3560 cm^{-1}, from Cailloud et al., 2004), less in the Fe-depleted E horizon. The 3570 cm^{-1} peak was also related with Fe-OH groups, particularly abundant in the Fe-rich Bs2 horizon.

Strong absorption bands at 3690 and 3620 cm^{-1} were detected, with increasing intensities in the E horizon, and are characteristics of a kaolinite spectrum. However, XRD did not detect kaolinite in the fine clay fraction. This mineral decreased from E to Bs and almost disappeared in the Bsm. The peak at 802 cm^{-1} represented vermiculite, and it confirmed the reduction from the most to the least weathered horizons. The 526 cm^{-1} peak (smectite) was probably masked by other substances.

In all the analyzed profiles, kaolinite, that was not observed with XRD, appeared with IR analysis. One of its characteristic peaks (916 cm^{-1}, according to Egli et al. 2001) was always visible in E horizons and sometimes also in the underlying Bs. Kaolinite was commonly present in smectite-rich samples though it is not detected by XRD (Caillaud et al. 2004).

P135

In the OH stretching region (fig. 4.8), trioctahedral occupancies were shown by the lack of a band at 3680 cm^{-1}, particularly in the A and Bs horizon. Mg was more strongly depleted in the E horizon (less trioctahedral occupancies). Fe-rich smectite was visible in the A and Bs horizons (absorption peaks around 3550-3560 cm^{-1}, from Cailloud et al. 2004), less in the Fe-depleted E horizon. This could be related to a partial transformation of Fe-rich (nontronite) to Al-rich (beidellite) smectite. The 3570 cm^{-1} peak was also related with Fe-OH groups, mostly in the Fe-rich Bs2 horizon.

The strong absorption band at 3671 cm^{-1}, typical of antigorite, almost completely disappeared in the A and E horizons.

Strong absorption bands at 3690 and 3620 cm^{-1}, with increasing intensities in the E horizon, were attributed to kaolinite. The strong absorption band at 3670 cm^{-1} could be related to the high antigorite content in the Bs horizon.

In the OH bending region (650-950 cm^{-1}), the 920 band could be due to kaolinite (916 cm^{-1}), which had the expected decreasing trend from E to Bs2; smectite (526 cm^{-1}) showed a similar trend; chlorite (660 cm^{-1}), was more abundant in the weakly weathered Bs2.

The difference between horizons showed a differential weathering of different minerals: the absorption bands at 830 cm^{-1} (showing the AlMgOH groups), 820 cm^{-1} (FeFeOH), 786 cm^{-1} (MgFeOH) decreased from the most weathered (E) to the least weathered (Bs, A) horizons.

There was a lower proportion of trioctahedral Fe in smectites in the E than in the A and Bs horizons (690-680 cm^{-1}). The higher quantity of Si-Al-O and of quartz (779, 799 cm^{-1}) in the E than in the Bs was verified. A tendency towards dioctahedral occupancy in clay minerals in the most weathered horizons was observed.

P134

The 920^{-1} band could be due to kaolinite (higher in the E horizon).

The difference between different horizons suggested a differential weathering of different minerals: the absorption bands at 830 cm^{-1} (showing the AlMgOH groups), 820 cm^{-1} (FeFeOH), 786 cm^{-1} (MgFeOH) decreased from the most weathered (E) to the least weathered (Bs, A) horizons.

Strangely, there was a lower proportion of trioctahedral Fe in smectites in the Bs than in the E horizons (690-680 cm^{-1}), maybe because of chemical reduction due to waterlogging.

The higher quantity of Si-Al-O and of quartz (779, 799 cm^{-1}) in the E than in the Bs was verified.

4.4 Discussion and conclusions

Mass transport calculations showed that the weathering of ultramafic and mafic material in the studied subalpine soils have similar paths as ophiolitic materials in temperate or boreal environments. For example, the strong Mg loss is nearly always observed in surface horizons (Kierczak et al. 2007, Bonifacio et al. 1997, Lee et al 2003, Bulmer 1992, Rabenhorst 1982). The strong Mg-loss was often observed in podzolic soils (Egli et al. 2006), in soils rich in Fe-Mg silicates.

The increase in Al concentration towards the surface is common in serpentinite soils, but not on mafic substrates. This trend was verified in the study area. It is often thought that this surface Al accumulation is due to input of alloctonous material, but in the 3 pedons the depth trend of the Ti/Zr ratio excluded important inputs of felsic materials on the surface. On serpentinite, Al was residually accumulated in the most weathered horizons because of the relative stability of Al-bearing minerals (mainly chlorite and its weathering products) in comparison to serpentine. The latter, in strongly acidic soil conditions, is particularly unstable and dissolves easily. Similarly, Ca was residually accumulated because of the relative stability of amphiboles and plagioclases in comparison with serpentine, and because of biocycling.

The progressive Mg loss and the Ca concentration are ecologically important: with time, weathering in temperate environments helps to reduce the strength of the “serpentine factor” (Alexander 1998).

Ni shows a strong leaching from surface horizon: this metal is often included in easily weatherable serpentine minerals (Kierczak et al 2007). A much stronger than usual weathering environment was evidenced by the strong Cr leaching from the upper horizons, which is unusual also in subalpine or boreal soils (for example, Bulmer 1992). Fe was also mobilized from weathered material. The mobility of these two elements, normally residually accumulated in the surface horizons of “serpentine soil”, was probably related with the extreme acidification caused by the vegetation and the subalpine wet and cold climate, and with the complexing agents associated with the podzolization process. The role of organic acids in removing heavy metals (included Fe and Cr) has been demonstrated by Schreier et al (1987).

Kierczak et al. (2007) showed how climate affects Ni and Cr mobility in temperate soils: humidity enhances Mg and Ni leaching, by decreasing pH values, while in the driest sites Ni was more stable and only Mg content was visibly diminished in the soil horizons. In the strong weathering environment found in subalpine forests, with precipitation values above 1000 mm, a deep and long-lasting snow cover and frequent summer rainfalls, associated with average yearly temperature between 0° and 2°C, also the least mobile elements were mobilized (Cr and Fe). In the Polish soils, developed under a quite cold and dry climate, Fe and Ni tended to be diluted in surface A horizons, probably because of the presence of alloctonous glacial materials; as already stated, this seems not to be the case in the studied soils in the western Alps. Bulmer (1992) verified the different leaching rate of Ni in response to a humidity gradient.

In the warmer and submediterranean climate of Monte Prinzera (Northern Apennines, Italy), element mobility was different: surface horizons were impoverished in both Ca and Mg, while Fe, Cr and Mn were the least mobile elements and accumulated in the topsoil (Venturelli et al. 1997). Mn, in subalpine areas of the western Alps, is one of the most mobile elements (chapter 5).

Mineralogical properties verified this particularly aggressive pedo-environment: resistant spinels were effectively dissolved in the most weathered soils horizons. Dissolution of spinels has been demonstrated in hydromorphic soils (Fisher 2008), but there are no evidences, in the literature, of their dissolution in extremely acidic podzolic soils because of low pH values and / or chelating organic acids. The same trend was shown by primary minerals.

Dissolution is probably the most important process affecting serpentine minerals, and this explains the extremely high Mg-loss from the most weathered horizons. Dissolution affecting these minerals was shown also by Buurman et al. (1988): ultramafic rocks usually weather to oxidic rather than clayey materials, so the clays found in serpentine soils are probably the result of chlorite weathering. In the studied subalpine soils, the pedogenic processes removed the oxides from the most weathered and acidic near-surface horizons, so that an unusual metal-poor E horizon could form.

The inverse correlation existing between the content in chlorite and smectites/vermiculites, though not significant from a statistical point of view because of the small number of samples and the lack of precision in quantification methods, is an evidence of the transformations of chlorite, while serpentine content is uncorrelated due to the scarcity of its weathering products. The weathering of chlorite to smectite and vermiculite in alpine acidic soils, via removal of hydroxy-interlayers and reduction of layer charge, was demonstrated by Carnicelli et al. (1997) and by Mirabella and Egli (2003). Normally, Mg is substituted by Al and Fe in the octahedral sheet (Mirabella and Egli 2003): in the studied ultramafic soils, the early transformation of primary Mg-rich chlorites into pedogenic Fe-rich chlorite was verified by XRD analysis. This was the first weathering reaction affecting chlorite minerals, which were mostly Fe-rich in the Bs horizons, probably because of removal of brucitic layers caused by low pH values, substituted by illuvial Fe^{3+} deposited in partially accessible interlayer space. According to Carnicelli et al. (1997), Al is deposited in the interlayer space, but in the studied soils the lack of Al and the abundance in Fe released by serpentine and magnetite dissolution increase the probability of Fe substitution.

In Bs horizons, hydroxi-interlayered minerals appeared, which represented the second step in chlorite weathering. Trioctahedral occupancies were still common, according to the IR spectra.

In the more weathered E horizons, a large quantity of Mg is removed from the clay mineral structure, and dioctahedral vermiculites and smectites formed. The interlayer charge of smectites was usually quite high, showing an incomplete evolution of these soils. The presence of Al-rich smectites (beidellites) is highly probable, because of mass balance calculations, but needs to be analytically verified (KOH, KCl and heat treatment); an Al substitution is in agreement with literature (Al usually accumulates in the most weathered horizons on ultramafic materials, Noack and Colin 1986). XRD spectra, however, showed a Fe-enrichment in soil chlorite minerals.

The pathway from chlorite to vermiculite, through loss of hydroxy-interlayers (Buurman et al. 1988) is well known and described worldwide, on many types of substrates.

The last weathering product of chlorite was probably kaolinite, which was detected by IR spectra in E and AE horizons. Its scarcity in surface horizons and its higher content in the E ones can be considered a proof that its origin was not aeolian (as often assumed in podzols). Smectite (particularly beidellite) transformation into kaolinite in acidic soils was demonstrated by Karathanasis and Hajek (1983).

Probably, the constant Al content with depth in the soil profiles depended from its inclusion in stable groups of chlorites and in their weathering products (Mg-rich chlorites, soil Fe-chlorites, hydroxy-interlayered minerals HIV and HIS, smectites and vermiculites). This mineral sequence is more stable than serpentine, which tended to dissolve in these extremely acidic soil environments.

The dominance of smectites in the mafic soils (P1) could be traced back also to the transformation of biotite (trioctahedral mica, Egli et al 2008), which is a quite abundant component in metamorphic gabbros.

The cementing agent of the deep Bsm and Cm horizons in P1 was probably composed of illuvial silica (opal), as often happens on mafic or ultramafic parent materials (Bulmer 1992, Alexander et al. 1994), produced by the dissolution of easily weatherable mafic and ultramafic primary materials.

The abundance of talc in the most weathered horizons needs further discussion; similar trends were shown by Chardot et al. (2007).

The weathering paths of the main ultramafic rock-forming minerals show how heavy metals are easily released from them. In fact, Ni and Cr (Manceau et al. 1985, de Caritat et al. 1993) are often located in the octahedral sheet of chlorite minerals, substituting for Mg or Fe^{2+}. The octahedral layer in trioctahedral chlorite is the first to be attacked by weathering, as demonstrated by the early transformation from Mg to Fe-rich mineral. An early release of heavy metals derived from chlorite weathering is highly probable. It is however possible that Ni and Cr are conserved in the octahedral sheet during Fe substitution for Mg, and are later released by subsequent pedogenic processes. The conservation of heavy metals through the weathering stages of serpentine is demonstrated by Caillaud et al. (2009), but the soil and environmental characteristics are extremely different from the ones observed in subalpine forests (pH values around 7, low metal mobility and leaching).

Serpentine dissolution in extremely acidic pedo-environment is, however, the main cause of Ni release into the potentially available form, as Ni^{2+} easily substitutes Mg^{2+} in serpentine minerals, because of similar ionic size and equal charge.

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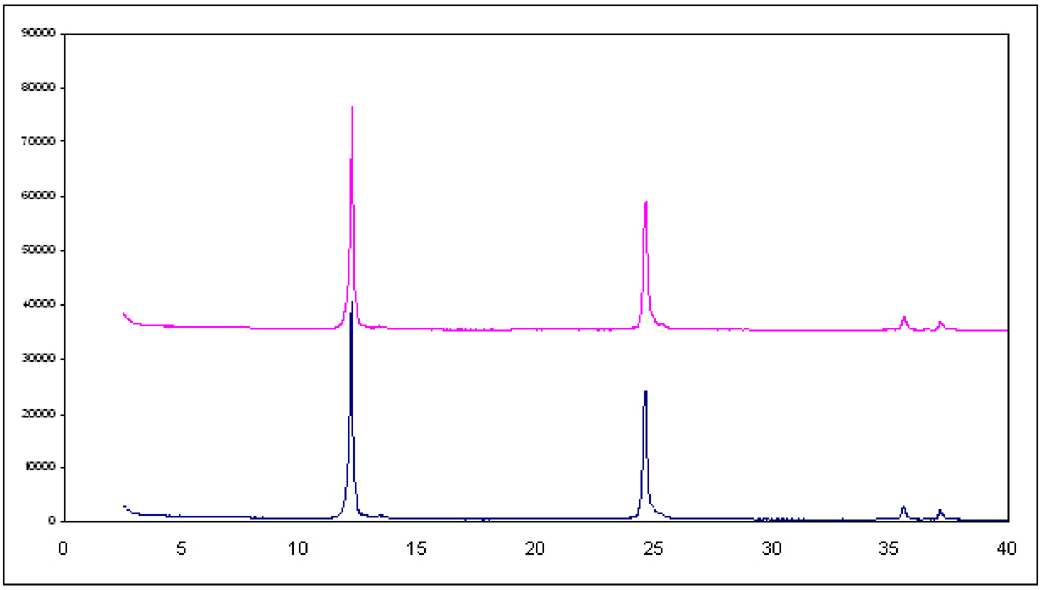

Fig. 4.1: diffraction patterns of weakly weathered serpentinite samples.

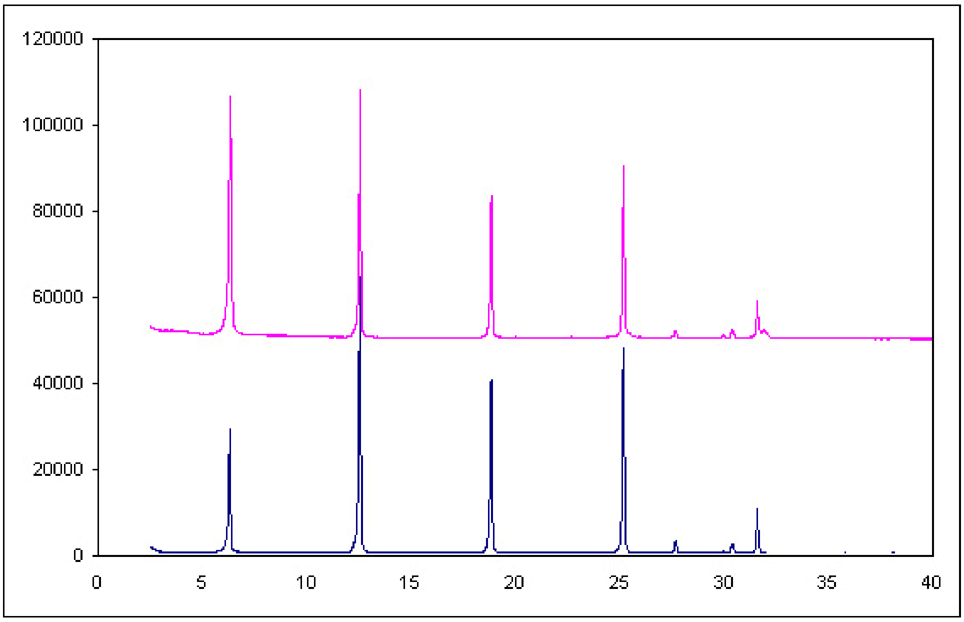

Fig. 4.2: diffraction patterns of a chlorite-schist sample.

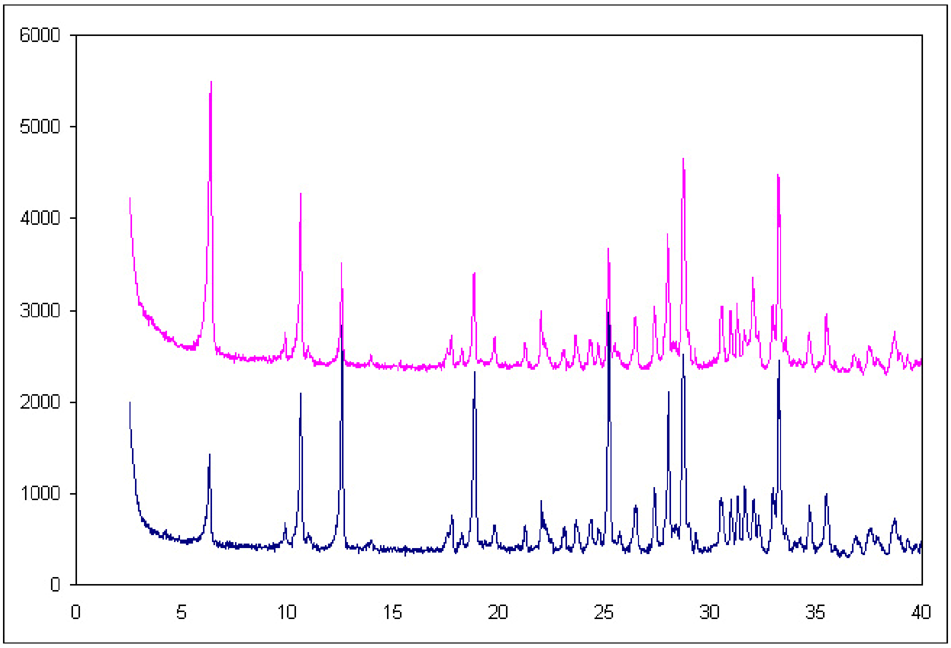

Fig. 4.3: diffraction patterns of a meta-gabbro sample. Chlorite peaks are clearly visible.

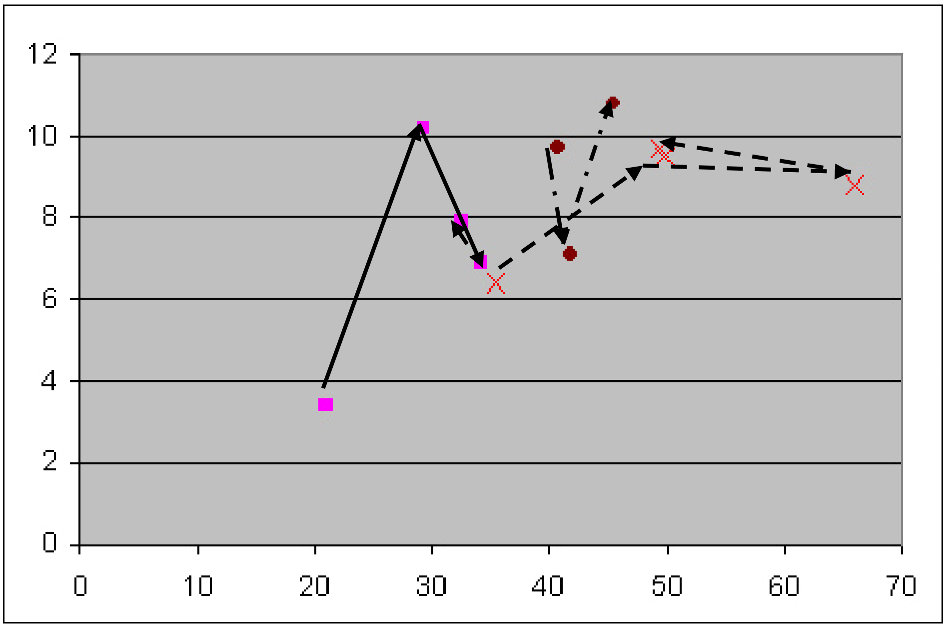

Fig. 4.4: silt (x axis) and clay (y) ratio in the 3 soils. Arrows indicate decreasing depths. Squares are P1, circles P135, crosses P134.

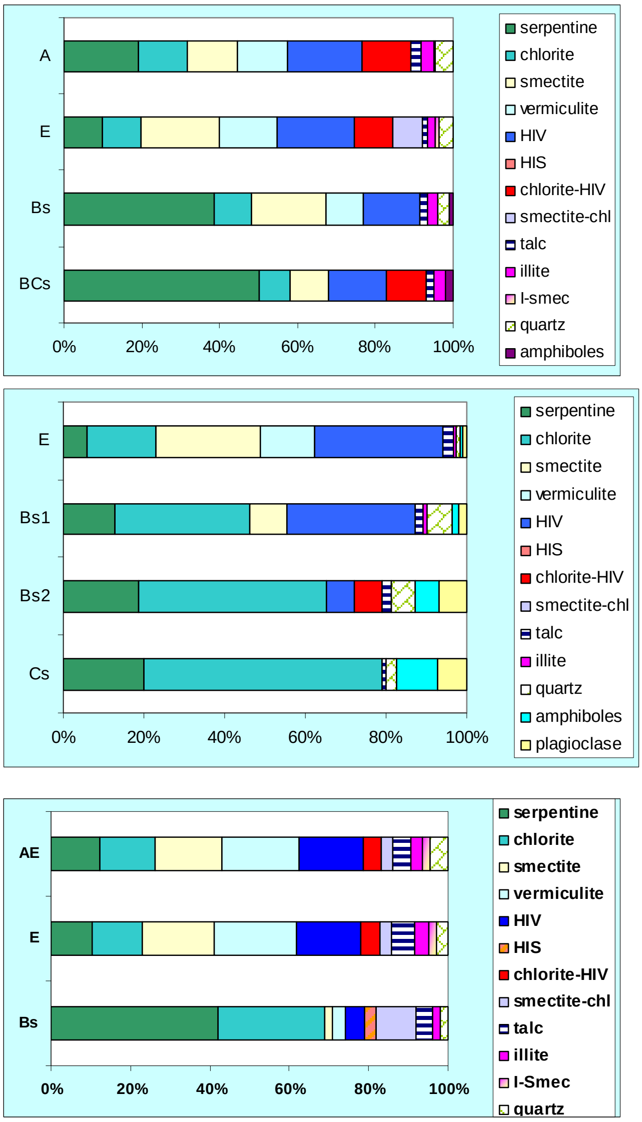

Fig. 4.5: clay minerals in the studied pedons (from semi-quantitative calculations); a (top left): P135; b (top right): P1; c (bottom left): P134

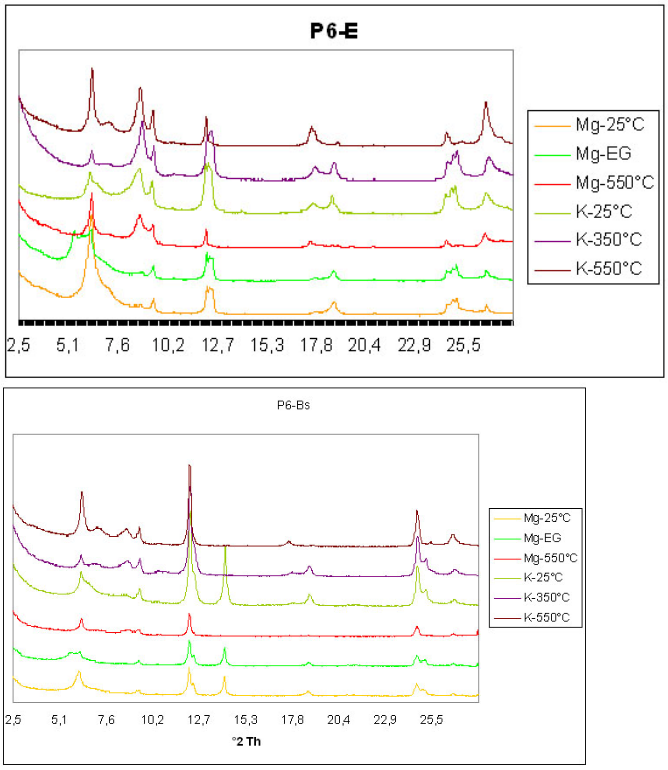

Fig. 4.6a, b: XRD diffraction patterns for P134 (E and Bs horizons).

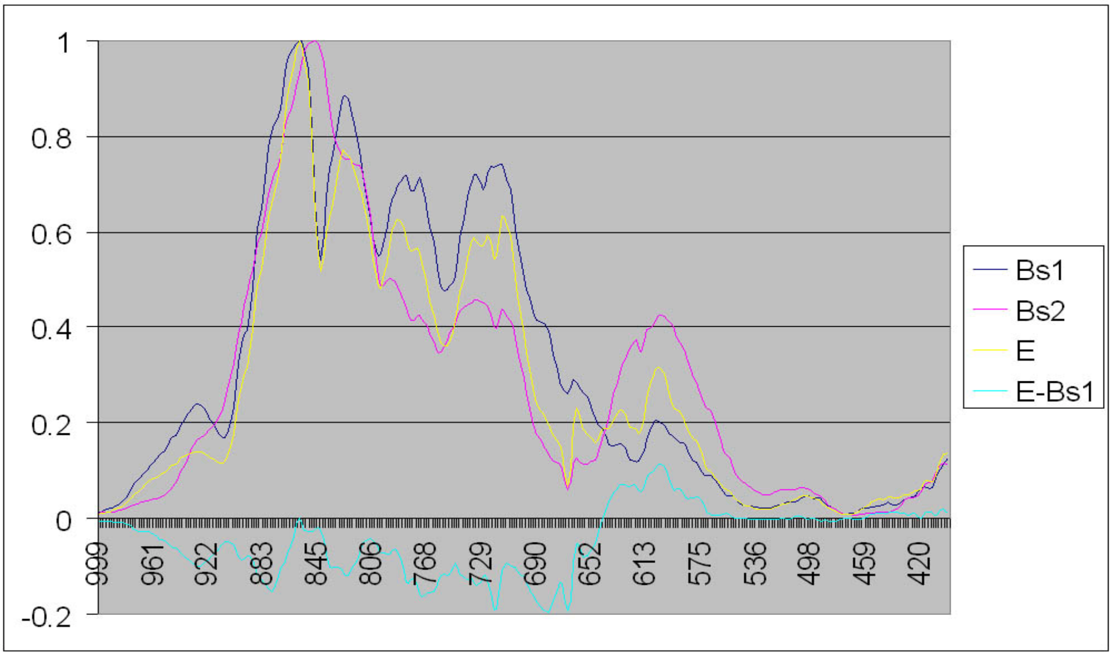

Fig. 4.7: IR spectrum of OH bending region of P1

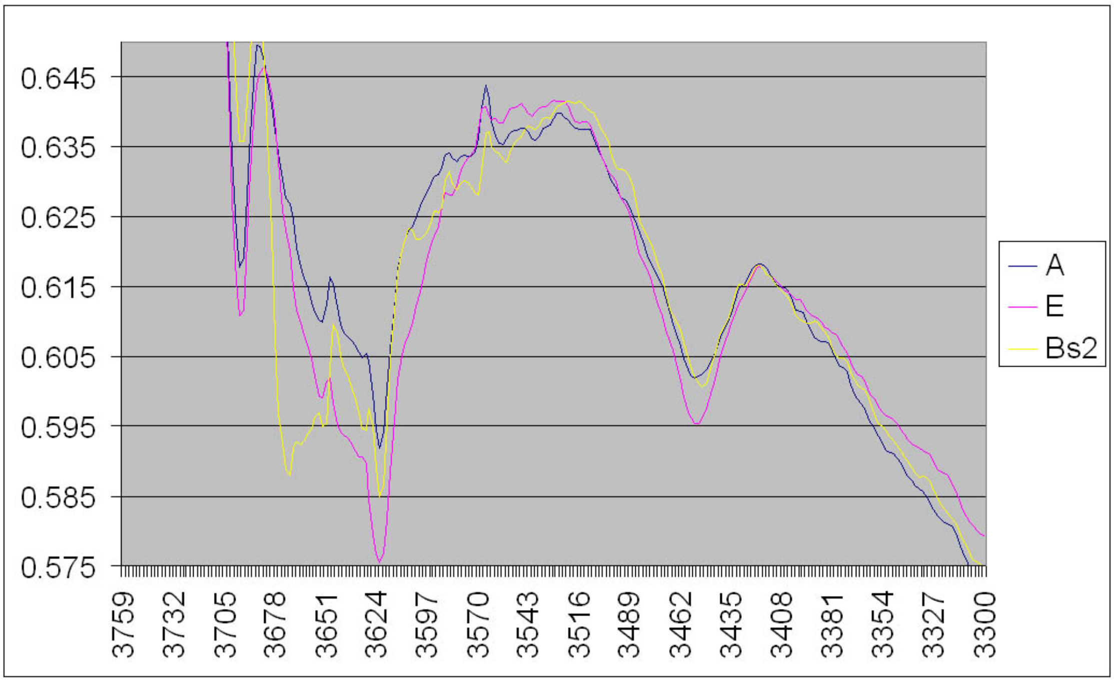

Fig. 4.8: OH stretching region of P135.

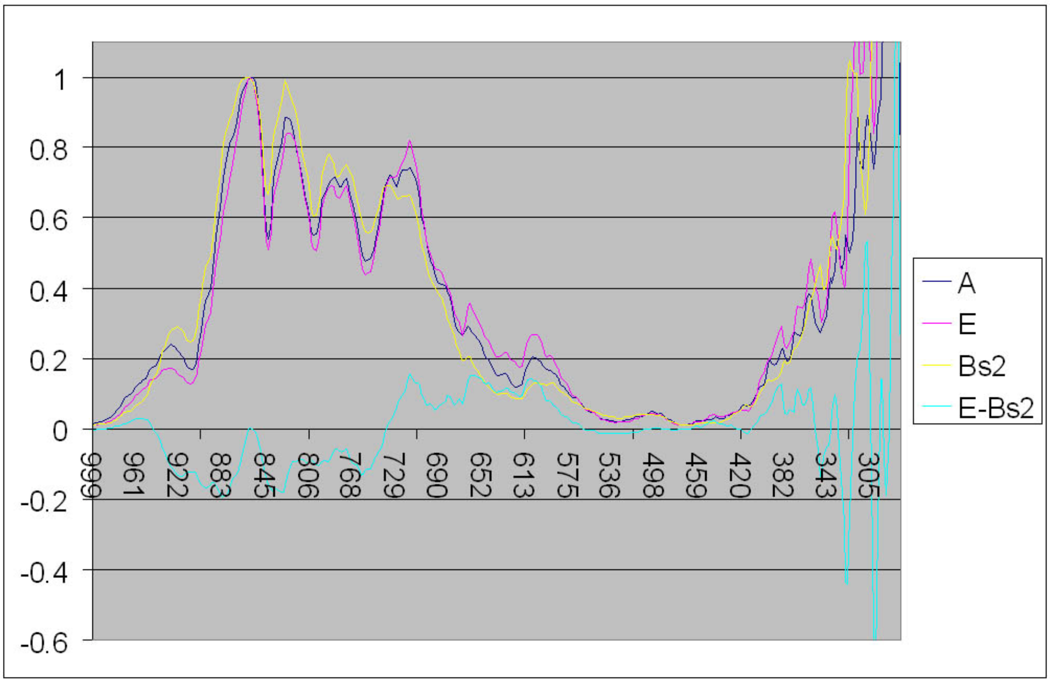

Fig. 4.9: OH bending region of serpentinic P135.

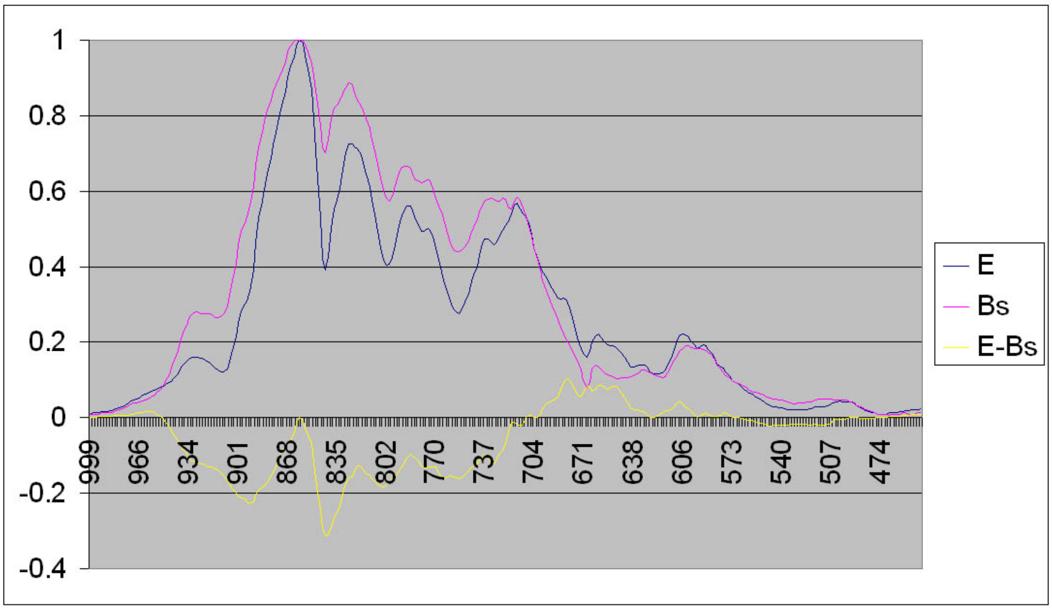

Fig. 4.10: OH bending region of serpentinic P134.

Tab. 4.1: chemical composition of weakly weathered serpentine samples in the study area.

	Na	Mg	Al	Si	Ca	Cr	Mn	Fe	Ni
	%	%	%	%	%	%	%	%	µg/g
SERP1	0.029	24.76	0.33	19.45	0.02	0.45	0.11	6.18	1325.0
SERP2	0.024	25.76	0.01	20.23	0.05	0.06	0.06	2.14	825.6

Tab. 4.2: chemical composition of weakly weathered chlorite-schist samples.

	Na %	Mg %	Al %	Si %	Ca %	Ti %	Cr %	Mn %	Fe %	Co µg/g	Ni µg/g	Cu µg/g
CLOR1	0,032	18,58	7,61	15,43	3,02	0,011	0,2383	0,1058	4,614	< 31	1274	< 3.4
CLOR2	0,030	20,07	7,171	14	0,033	0,02	0,00997	0,06797	4,469	< 29	998,2	2,7

Tab. 4.3: chemical composition of mafic rocks in the study area.

	Metagabbro	*Prasinite*	*Anfibolite*
SiO_2 (%)	46,1	42,4	36,2
Al_2O_3 (%)	15,7	10,6	11,8
Fe_2O_3 (%)	4,3	10,6 (±3)	7,8
MgO (%)	15,6	18,2 (±5)	31,0 (±2)
CaO (%)	10,5	7,6 (±2)	7,8 (±4)
K_2O (%)	Trace	Trace	trace
P_2O_5 (%)	Trace	Trace	trace
Na_2O (%)	2,15 (±1)	0,6	0,05
Cr_2O_3 (µg/g)	2654	506 (±200)	860
NiO (µg/g)	310	284	1390
Cu_2O (µg/g)	11,2 (±7)	12,3	5,6
TiO_2 (%)	0,23	3 (±2)	0,05
Zr (µg/g)	7	72	1,8
MnO (%)	0,06	0,21 (±0,1)	0,09

*Tab. 4.4: open system mass transport functions (Tj,i) of the main elements in the 3 studied soils. BD: Bulk density, g*cm*$^{-3}$

T j,w (Ti)	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	Ni	Cr	Cu	BD
P1E	-0,62	-0,50	-0,37	-0,48	-0,60	-0,70	-0,54	-0,98	1.25
P1Bs1	-0,60	-0,51	-0,49	-0,60	-0,32	-0,66	-0,48	-0,94	0.96
P1 Bs2	-0,42	-0,32	-0,39	-0,57	-0,17	-0,33	-0,29	-0,39	1.42
P1 CB	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1.51
P135AE	-0,18	0,06	-0,11	-0,35	-0,05	0,16	-0,05	-0,14	0.88
P135E	-0,42	-0,02	-0,22	-0,34	-0,43	-0,50	-0,36	-0,79	0.77
P135Bs	-0,13	0,00	-0,06	-0,14	-0,06	-0,11	-0,10	-0,46	1.41
P135BCs	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1.56
P134AE	-0,77	1.04	-0,45	0.91	-0,49	-0,86	-0,81	-0,76	0.98
P134E	-0,75	0.84	-0,41	0,33	-0,50	-0,86	-0,80	-0,90	1.16
P134Bs	-0,56	0.61	-0,30	0.04	0,02	-0,68	-0,64	0,64	1.21

*Tab. 4.6: clay minerals detected in the studied soils. ****>50%, ***25-50%, **12-25%, *5-12%, ++3-5%, +1-3%, . <1%. Plg is plagioclase*

Pedon	Hor.	Serp	Chl	HIS	HIV	Smect.	Verm.	Amph	Plg.	Mica/ illite	Talc	Qtz
P1	E	*	**		***	***	**	+	+	+	++	*
	Bs	**	***		***	*		+	+	+	+	*
	Bsm	**	***		*			+	*		+	++
	Cm	**	****					*	*		.	++
P135	A	***	**		**	**	**			++	*	*
	E	**	**	**	***	***	***			+	+++	+
	Bs1	***	*		*	*	*	+		.	+	+
	Bs2	****	*		+	*		+		++	+	
P134	AE	**	**		**	**	**			+	++	++
	E	*	**		**	**	**			++	*	+
	Bs	****	***	+	+	+	+			+	+	.

Tab. 4.7: magnetic mineral content (%) in the studied soils.

	Magnetic minerals %		Magnetic minerals %
P1E	0.92	P135Bs1	4.10
P1Bs	0.86	P135Bs2	5.45
P1Bsm	0.80	P134AE	1.42
P1Cm	1.30	P134E	1.03
P135A	4.20	P134Bs	4.09
P135E	2.57		

5. Heavy metal speciation and mobility along altitudinal gradients on ophiolites.

Abstract

Soils on ultramafic materials are usually rich in Mg, Fe and heavy metals (particularly Ni, Cr, Mn, Co). These chemical properties could cause toxicity effects on biological communities.

Metal fractionation/speciation/partitioning shows the soil phases to which metals are associated (i.e., soluble, exchangeable, associated with organic matter, with amorphous or crystalline Fe and Mn oxides, residual), and thus it is strictly related with their bioavailability.

Ni, Cr, Mn and Co partitioning (6 fractions) have been analysed in 7 montane, 6 subalpine and in 17 alpine (i.e., above the present-day treeline) soils in the ophiolitic area of Mont Avic Natural Park (Valle d'Aosta, Italian Alps), on soils formed from metal-rich serpentinite or from metal-poor mafic rocks and calcschists. The results show a tight relationship between vegetation, soil forming processes, metal speciation and bioavailability: below and above the present-day treeline soil forming processes and metal fractionation change dramatically.

Under subalpine forest, the main pedogenic process is podzolization. In these extremely acidic and leached soils, all metals are mobilized and their lowest concentration is in the bleached E horizons, while there is a higher value in organic matter-rich surface horizons and in the illuvial Bs. All the fractions of Ni, Co and Mn are strictly correlated with each other: in A and Bs horizons, the greatest fraction (not in the primary minerals) is associated with organic matter and with crystalline Fe-oxides. Cr is less released by weathering, and the greatest fraction is together with organic matter and amorphous Fe-oxides. No Cr could be detected associated with Mn oxides.

Above the treeline, the situation changes dramatically. Leaching is important only in stable, flat areas, while usually metal concentration increases in surface horizon because of stabilization by organic matter. Co and Ni are not correlated with Cr and Mn. The most important factors in determinibg available metal content are erosion and cryoturbation.

5.1 Introduction

Soils over ultramafic materials (often called "serpentine soils" by ecologists) usually contain very high Mg (18–24%), Fe (6–9%) and heavy metals (particularly Ni, Co, Cr and Mn), but very low Ca (1–4%) and Al (1–2%) (Alexander 2004). Mg and Ni probably cause the most significant ecological effects. Ni impact on serpentine ecological systems is controversial: according to many researchers, its effect is negligible if sufficient nutrients are available (e.g., Chiarucci et al. 2001). However, the importance of metals in serpentine plant ecology is shown by the presence of species which hyperaccumulate them, normally endemic to ophiolitic habitats.

The identification of metal-bearing phases is a primary step to understanding the fate of trace elements in the soil–plant system. Thus, the solid fractionation/speciation/partitioning of elements in the soil matrix is of primary interest in order to predict their potential mobility, availability and toxicity for plants and other soil-dwelling creatures.

Pedogenesis and weathering of the parent material release metals from the crystal structure of primary minerals (depending on their weatherability) and create "new" materials with different stability, chelating properties and cation exchange capacity (CEC), depending on climate, vegetation, organic matter biocycling, topography and drainage. Climate is one of the most influential factors (Kierczak et al. 2007): in tropical environments, climax soils on serpentinite are strongly weathered lateritic soils, and heavy metal chemistry depends on Fe and Mn oxi-hydroxides, and their concentration often reaches extremely high values (Becquer et al. 2006).

In temperate soils, weathering leads to the formation of clay minerals, and metal geochemistry depends more on primary and secondary phyllosilicates and on organic matter bio-geo-cycling (Chardot et al. 2007).

Very few data are available about metal speciation in boreal, subalpine or alpine environments (Roberts 1980, Bulmer and Lavkulich 1994, Gasser et al. 1994, Wenzel and Jockwer 1999). Nevertheless, this is an interesting subject, as subalpine and alpine environmental conditions (acidifying vegetation, high humidity and leaching) should enhance metal mobility and, perhaps, bioavailability and toxicity. Moreover, it is often thought that mineral weathering should be higher in warm and wet climates in respect to cold ones, but this is not always true (Hall et al. 2002). In temperate mountain habitats, in particular, mineralogical evidences show that the highest weathering rates should be at the subalpine altitudinal level, where the balance between cool temperatures and high humidity and acidity produced by the vegetation enhance the mineralogical transformation and the element mobilization (Egli et al. 2004). Weathering rate is slower in the warmer montane level.

Metal availability depends also on their origin and on other edaphic properties. Soil pH is probably one of the most influencing factors, and it is often inversely related with labile and bioavailable forms of many metals, particularly Ni in acidic soils (Echevarria et al. 2006), but previous works in alpine and temperate areas (Chardot et al. 2007) show a direct correlation, probably due to high leaching at low pH values.

It is thus suspected that at different altitudes (meaning different climates and plant covers) the metal speciation, mobility and bioavailability should be different.

The goals of this study were to investigate heavy metal partitioning and bioavailability on different ophiolitic rocks, at different altitudes and under different plant covers and climates. As already stated, metal speciation, mobility and availability have seldom been studied in mountain or boreal habitats, particularly in high altitude or subarctic habitats. How pedogenic processes and environmental properties influence metal speciation is of crucial importance to understand the fate of anthropogenic pollutants and metal ecology. Metal speciation, mobility and availability in soil catenas can also represent a changing metal geochemistry in naturally metal-rich soils under a changing environment.

5.2 The studied soil profiles

The investigated soil pits were developed under montane forests (*Pinus sylvestris* on xeric south-facing slopes, and *Fagus sylvatica* on humid north-facing ones), *Pinus uncinata* Miller and *Larix decidua* subalpine forests and ericaceous shrubs, and under alpine and snowbed vegetation (chapter 2, and D’Amico and Previtali 2009). Substrate and climate is described in chapter 1 and 2.

Soil forming processes are different at different altitudes according to many factors (chapter 2), the most important of which are aspect, vegetation and disturbances (erosion-deposition and cryoturbation). Under xerophilous Scotch pine (*P. sylvestris*) forests at the montane level, acidification is limited, while the low humidity inhibits weathering and leaching. Soils were often classified as Regosols or Cambisols. In the humid beech forests on north-facing slopes, weathering and leaching are more intense: soils are strongly acidic Dystric Cambisols.

Under subalpine vegetation (dominated by *Pinus uncinata* M. and *Larix decidua*), the podzolization is the most important process (D’Amico et al. 2008). Above the treeline, the pedogenic processes diverge in relation to topography and substrate. No single typical soil-forming process is recognizable: acidification is important on stable surfaces under high vegetation coverings, while cryoturbation and erosion/deposition are widespread and “rejuvenate” soils by mixing and removing surface layers.

5.3 Materials and methods

The 33 investigated soil pits were representative of the typical soils formed in the study area in the different phyto-climatic conditions. They were selected as representative among 198 previously observed and analyzed soil pits (chapter 3). Soil sampling took place in late August 2008 (except for subalpine podzols, D'Amico et al. 2009). Around 500 g of soil from each genetic horizon were collected in order to make chemical analyses. Rock fragments were separated, cleaned (using a Calgon solution), observed, divided according to the different lithologies and weighted, in order to distinguish the proportions of the different rocks in the morainic or detritic parent material.

The pedons were classified according to the WRB (IUSS Working Group 2006).

The following chemical analyses were performed on each sample, after drying at air temperature and sieving at 2 mm, according to standard methods (Ministero delle Politiche Agricole e Forestali 2000): pH (in water and KCl, 1:2.5 solution), exchangeable bases (extracted with $BaCl_2$ – TEA and ascertained using Flame Atomic Absorption Spectroscopy, FAAS) and total exchangeable acidity; spodic properties were determined by oxalate extractable Fe and Al. The CEC was calculated by sum of exchangeable bases and acidity. Total Organic Carbon (TOC) and N were analyzed by CN elemental analyzer (Thermo Electron, NC Soil); particle size distributions were determined by the pipette method and sieving. The chemical composition of rock samples was determined by X Ray Fluorimetry (XRF).

"Available" Ni, Co, Cr and Mn (Ni_{av}, Co_{av}, Cr_{av}, Mn_{av}) were extracted by 0.1M ammonium acetate-EDTA (2.5 g of soil in 25 ml of solution, shaken for 30'). Cr(VI) was measured using the diphenyl-carbazide method (Bartlett and James 1996) after 0.1M KH_2PO_4 extraction on field-humid samples.

The "operationally defined" fractionation of metals among the compartments of the soil solid phase was investigated by selective sequential extraction (SSE). It was performed on 1 g of soil. Ni, Co, Cr, Mn and Fe were determined with FAAS. After each extraction, the samples were washed with 10 ml demineralised water, centrifuged and dried at 50°C. A seven step scheme, modified from Tessier et al. (1979), was implemented (Table 5.1). A shortcoming of SSE analytical methods is the absence of a standard sequence of extractants. As Quantin et al. 2002, we choose to extract metals associated with organic matter before the crystalline oxide-associated fraction, but this could lead to a partial oxidation and solubilization of Cr (overestimation Cr associated with TOC and an underestimation of crystalline oxide fraction). Oxalate is also known to extract fulvic acids, thus decreasing the fraction of metals extracted in the following step.

5.4 Results

5.4.1 Nickel speciation

On serpentinite, the Ni_{tot} contents were in the normal range for "serpentine soils" worldwide (Brooks 1987). Above the treeline, the values were similar to the ones found in primitive and non-acidified "serpentine" soils, in alpine (Roberts 1980) and in temperate mountain habitats (Robinson et al. 1997). These values were much higher than in typical subalpine or montane soils in the study area (tab. 5.2). Above the treeline, Ni_{tot} was particularly high also in deep horizons on calcschists and gabbros (nearly 10 times higher than its typical content in soils formed from similar rocks). Abrupt changes in the Ni_{tot} depth trend depended mostly on lithological discontinuities (P11, P37) among different horizons, related with solifluction and erosion-deposition processes.

On all parent materials in the typical subalpine soils, Ni_{tot} (table 5.2) was similar to the contents found in acidified soils formed in temperate or tropical humid montane climates on similar substrates (Brooks 1987, Hseu 2006, Chardot et al. 2007).

On serpentinite, labile forms of Ni (Ni_{aq}, Ni_{ex}, Ni_{mn}) changed widely with altitude (tab 5.3). The lowest values (% Ni_{tot}) were in subalpine podzols. This was probably due to the leaching caused by the complexation and cheluviation related with the podzolization process, the high acidity and the temporary reductive conditions at snowmelt. The low Ni_{mn}/Ni_{tot} and Ni_{ex}/Ni_{tot} in the most acidified forest soils verified this leaching. Moreover, Ni_{aq} usually was below the detection limit in subalpine podzols (an exception was P135, where illuviation from upslope areas increased its content in the top horizon). The strong acidity and humidity did not permit the accumulation of Ni associated with Fe oxides in deep horizons of soils formed on serpentinite, differently from what shown by Bulmer (1992).

P148 is a subalpine soil, but it is developed in a serpentinic rock crevice, and its pedogenesis is blocked by the extreme steepness and the hardness of the substrate. Waters flowing on the rock surface collect the released elements from the weathering of the rock, and the high CEC of the soil material (these soil types are characterized by a great enrichment in organic matter) blocks them within the pedon.

In montane soils, Ni speciation was somehow similar to subalpine soils (tab. 5.2), but its pedogenic/total ratio was often higher because of the weaker leaching, caused by the weaker acidity, humidity and cheluviation processes. Montane soils in the Alps are usually less developed than subalpine ones, because of lesser humidity and a higher evapotranspiration (Egli et al. 2004). On serpentinite-dominated substrates, Ni_{ex} was everywhere higher than 1 $mg*kg^{-1}$, which is the limit above which toxic effects are highly probable (Wenzel and Jockwer 1999). In Austrian raw montane soils formed on serpentinite, the values were much lower than in analogous habitats in Mont Avic Natural Park.

Above the treeline, the Ni partitioning radically changes. Labile forms represent a larger fraction of total Ni. The high values observed in deep horizons on calcschist are notable.

In these high-altitude soils, Ni_{org} usually showed a decreasing trend with depth, in good correlation with TOC. In subalpine podzols this trend was different because of the illuviation of organic matter associated with metals in the spodic Bs horizons (fig. 5.1). Above the treeline, Ni_{org}/Ni_{tot} was higher than in montane and subalpine soils, probably because of the slower TOC decomposition rate caused by low temperatures.

In most soils, under forest or alpine vegetation, the Ni_{ox} and Ni_d depth trend was significantly correlated with the respective forms of Fe and Co, while Mn and Cr showed different geochemistry, particularly above the treeline. The association of Ni with primary minerals (Kierczak et al. 2008) seemed not to be important.

5.4.2 Chromium speciation

Total Cr was highest on serpentinite (Table 5.3) but in soils formed from mainly mafic materials it was much higher than usual (on mafic rocks it is usually around 200-300 mg kg^{-1} [Brooks 1987]), maybe because of the presence of Cr-rich chlorite in the parent material (chapter 3). The lowest Cr_{tot} values were found on calcschists.

The Cr_{tot} depth trend in subalpine soils suggested an unusual mobility of this element, which should be residually accumulated in the most weathered pedogenic surface horizons because of the high stability of Cr-bearing chromite and magnetite (Bulmer and Lavkulich 1994, Roberts 1980). The high Cr mobility was probably related to its high concentration in easily weatherable chlorites, and to a strong podzolization process (chapter 2). The low values in E horizons were not caused by dilution due to organic matter accumulation (Kierczak et al. 2008), as these layers were usually TOC-poor, neither to aeolian inputs of alloctonous sialic materials (D'Amico et al. 2008).

In alpine and in "xeric" montane soils, the Cr_{tot} often decreased with depth, in agreement with the literature. Increases in deep horizons were observed in some alpine soils, owing to lithological discontinuities among different soil layers caused by solifluction and erosion-deposition processes.

On serpentinite, Cr was mostly included in the crystal structure of primary minerals (residual fraction), particularly in montane and subalpine soils. The higher values of pedogenic Cr in young and disturbed soils above the treeline are not easily interpreted, as normally it is slowly released from primary minerals and included in "pedogenic" materials as time and weathering proceed. For example, in tropical mountain forest habitats in Taiwan (Hseu 2006), young soils in the high part of the landscape had a lower proportion of pedogenic forms and a higher residual fraction. In ancient soils in New Caledonia, in tropical climates, Cr was mostly included in secondary minerals (Garnier et al. 2006).

Cr_{aq} and Cr_{ex} were usually below the detection limit. Cr_{org}, Cr_d and Cr_{ox} values were high in montane and alpine soils. These forms were significantly correlated with the respective Fe forms particularly in the subalpine podzols, showing both the association of Cr with the respective Fe pedogenic oxi-hydroxides and a similar susceptibility to the cheluviation and illuviation processes of podzolization; here, the $Cr_{mn+ox+org+d}/Cr_{tot}$ ratio (fig. 5.2) was lower than in the other studied habitats, probably because of cheluviation and leaching.

Cr_{org} was very high in subalpine and alpine soils, showing the strength of Cr-organic matter complexes. The strong association with organic matter was also recognized by Juchler (1988) in subalpine soils in Switzerland.

The extremely low Cr_{mn} values verified the impossibility of the association between Cr and Mn: in fact, the first is easily oxidized, mobilized and leached in presence of Mn oxides (Fendorf 1995). The low Cr_d content could be due to analytical problems: this extraction was performed after the H_2O_2 one, which could have oxidized and solubilized also a part of the Cr associated with crystalline Fe-oxides.

The toxic Cr(VI) was high in some deep horizons (B and BC horizons in subalpine soils, or BC and C in alpine ones), despite the low pH and the high organic matter content. In fact, this form should be readily reduced to Cr(III) in acidic conditions in the presence of Fe^{2+} and organic matter (Fendorf 1995), but the high levels of Mn oxides oxidized Cr to the toxic forms. Temporary waterlogging at snowmelt, causing moderate reducing conditions, followed by drying, was in favour of the temporary reduction of Mn oxides and the simultaneous oxidation of Cr(III). While drying, Mn oxides could form again (Cooper 2002). The mobile and toxic Cr(VI) was scarce in montane soils, probably because of the weaker and shorter periods of waterlogging.

5.4.3 Cobalt speciation

In subalpine and montane forest soils, total Co was particularly low and similar on all substrata (tab. 5.4). At the alpine level, the Co_{tot} values changed widely on different substrata (they were highest on serpentinite, where its contents were similar to the alpine soils found by Roberts 1980), despite the higher leaching occurring here than in montane soils. The higher age and stability of montane and subalpine soils probably are the causes of the Co loss from forest soils.

The high weatherability of Co-bearing minerals was shown by the high fraction of Co associated with pedogenic materials ($Co_{aq+ex+mn+ox+org+d}/Co_{tot}$). In every soil, Co_d and Co_{ox} (Table 5.4, fig. 5.3) were in the same order of magnitude as in other subalpine soils (Bulmer and Lavkulich 1994).

In the forest soils, all forms of Co were quite well associated with the respective Mn and Ni forms, in agreement with Gasser et al (1994), while above the treeline they are correlated only with the respective Ni forms. A podzolic trend (accumulation in the Bs horizon) was visible for Co_{mn}, Co_{ox} and Co_{org}. The strong association with TOC, and with primary minerals, observed by Kierczak et al (2008) in montane serpentinite soils from Poland, was not observed here.
At the alpine level, Co_{av} (tab. 5.6) is much more concentrated than in Spanish alpine soils (Sanchez –Maranon et al. 1999), but slightly lower than in toxic Scottish soils (Slingsby and Brown 1977). The depth trend of pedogenic fractions changed according to the TOC content (which stabilizes metal oxides), to the solute inputs via waters flowing at the interface between permeable and impermeable layers, and to lithological discontinuities.
Weatherability of primary minerals, strong association with organic matter and leaching suggested high potential bioavailability of this metal in the studied mountain environments.

5.4.4 Manganese speciation

Mn_{tot} (tab. 5.5) depended on serpentinite content in forest soils, while, above the treeline, the highest values were found in soils formed from calcschists. On serpentinite, the values were normal for soils developed on such materials (Oze et al. 2004). The lowest values were on metagabbros.
In heavily cryoturbated alpine soils, Mn_{tot} was higher than in stable ones, because of the input of “fresh” weatherable materials on the surface, caused by pedoturbation, while in stable, older soils leaching reduces the contents. Its depth trend depended on chemical reductive processes (common at snowmelt) and the difference from impoverished surface horizons to deep ones sometimes was extremely high. Illuviation to B or BC horizons was also verified, particularly in calcschist soils under bleached AE horizons.
In subalpine forest soils, the cheluviation related with the podzolization process was active also on Mn, with a typical low values for most forms (tab. 5.5 and fig. 5.4), but not in hydromorphic ones, where Mn leaching characterizes also deep horizons (P134). These values were lower than in other subalpine, less acidic soils (Bulmer and Lavkulich 1994), because of the podzolization process, high acidity and seasonal waterlogging, which favoured strong leaching.
Water-soluble Mn_{aq} is above detection limit on calcschist and serpentinite, particularly in deep horizons, while it is often scarce or absent in top ones because of leaching. Subalpine podzols are particularly poor in the extremely labile form, because of the high acidity and the cheluviation process related with podzolization.

5.4.5 Bioavailable metals

The “bioavailable” Ni, Co and Mn showed different depth trends at the different altitudinal levels (tab. 5.6 and fig 5.5). Under montane forest, their concentration usually decreased at increasing depth, following mainly the TOC content and the weathering degree of the soil material. Under subalpine forest, the depth trend showed a maximum in the surface, TOC-rich horizons, a minimum on the severely leached and extremely acidic E and a slightly higher value in the Bs, probably resulting from the association between illuvial organic matter and amorphous, easily reduced Fe oxy-hydroxides. Above the treeline, a greater variability of morpho-pedogenetic processes caused the irregular depth trend and the differences between different soil profiles. The increase in deep horizon in alpine soils could be related with lithological discontinuities (for example, the C horizon of P11 was composed of serpentinite, while upper ones were developed from meta-gabbro debris, slowly flowing on top of the serpentinitic substrate because of cryogenic solifluction), or to lateral illuviation caused by the solute transportation if metals in the waters flowing at snowmelt. In fact, there are serpentinite outcrops upstream from these soils.

In alpine soils, EDTA extractable metals usually increased with depth on calcschists and metagabbros, whereas they were highest in the most weathered horizons on serpentinite.

Ni_{av}, Co_{av} and Mn_{av} were strictly correlated with each other in forest soils. Their highest correlation values were with the respective Mn-associated form, followed by the oxalate-extractable fraction, as shown for Mn by Gambrell (1996) and Quantin et al. (2002b). Organic forms and the ones associated with crystalline Fe oxides are less related with the so-called "bioavailable" fraction.

The comments will be mostly about Ni, which is probably the most biologically important metal (Chardot et al. 2007)

On serpentinite, Ni_{av} was particularly high at the alpine level, sometimes higher than in most alpine soils worldwide (tab. 5.6). For example, in the toxic soils of the Keen of Hamar, in Scotland (Slingsby and Brown 1977), the values were lower than in some heavily cryoturbated soils in Mont Avic ophiolitic areas. Alpine soils in Spain (Sanchez-Marañon et al. 1999) and in Newfoundland (Roberts 1980) showed 100 or 1000 times lower Ni_{av} values. On serpentinite, the highest Ni_{av} values were found in TOC-rich horizons, and rarely in B horizons (probably related with incipient podzolization processes and associated with illuvial organic matter and amorphous Fe and Mn oxides. Its values were normally higher than the toxic level (according to Gasser et al. 1994, this value is around 6 mg kg^{-1}). However, according to Angelone et al. (1990), Ni_{av} is toxic when above 20 mg kg^{-1}: this level is often surpassed in montane and alpine soils, while in the more leached subalpine ones they are only seldom found.

On different substrata, the Ni_{av} highest values were often found in deep horizons, probably because of inputs due to solute transportation in the waters flowing at the interface between soils and rocks and between soils and (temporary or perennial) frozen materials. This process was verified by the good correlation between the high Ni_{av} values, the abundance of labile forms and the high pedogenic fractions values on Ni-poor calcschists (P38, P37, P52, P56). It is known, in fact, that Ni in solution is easily sorbed onto reactive surfaces of oxi-hydroxides, organic matter and phyllosilicates at pH values higher than 5.5 (Juchler 1988).

High values were also found in montane soils. Ni_{av} content was lower in the extremely acidic and leached subalpine soils. In alpine soils, weathering released metals from the crystal structure of parent minerals, but the weak acidity and the continuous enrichment with fresh materials related with cryoturbation and erosion-deposition processes inhibit leaching. Subalpine podzols contained the lowest values, lower than in many temperate or boreal, well developed soils formed on ultramafic materials (Slingsby and Brown 1977, Lombini et al. 1998).

The most important factor influencing Ni_{av} content was TOC. There was a positive correlation with pH. This result is unusual: worldwide, Ni_{av} is negatively correlated with pH (Echevarria et al. 2006): low pH values increase metal mobility and bioavailability.

Ni_{av} was extremely high in some subalpine soils (P148), probably for the same reason explained in par. 5.4.1.

5.5 Discussion and conclusion

The stability of primary minerals influences the translocation rate of elements from resistant to bioavailable and labile forms. The main Ni and Cr-bearing rocks are ultramafic serpentinite and chloriteschists, while Mn was most concentrated in calcschists and Co in prasinites (table 3.1). Unfortunately, the metal content of the single metal-bearing rock-forming minerals in the study area is not available, but we can make some additional assumptions according to the literature. Cr usually substitutes Fe in resistant magnetite and chromite. In the studied soils, however, a large fraction was also included in weatherable chlorites (tab 3.1), which was the only rock-forming mineral in chloriteschists. Despite the high content also in easily weathered minerals, its mobility was weak in xeric montane and in alpine soils (residual concentration in the surface horizons). Up to 50% of Cr was however associated with pedogenic materials in alpine soils, particularly on Cr-poor calcschist, where the presence of resistant spinels was unlikely.

Ni is mostly included in easily weatherable serpentine minerals, substituting Mg. Thus, the release of large quantities of this metal into labile pedogenic forms is fast. Labile fractions (Ni_{aq}, Ni_{ex}, Ni_{mn}) reached high values, which are strongly correlated with the presence of serpentine-endemic species (chapter 2), where acidity and humidity were less important (montane soils) and where unweathered materials were added to surface horizons because of cryoturbation (alpine habitats).

Co is included in serpentine minerals as well, and, in some areas, also in spinels (Kierczak et al. 2007), but in the study area this was unlikely, as the pedogenic fraction was much larger than the one associated with the residual primary minerals in most soils, and its concentration was highest in spinel-poor prasinite. Its high content in mafic rocks could be due to an inclusion in amphiboles.

Soil-forming processes and development degree clearly influence metal partitioning, mobility and, perhaps, bioavailability and toxicity. The podzolization process is probably the most important one, and causes the strikingly different speciation and depth trend in subalpine forest soils, compared to montane or alpine ones. The difference with metal speciation in other soils developed on ultramafic materials in temperate (e.g., Caillaud et al. 2009) or tropical environments (e.g., Becquer et al. 2006) is great. Usually, the weathering processes concentrate metals in the secondary phases and increase the peculiarity of serpentine soils towards the soil surface, particularly where the hydrolysis strength is strong as in tropical environments. Metal oxide accumulation is the main feature of serpentine soils worldwide, because of the lack of Al in the parent material which inhibits clay genesis and transformation (Caillaud et al. 2009).

Comparing metal mobility on serpentinite in the mountain habitats in the study area (Italian Western Alps) with other soils developed in ultramafic materials in temperate or boreal environments, some common trends and some differences are visible. In the quite dry Polish climate (Kierczak et al. 2007), vertical variations in metal content in weakly developed soils were due to the presence of alloctonous glacial materials in surface layers. In well developed soils, Mg was strongly leached from pedogenic horizons, Fe was concentrated and Ni and Cr were diluted because of organic matter accumulation. Similarly, in soils formed from serpentinite in Central France (Caillaud et al. 2009), weathered horizons were enriched in Ni, Cr, Mn and Co, and only Mg was significantly leached and depleted in B and C horizons compared to the parent rock.

In wetter mountain habitats in France (Vosges mountains), Cr was accumulated in soil horizons, while Ni was strongly leached (Chardot et al. 2007). The same trend was observed by Quantin et al (2008) in the drier Czech republic; in this case, Ni was mostly included in amorphous Fe/Mn and crystalline Fe oxides, while Cr was mostly included in primary minerals.

In slightly warmer submediterranean climates on the Apennine range in Liguria, north-western Italy (Bonifacio et al. 1997), metal leaching was inhibited and metals accumulated in soil horizons in respect to the parent material in shallow and well drained summit soils, while a strong leaching was visible for Ni in the more humid and evolved soils downslope. Cr was always residually accumulated.

In soils developed in the cool and seasonally humid habitats in the mountains of British Columbia, Canada (Bulmer 1992), metal mobility strongly depended on average annual precipitation, which also influenced pedogenic evolution. In podzolic soils in the most humid areas, Ni, Mn and Co were mobilized and leached, while, in drier sites, only Ni was translocated from the surface horizons: the most mobile element was Ni. Cr was always the least mobile and available metal, also in the well developed podzolic soils, and showed a residual accumulation in the most weathered horizons.

In the subalpine podzols of Mont Avic Natural Park, all the metals were mobilized and strongly leached, Cr included. This was possibly due to the more humid summers of the European Alps, or to differences in the Cr-bearing primary minerals (high Cr concentration in easily weatherable chlorite instead of resistant spinels). A particularly "aggressive" environment in the studied forest soils is demonstrated by the decrease in magnetic minerals in the E horizons.

On mafic substrates (basalt, Néel et al. 2007), Ni is usually geochemically associated with Cr, and both are characterized by a low mobility and a low association with pedogenic materials. On mafic parent materials (meta-gabbros, amphibolites and prasinites) in the study area, the trend was similar to the one observed on serpentinite, but the absolute values were much smaller.

Overall, in temperate soils formed from ultramafic materials worldwide, Co, Mn and Cr leaching is not an important geochemical process, particularly in shallow and well drained soils. This is in agreement with what was observed in Mont Avic Natural Park in montane (particularly for Cr) and in alpine soils, where the general trend was similar (for Cr, Co and Ni), but with local changes caused by waterlogging at snowmelt and periglacial processes.

In subalpine soils, the leaching related with the podzolization process radically changed the metal distribution and speciation: the strong weathering caused by acidity and chelating agents released metals from the crystal structure of primary minerals, and the acidity and cheluviation solubilized the released forms. The result was the leaching of metals away from the profile, particularly from the most strongly weathered E horizons. A partial accumulation is observed in the underlying Bs horizons, but the total metals are usually less concentrated than in the parent material, as often observed in podzolic soils (Egli et al. 2000). As shown by Burdick et al. (1983), podzolic Bs horizons were a weak source of bioavailable heavy metals, as they prove to be mostly sinks: Fe oxyhydroxides tend to immobilize metals. EDTA-extractable Ni, Co, Mn, Cr were usually less concentrated than in the overlying A and AE horizons.

The high contents in labile and pedogenic fractions in weakly weathered alpine soils in the study area agreed with what found by Bulmer (1992), who stated that heavy metals are very easily released from serpentine minerals in the first stages of weathering. This was caused by the surface input of fresh, easily weatherable materials, which soon released metals into the pedogenic "forms".

Pedogenetic fractions are mostly associated with organic matter, probably because TOC strongly binds oxides and ions.

Cr(VI) was common in soils formed from serpentinite, where acidic condition enhanced its formation and maintained high levels in surface and ground waters (Oze et al. 2007), which brought this toxic metal form to deep horizons of soils formed from Cr-poor parent materials.

The contamination risk for surface and ground waters associated with heavy metals released from soils was quite high in the studied habitats, particularly on serpentinite, as revealed by the high labile fractions of Ni, Co and Mn, and the high Cr(VI) content. They were due to different soil-forming processes at the different altitudinal levels. A particularly high mobility of potentially toxic elements was verified above the treeline, where deep layers of soils formed on metal-poor parent materials were often enriched in labile (easily reducible, or associated to organic matter) fractions of many metals. The results shown above are of special interest for geochemists and environmental scientists concerned with the mobility and availability of heavy metals in terrestrial environments: pedogenic processes are active on primary minerals and on anthropogenic contaminants,

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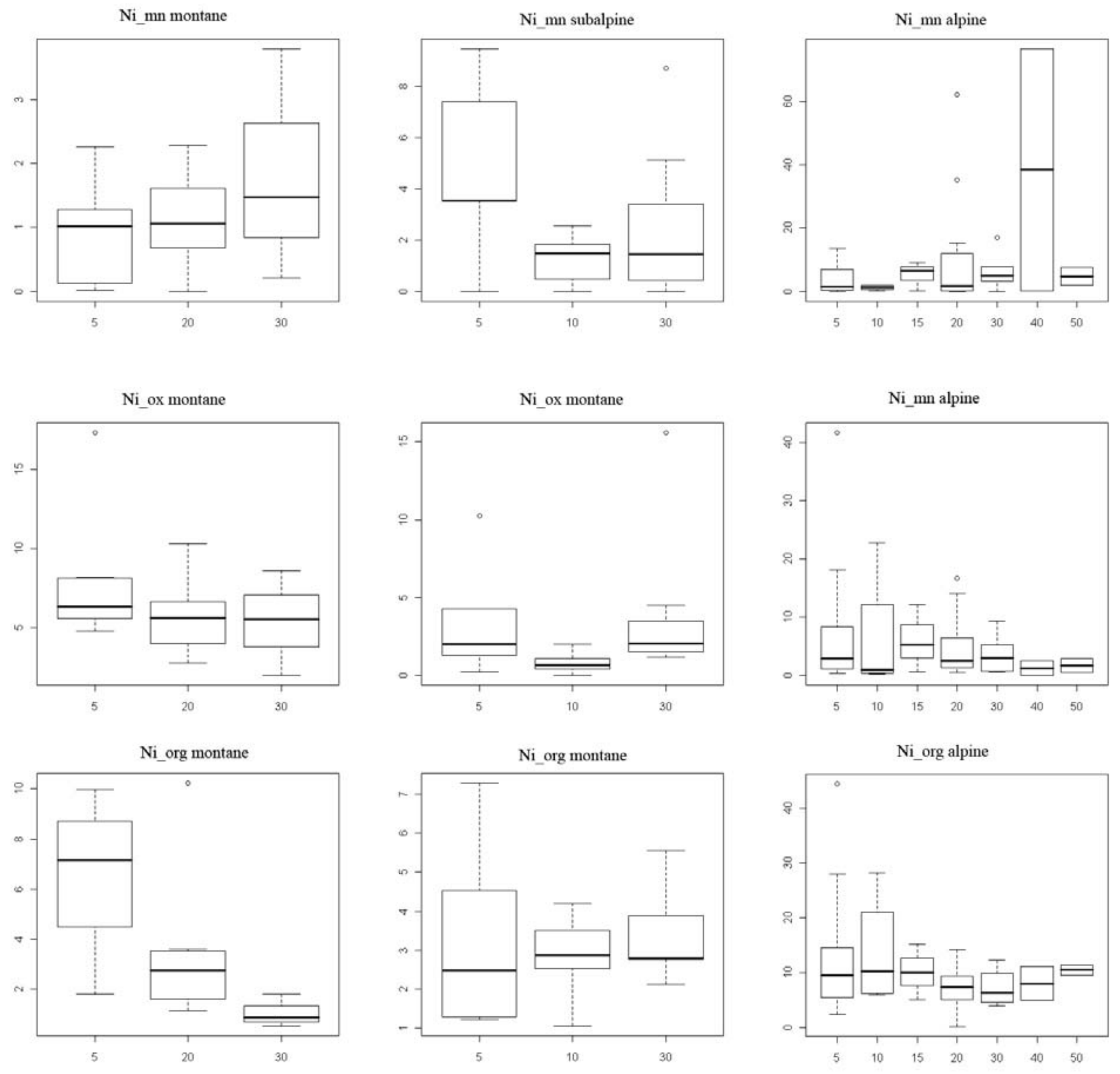

Fig. 5.1: Ni speciation (% tot) compared to depth in the studied montane, subalpine and alpine soils.

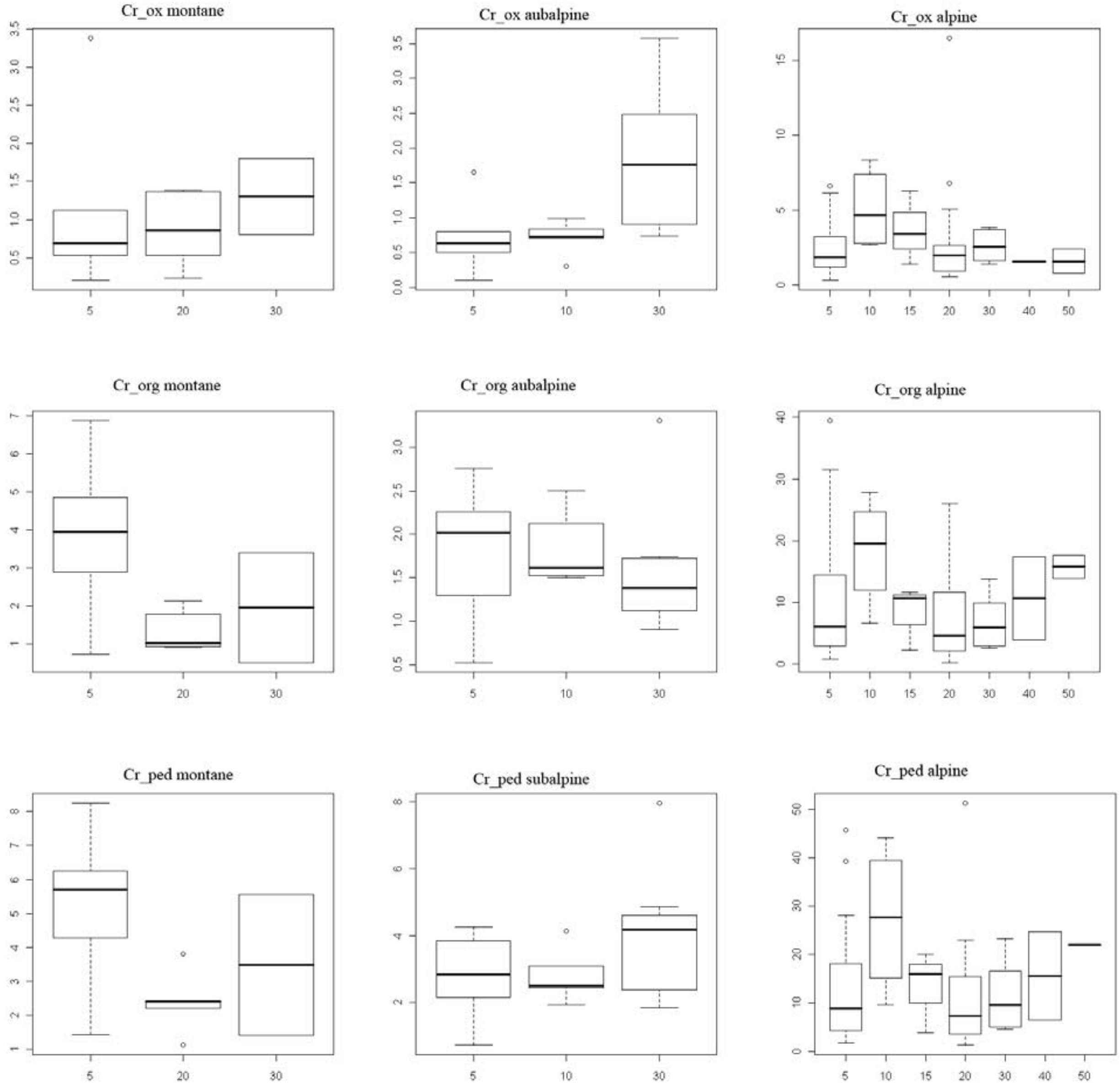

Fig. 5.2: some forms of Cr (% on Cr_{tot}) in the studied montane, subalpine and alpine soils. Cr_{ped} is $Cr_{mn+ox+org+d}$.

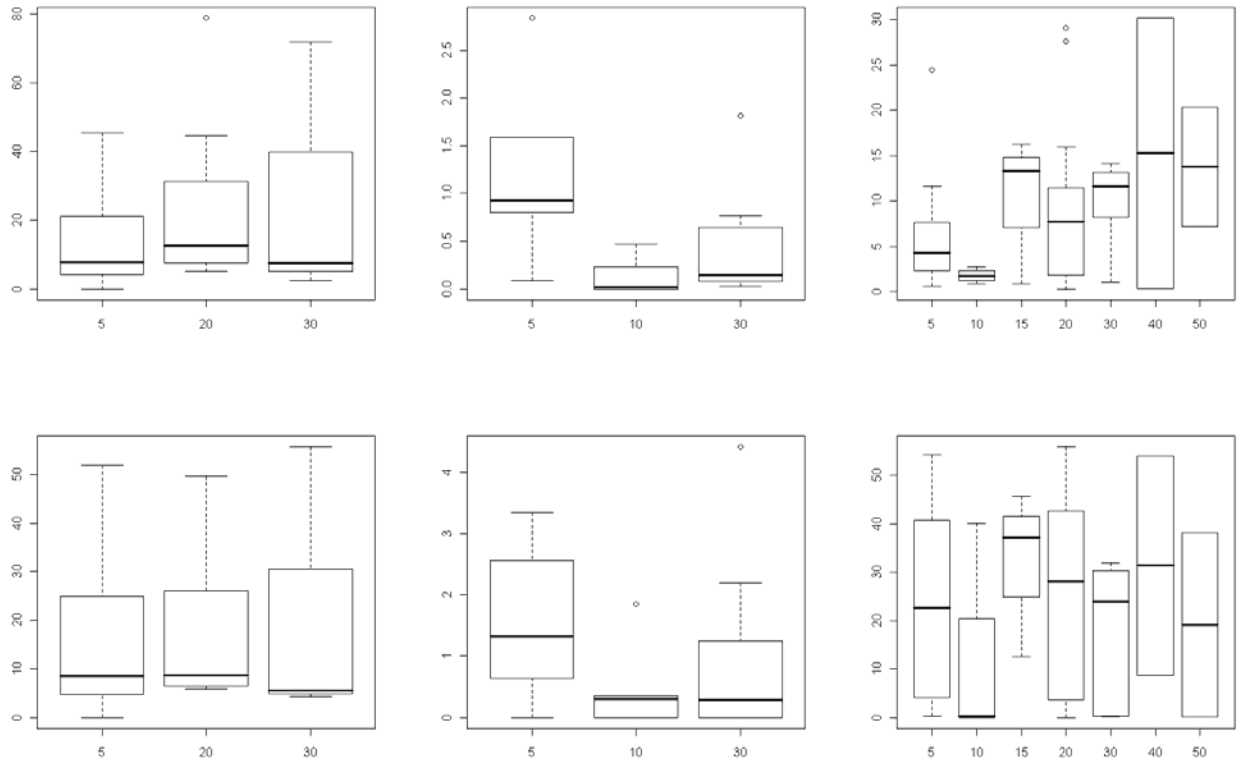

Fig. 5.3: Co$_{mn}$ *(top graphics) and Co*$_{ox}$ *in the studied mountain, subalpine and alpine soils (from left to right)*

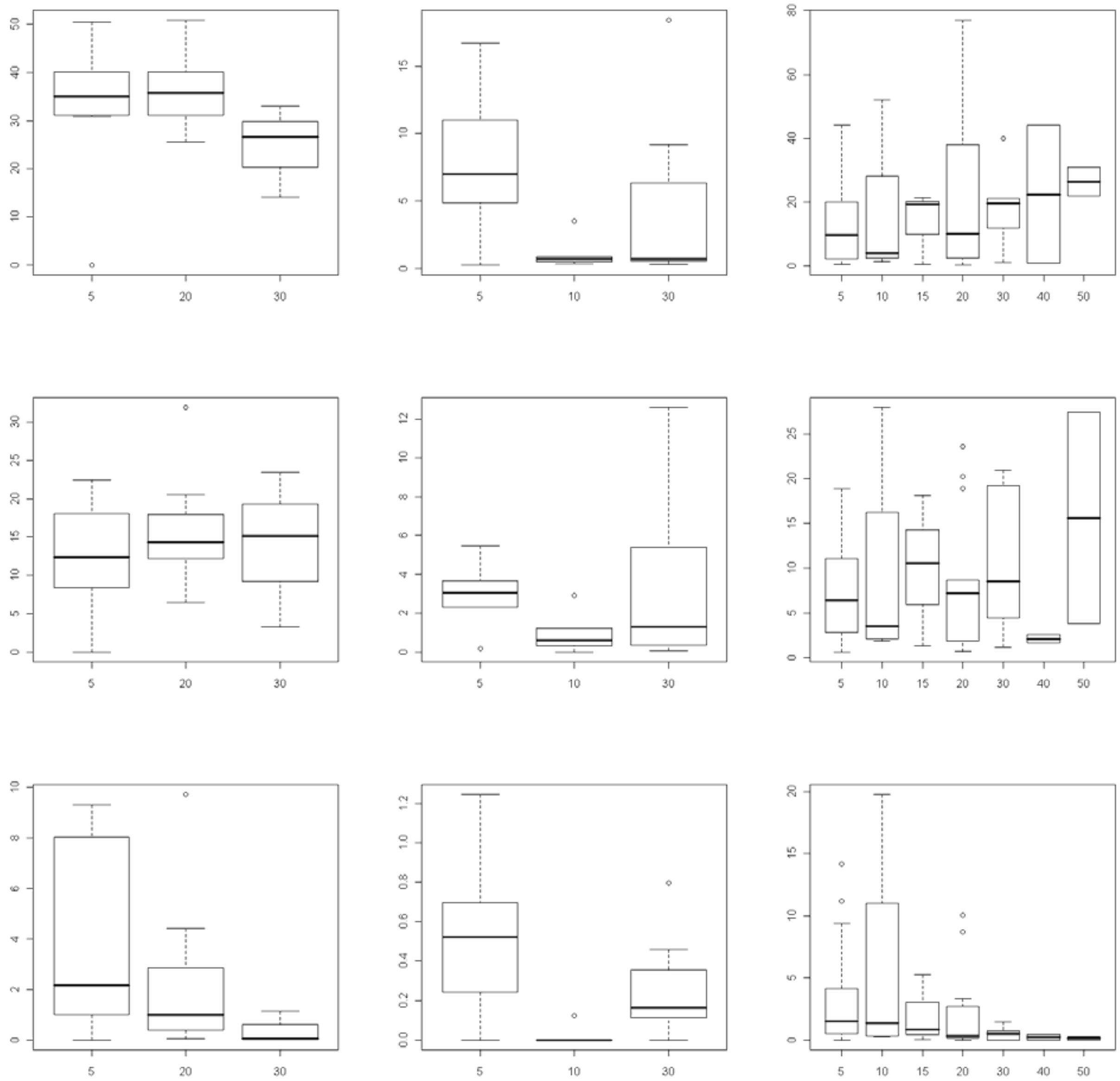

Fig. 5.4: from top to bottom, Mn_{mn}, Mn_{ox}, Mn_{org} in the studied montane, subalpine and alpine soils

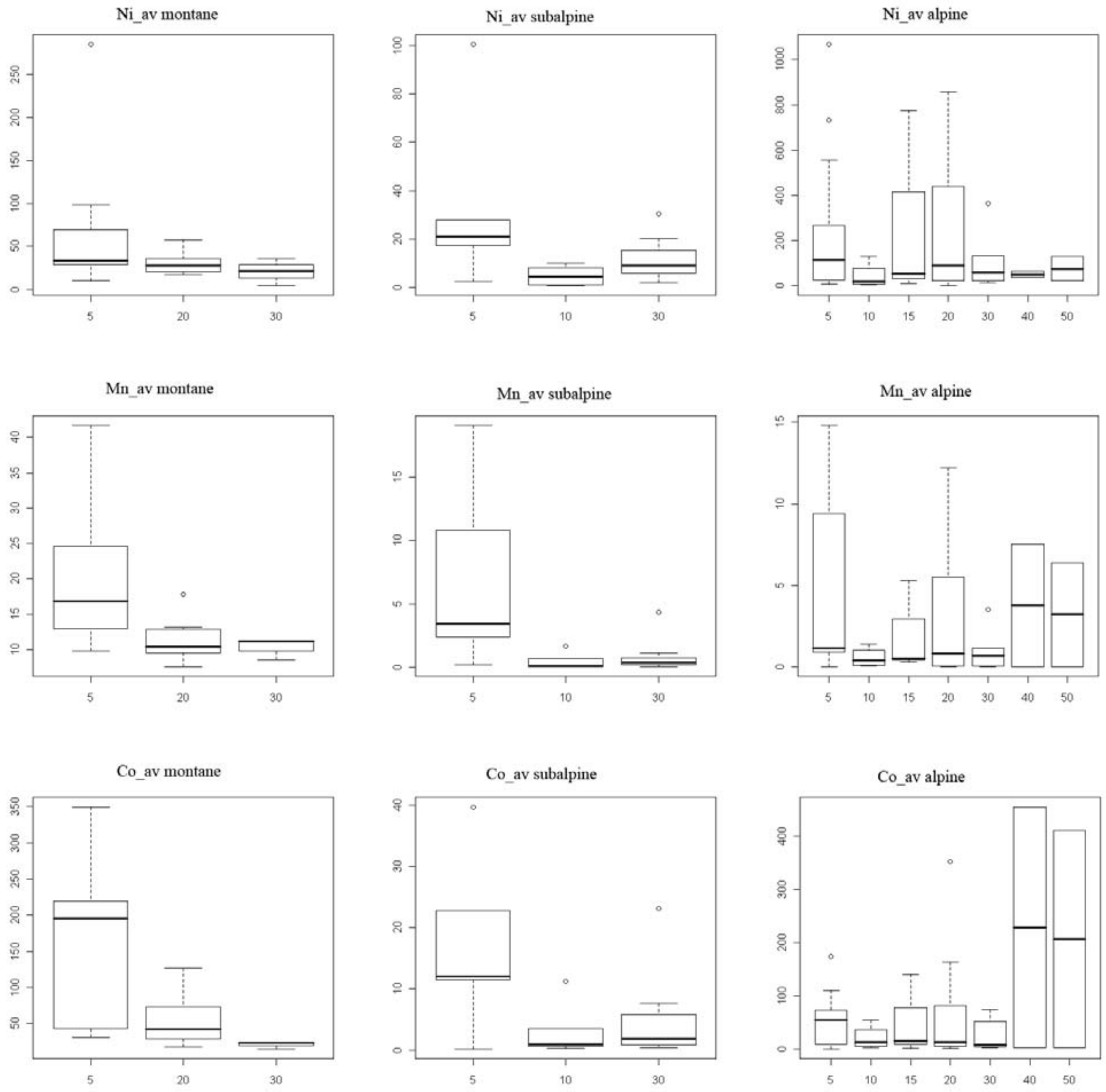

Fig. 5.5: Ni_{av}, Mn_{av} and Co_{av} , in montane, subalpine and alpine soils (mg kg^{-1}).

Table 5.1: Reagents and methods used in the sequential extraction

Extractant	Volume	Time	Temp.	Fraction extracted
H_2O	20 ml	1 hour	25°C	Water-soluble (Ni_{aq} Co_{aq}, Cr_{aq}, Mn_{aq}).
CH_3COONH_4 (1M)	20 ml	45 min.	25°C	Exchangeable. (Ni_{ex} Co_{ex}, Cr_{ex}, Mn_{ex})
NH_2OH-HCl (0.1M)	20 ml	30 min.	25°C	Bound to Mn oxides and highly amorphous Fe oxi-hydroxides. (Ni_{Mn}, Co_{Mn}, Cr_{Mn}, Mn_{Mn})
Oxalate (1M)	20 ml	4 hours	25°C	Bound to amorphous Fe oxi-hydroxides. (Ni_o, Co_o, Cr_o, Mn_o, Fe_o)
H_2O_2 (30%)	20 ml	10 hours	65°C	Bound to organic matter (and sulphides).
Ammonium-acetate (0.1M)*	20 ml	30 min.	25°C	(Ni_{org}, Co_{org}, Cr_{org}, Mn_{org} Fe_{org})
DCB**	40 ml	14 hours	25°C	Associated with crystalline pedogenic Fe oxides. (Ni_d, Co_d, Cr_d, Mn_d, Fe_d)
Aqua regia	10 ml	90 min.	MW owen	Residual

*H_2O_2-solubilized metals are easily readsorbed on the residual CEC of the soil (Filgueiras et al. 2002). After drying at 50°C, the metals were re-dissolved with a solution of ammonium acetate (CH_3COONH_4). **DCB is Na-Dithionite-Citrate Bicarbonate.

Tab. 5.2: chemical speciation of Ni in the studied soils. Missing values were below the detection limit.

		Ni_{aq}	Ni_{ex}	Ni_{mn}	Ni_{ox}	Ni_{org}	Ni_{d}	$Ni_{tot.}$			Ni_{aq}	Ni_{ex}	Ni_{mn}	Ni_{ox}	Ni_{org}	Ni_{d}	$Ni_{tot.}$
Alpine soils																	
A1	**P37**		0	0.39	29.92	46.06	21.02	164.68	**A**	**P11**		1.4	0.32	2.1	52.72	2.31	530
AC1			0	3.99	45.86	27.92	16.21	202	**B**			0.78	0.19	3.24	54.33	0	540
CB1			0	146.69	9.45	17.39	0.67	236.22	**C**			0.34	2.2	0.37	57.2	0	1148.81
CBn			0	198.81	6.33	28.88	7.27	259.92	**A**	**P12**	1.32	20.88	64.15	92.9	147.79	121.07	900
Bw			0	5.6	8	26.8	8.71	281.37	**BC**		0.78	20.05	61.14	157.21	158.41	9.5	1120
A1	**P38**		0.89	4.69	1.21	19.63	23.21	267.44	**AC**	**P139**		1.43	7.55	18.76	75.45	0	1270.59
AE			0.04	3.91	0.87	15.44	12.67	234.13	**C**			1.73	0.14	18.68	72.76	0	1442.8
B				0					**C1**	**P140**	4.06	22.21	402.44	261.14	195.27	797.56	3155.64
CB			0.43	89.67	16.38	26.29	183.11	256.97	**C2**		1.64	22.13	479.01	366.48	222.48	787.45	3308.88
C			0.34	25.54	13.73	36.86	6.12	812.75	**A**	**P4**		0	0	11.81	38.58	0	1076.21
A	**P52**	0.11	5.58	26.8	12.95	47.11	11.75	470.24	**Bw**			0	0	4.71	66.67	0	1130.77
AC		0.50	2.62	30.62	26.67	77.37	53.1	510	**A**	**P141**	1.81	9.49	9.69	37.56	122.68	122.45	1275.79
C		0.63	1.82	95.73	29.81	56.6	79.46	571.71	**AC**		0.27	7.21	49.88	57.88	149.85	220.14	1742
A	**P56**		0.44	5.08	0.39	28.01	8.43	63.00	**C**		0.92	6.07	46.22	69.98	108.55	137.21	1649.02
E			0.02	0.17	0.21	23.46	4.36	83.00	**A**	**P142**		3.26	0.72	13.88	56.29	0.00	1154.85
B			0	1.69	1.05	23.64	5.89	225.1	**CA**			2.72	0.39	12.8	66	0	1337.94
BC			0	17.21	1.21	26.99	3.21	220	**C**			2.42	0.58	11	61.69	0	1554.22
C			0	17.59	1.19	26.48	0.07	231.48	**A**	**P143**		5.74	0.21	47.97	109.42	0	815.5
A	**P138**	0.21	16.87	104.81	160.89	100.63	35.82	1864.21	**A**	**P144**		1.02	0.97	15.11	55.27	0	378.97
Bw		1.88	22.9	193.32	285.89	120.52	50.44	2356.57	**A1**	**P145**	0.21	0.19	1.94	193.61	77.44	0	464.29
C		1.55	14.4	120.82	184.93	123.92	24.74	1992.09	**A2**		0.74	0.29	0.49	80.78	45.66	0	483.39
A	**P10**	0.21	4.97	7.35	10.39	52.79	11.34	783.73	**AC1**	**P146**	2.72	28.64	226.99	74.58	252.44	292.62	2716.54
Bw			4.42	3.88	10.39	41.7	15.61	550.00	**AC2**		3.33	16.86	343.99	80.23	218.71	445.92	3009.77
Ah	**P41**		0	4.37	2.89	9.91	1.86	421.67	**A**	**P171**	0.46	10.21	31.08	54.65	43.07	30.58	1476.39
AE			0	0.72	4.95	0.72	1.03	395.35	**BC**		0.90	6.34	21.98	38.61	29.90	21.67	1641.53
Subalpine soils																	
E	**P1**		0	6.32	6.89	9.95	6.46	347	**A**	**P65**		5.1	44.61	22.40	38.31	10.62	526
Bs			0	0.95	8.00	11.05	14.40	395	**E**			0.9	1.98	6.15	24.81	15.64	590
A	**P135**	0.54	29.83	7.66	13.74	26.50	117.75	1071	**Bsg**			3.85	4.85	14.70	28.05	26.51	597
E			31.24	7.75	2.35	15.44	28.69	612	**AE**	**P137**		0.37	0.1	1.57	10.78	0.42	845
Bs1		0.10	28.55	6.53	10.17	17.79	56.15	838	**E**			0	0	0.00	9.54	0.00	901
AE	**P134**		8.25	17.03	6.79	15.47	6.48	342	**Bs**			0.38	0.83	15.08	23.02	7.02	835
E			5.29	3.53	2.30	12.08	4.48	344	**Ah1**	**P198**	0.21	64.58	166.5	668.83	79.12	293.13	6535
Bs			4.97	4.96	6.88	18.34	0.80	597	**BC1**		0.17	18.63	68.12	155.31	27.7	110.13	996
A	**P148**	4.56	181.18	36.43	940.89	208.56	61.21	1632	**BC2**			7.08	33.45	35.34	43.88	25.56	790
Montane soils																	
A	**P59**		3.7	4.42	38.02	36.04	11.88	451	**AC**	**P60**		5.43	4.51	71.35	39.18	22.51	821
AC		2.44	1.21	4.05	31.42	24.77	15.71	521	**C**		0.21	5.54	11.05	110.32	109.55	39.92	936
Ah	**P62**	0.05		0				311.82	**A**	**P82**	1.70	19.92	10.58	233.37	102.76	19.04	1173.69
C1		0.20	6.02	3.52	43.86	14.21	7.01	792.93	**BC1**		0.56	8.7	8.88	55.35	15.76	5.45	755
C2		0.09	2.66	0.55	29.69	13.04	8.12	1006.17	**BC2**		0.21	6.15	6.88	48.60	4.76		1021
A	**P99**	0.06	0.1	0.1	76.98	147.02	30.65	936	**A**	**P123**	0.11	0.21	0.38	32.00	28.49		398.22
CB		0.54	6.82	0.92	81.04	48.74	22.63	921	**Bw1**		0.30	5.03	2.11	23.94	4.83		426.18
A	**P124**		0.06	0.14	13.04	20.66		206.72	**Bw2**		0.21	4.59	13.36	40.68	8.57	2.62	473.21
Bw			0.14	0.06	6.70	6.70		242.97									

Tab. 5.3: Chemical speciation of Cr in the studied soils in Mont Avic Natural Park. Cr_{ex} is always below or very close to the detection limit.

		Cr_{mn}	Cr_{ox}	Cr_{org}	Cr_d	CrVI	Cr_{tot}			Cr_{mn}	Cr_{ox}	Cr_{org}	Cr_d	CrVI	Cr_{tot}
A1	**P37**	0	0.79	31.5	1.10	1.94	218.25	**A**	**P11**	0	45.46	78.32	1.23	0	690.00
AC1		0	6.38	37.89	1.21	0	218.00	**B**		0	37.01	68.9	11.74	0	589.00
CB1		0	2.27	28.36	6.63	0	242.06	**C**		0	22.8	56.07	13.12	0	1440.48
CBn		0	2.77	29.67	9.87	0	171.10	**A**	**P12**	0	23.03	76.78	4.21	3.42	1790.00
Bw		0	1.6	36	7.87	0	204.72	**BC**		0	29.05	75.62	9.31	0.55	1710.00
A1	**P38**	0	9.62	46.2	6.21	0	298.45	**AC**	**P139**	0	41.12	101.8	4.32	5.13	1537.25
AE		0	11.68	39.55	12.05	0	182.54	**C**		0	37.35	83.66	7.88	4.8	1789.67
B								**C1**	**P140**	0.2	33.93	72.98	8.56	6.51	2758.75
CB		0	15.62	24.76	8.27	0	95.00	**C2**		0	30.1	62.86	7.93	9.41	3735.52
C		0	12.94	31.37	11.20	0.07	699.20	**A**	**P4**	0	27.17	61.02	4.21	0	1308.55
A	**P52**	0	13.35	58.88	4.20	5.04	448.41	**Bw**		0	23.92	50.98	8.06	0	1059.62
AC		0	15.02	46.95	8.69	7.75	441.18	**A**	**P141**	0	43.96	79.92	4.00	11.43	2714.29
C		0	11.32	30.19	9.32	0	306.77	**AC**		0	49.16	91.18	6.80	14.65	2550.00
A	**P56**	0	4.73	37.48	1.21	1.66	95.00	**C**		0	41.75	75.55	10.71	9.63	2580.39
E		0	9.08	30.27	8.78	0	109.00	**A**	**P142**	0	38.45	101.09	4.54	0	1313.43
B		0	13.13	33.77	9.52	0	258.96	**CA**		0	41.6	96	7.21	0	1610.67
BC		0	6.65	24.03	9.76	0	174.00	**C**		0	45.97	104.13	9.42	0	1425.70
C		0	4.74	27.67	10.82	0	198.15	**A**	**P143**	0	38.06	99.11	3.21	0	1324.72
A	**P138**		19.80	22.77	3.96		2765.21	**A**	**P144**	0	14.71	75.55	4.11	0	240.08
Bw		0	52.05	84.08	9.58	2.22	3743.03	**A1**	**P145**	0	30.2	108.42	3.21	0	503.97
C		0	23.73	43.31	8.63	0.55	1669.96	**A2**		0	58.54	134.63	4.54	0	859.78
A	**P10**	0	26.59	60.61	1.21	0	1700.40	**AC1**	**P146**	0.2	31.11	71.78	3.12	0	2498.03
Bw		0	44.02	75.29	2.11	3.29	1666.00	**AC2**		0.19	31.63	57.86	6.54	0	2708.98
A	**P41**	0	3.09	3.95	5.94	3.21	421.43	**A**	**P171**	0	15.80	18.77	3.96	0	1895.56
AE		0	2.84	2.97	3.09	3.97	384.90	**BC**		0	9.90	4.95	9.90	0	1795.45
Subalpine soils															
E	**P1**	0.02	2.90	15.31	0.05	2.21	948.21	**A**	**P65**	0.00	12.06	38.31	3.54	2.12	1900
Bs		0.27	31.10	13.33	4.12	1.52	1002.43	**E**		0.06	11.40	24.04	3.56	1.94	1600
A	**P135**	0.02	14.10	36.31	10.08	3.28	2800	**Bsg**		0.00	17.46	16.44	4.75	9.98	1800
E		0.14	20.89	38.12	3.28	3.57	2500	**AE**	**P137**	0.53	14.33	19.61	2.52	1.49	868
Bs1		0.29	47.54	46.92	22.79	12.08	2700	**E**		0.33	6.49	16.55	3.99	0.18	660
AE	**P134**	0.02	11.18	38.68	4.05	3.46	1401	**Bs**		0.52	23.60	21.83	6.60	1.76	660
E		0.17	10.19	29.72	2.99	1.12	1400	**Ah1**	**P198**	0.08	13.00	62.92	11.94	1.07	12000
Bs		0.23	35.60	32.47	11.19	2.83	1901	**Ah2**		0.81	29.61	36.40	7.63	1.73	4020
A	**P148**	0.55	7.01	25.23		0.05		**BC**		0.15	16.12	26.21	7.30	0.00	1900
Montane soils															
A	**P59**	1.98	8.91	54.65	4.16	4.16	794.87	**AC**	**P60**	1.56	4.68	6.24	16.96	16.96	875.00
AC		3.02	6.24	6.65	30.51	30.51	722.89	**C**		0.00	2.51	9.64	17.36	17.36	1071.11
Ah	**P62**	0	29.54	25.21		9.21	871.21	**A**	**P82**	2.46	9.21	65.30	25.79	25.79	1346.73
C1		0.20	16.65	12.18	18.58	18.58	1205.74	**BC1**		2.42	10.51	16.36	26.06	26.06	770.00
C2		1.40	12.04	7.62	30.99	30.99	1500.00	**BC2**		3.10	15.93	73.63	9.93	9.93	882.93
A	**P99**	1.98	3.17	59.13	0.89	0.89	442.15	**A**	**P123**	1.37	5.85	37.27	0.59	0.59	321.76
CB		1.35	7.16	23.98	5.51	5.51	767.77	**Bw1**		4.44	7.34	23.36	4.92	4.92	368.42
A	**P124**	4.61	7.62	36.51			328.89	**Bw2**		4.19	6.58	19.74			467.89
Bw1		4.67	8.12	31.07	10.05	10.05	488.26								

Tab. 5.4: Chemical speciation of Co in the studied soils in Mont Avic Natural Park. Missing data are below the detection limit.

		Co_{ex}	Co_{mn}	Co_{ox}	Co_{org}	Co_{d}	Co_{tot}			Co_{ex}	Co_{mn}	Co_{ox}	Co_{org}	Co_{d}	Co_{tot}
A1	**P37**	0.15	0.15	0.69	5.41	2.91	47.62	**A**	**P11**	0.51	0.74	9.54	2.48	0.59	54.02
AC1			0.97	0.3	4.89	5.95	52	**B**		0.25	0.45	9.86	2.66	6.69	78.12
CB1			7.05	16.92	3.59	0.57	61.51	**C**		0	0.41	9.58	1.96	0.93	109.13
CBn		0.17	15.33	27.75	4.35	6.13	51.33	**A**	**P12**	0.38	13.02	71.53	2.88	21.39	175.21
Bw			12.43	23.26	5.5	1.24	61.02	**BC**		0.3	14.87	63.97	4.68	2.90	156.45
A1	**P38**		1.25	0.1	3.56	3.05	46.51	**AC**	**P139**	0	1.73	44.85	1.1	9.83	111.76
AE			0.48	0	4.9	3.53	55.56	**C**		0	2.75	43.48	2.04	5.61	151.29
B			0					**C1**	**P140**	0	62.43	138.72		8.95	254.86
CB		0.32	15.32	0.1	3.43	6.51	53.78	**C2**		0.05	73.12	147.94	1.52	12.94	264.48
C			9.44	0.2	3.73	0.48	77.69	**A**	**P4**	0	0.91	36.24		8.47	141.26
A	**P52**		3.82	13.51	4.71	5.04	89.29	**Bw**		0	0.45	37.45	0.2	8.06	150
AC			7.53	20.96	4.98	13.18	56.21	**A**	**P141**	0.37	13.71	61.82	0.1	11.02	216.27
C		0.02	9.99	18.98	3.58	14.97	75.7	**AC**		0	32.41	86.36	0.89	11.39	202
A	**P56**	0.04	0.89	0.1	5.13	2.91	21.65	**C**			30.49	68.8	0.4	10.43	215.69
E			0.47		2.27	3.96	17.21	**A**	**P142**	0.19	2.5	46.63		1.25	151.12
B			0.51		2.16	0.34	83.67	**CA**		0	2	45.75	0.2	8.98	160.08
BC			5.77	0.09	2.22	7.84	70	**C**			1.51	44.41		4.24	146.59
C			6.36	0.1	3.16	0.98	88.89	**A**	**P143**	0.38	2.24	46.27	0.69	5.63	95.94
A	**P138**	0	20.4	5.25	13.66	4.41	175.21	**A**	**P144**	0.17	1.49	42.82	0.89	8.19	101.19
Bw		0.25	32.79	92.82	4.8	2.36	203.19	**A1**	**P145**	0.39	3.98	57.52	0.39	1.41	126.98
C		0.1	17.3	35.4	3.3	0.96	156.13	**A2**		0	8.94	51.35	0.2	3.13	108.86
A	**P10**	0.92	5.05	19.56	3.03	8.49	99.21	**AC1**	**P146**	0.09	12.38	85	0.5	17.54	216.54
Bw		0.18	2.35	13.64	2.41	7.39	117.21	**AC2**			24.55	97.54		12.08	216.8
Ah	**P41**	0.11	7.12	2.67	4.12	2.38	65.56	**A**	**P171**	0.05	12.71	11.21	5.76	12.48	131.54
AE		0.06		0.61	2.28	0.72	73.89	**BC**		0.08	9.13	4.65	6.93	2.38	126.43
Subalpine soils															
E	**P1**	0	0	0.48	0.48	0.4	26	**A**	**P65**	0.82	0.11	0.69	5.30	10.18	27
Bs		0	0.01	0.10	1.05	5.76	33	**E**		0.09	0.04	0.10	3.37	3.56	29
A	**P135**	4.04	1.01	0.49	3.43	11	37	**Bsg**		0.16	0.09	0.10	3.00	11.08	35
E		1.36	0.8	0.10	3.13	4.51	34	**AE**	**P137**	0.09	0.04	0.00	6.86	7.97	36
Bs1		0.79	0.41	0.00	4.01	8.95	38	**E**		0	0.01	0.00	5.06	6.79	43
AE	**P134**	0.94	0.04	0.19	4.06	4.46	30	**Bs**		0	0.03	0.00	5.75	7.43	64
E		0.33	0.34	0.00	2.68	4.48	30	**Ah1**	**P198**	0.54	0.99	6.39	4.19	16.12	191
Bs		0.13	0.61	0.00	3.15	6.79	36	**BC1**		0.16	0.51	3.84	6.07	6.67	87
A	**P148**	1.15	10.56	72.86	4.64	5.32	121	**BC2**			1.45	1.75	6.21	7.30	80
Montane soils															
A	**P59**	1.34	1.73	1.68	2.08	2.67	41.03	**AC**	**P60**	0.55	2.57	2.14	0.39	6.63	40.38
AC		0.45	4.18	1.51	0.81		25.7	**C**		0.19	4.73	3.38	0.77	8.87	39.11
Ah	**P62**		0					**A**	**P82**	1	4.94	6.14	0.72	1.23	38.19
C1		0.62	2.12	2.94	1.42	1.22	42.11	**BC1**		0.77	1.65	2.93	0.1		48
C2		0.64	0.66	2.21	0.2	0.4	52.43	**BC2**		0.6	2.81	2.48	0.52	1.24	44.88
A	**P99**	0.69	0.01	4.46	2.08	3.97	23.14	**A**	**P123**	0.87	1.96	3.22	1.37		
CB		1.04	2.34	4.93	0.68	2.71	28.44	**Bw1**		0.98	3.17	2.61	0.58		5.26
A	**P124**	0.55	1.36	2.41	1.5		7.11	**Bw2**		0.28	5	4.09	0.6		7.34
Bw		0.46	2.89	2.94	0.3		7.51								

Tab. 5.5: Chemical speciation of Mn in the studied soils in Mont Avic Natural Park. Missing values are below the detection limit.

		$\mathrm{Mn_{aq}}$	$\mathrm{Mn_{ex}}$	$\mathrm{Mn_{mn}}$	$\mathrm{Mn_{ox}}$	$\mathrm{Mn_{org}}$	$\mathrm{Mn_{d}}$	$\mathrm{Mn_{tot}}$			$\mathrm{Mn_{aq}}$	$\mathrm{Mn_{ex}}$	$\mathrm{Mn_{mn}}$	$\mathrm{Mn_{ox}}$	$\mathrm{Mn_{org}}$	$\mathrm{Mn_{d}}$	$\mathrm{Mn_{tot}}$
A1	**P37**		5.14	136.59	114.57	101.18	65.86	714.29	**A**	**P11**		0.76	1.72	4.97	9.55	2.96	776.89
AC1			4.21	540.76	293.52	207.38	127.23	1050	**B**			0.32	3.03	11.81	0.39	14.23	894.23
CB1			2.04	1066.96	107.75	3.78	7.81	1388.89	**C**			0.18	7.48	16.45		1.14	1011.9
CBn		0.31	0.57	1160.85	67.66	11.47	71.57	2633.08	**A**	**P12**	0.49	18.74	405.44	92.9	34.93	79.14	960.78
Bw		1.26	0.61	745.99	92	6.8	60.58	2421.26	**BC**		0.35	15.89	463.51	197.01	90.75	20.06	1043.31
A1	**P38**		32	22.28	43.12	29.26	40.85	639.53	**AC**	**P139**		2.75	40.96	18.76	2.4	24.36	1019.61
AE			0.46	5.75	12.43	2.26	45.14	515.87	**C**			1.64	36.49	18.68		18.82	1014.76
B		0.06		0					**C1**	**P140**	0.45	4.36	789.53	261.14	6.71	106.61	1828.79
CB		0.31	7.59	1019.65	638.1	21.33	62.67	2709.16	**C2**		0.09	5.21	698.41	366.48	6.48	157.65	1814.67
C		0.67	4.97	327.19	301.96	11.37	5.25	1573.71	**A**	**P4**		1.93	13.03	11.81		21.77	789.96
A	**P52**	0.11	5.49	84.6	106.38	8.64	49.11	684.52	**Bw**			0.22	3.31	4.71		16.11	701.92
AC		0.39	2.62	257.1	245.26	70.99	151.16	1352.94	**A**	**P141**	0.12	9.01	87.69	37.56		31.84	1011.9
C		0.97	2.38	498.37	129.06	4.91	56.81	1254.98	**AC**		0.06	4.32	168.33	57.88	1.59	50.86	940
A	**P56**	0.32	3.86	349.79	181.85	89.94	81.5	961.54	**C**			0.79	122.87	69.98	15.11	81.04	1039.22
E			1.04	20.15	27.63	13.62	144.41	611.11	**A**	**P142**		3.88	15.55	13.88		14.61	951.49
B		1.54	6.72	25.36	85.18	26.64	8.15	986.06	**CA**			2.15	14.05	12.8		24.08	1027.67
BC		0.21	2.21	318.49	339	9.98	32.13	1620	**C**			0.5	10.31	11		15.68	943.78
C			0.49	298.13	372.73	0.00	3.6	1361.11	**A**	**P143**		7.16	6.72	47.97	10.7	64.79	673.43
A	**P138**		4.84	170.01	72.57	17.39	22.87	1435.21	**A**	**P144**	1.16	19.61	5.04	15.11	11.53	49.16	605.16
Bw		0.35	6.06	387.93	195.8	15.22	37.68	1862.55	**A1**	**P145**	1.34	49.8	251.26	193.61	195.16	155.5	1746.03
C		0.03	2.21	239.97	55.74		11.82	1254.94	**A2**		1.06	2.33	145.77	80.78	112	227.68	1116.24
A	**P10**	1.65	54.21	28.1	99.71	37.93	124.25	922.62	**AC1**	**P146**	0.43	5.5	272.86	74.58	5.98	53.9	1240.16
Bw		0.07	2.12	22.98	81.47	33.98	194.25	1029.41	**AC2**		0.53	3.22	395.62	80.23	4.63	43.5	1474.61
Ah	**P41**		0.51	12.05	18.62	9.50	12.45	659.49	**A**	**P171**	0.40	5.21	116.46	49.31	30.57	35.75	1254.89
AE			0.26	1.18	5.88	1.65	14.03	521.53	**BC**		0.36	3.78	71.07	76.53	9.10	27.54	1068.37
Subalpine soils																	
E	**P1**		0.24	3.2	5.74	0.57	6.87	468	**A**	**P65**	0.73	5.98	32.53	16.90	6.88	22.57	552
Bs			0.18	2.68	2.29	0.76	9.88	487	**E**			1.51	0.61	3.46	0.00	4.98	572
A	**P135**	1.61	247.76	196.01	53.39	3.53	25.66	1459	**Bsg**			0.83	3.43	7.74	0.97	17.01	595
E			7.25	19.73	22.29	0.00	11.48	771	**AE**	**P137**		0.49	0.88	0.78	0.00	7.56	521
Bs1		0.15	6.19	26.07	19.94	2.35	48.42	938	**E**			0.64	1.89	0.00	0.00	4.79	507
AE	**P134**	0.39	14.4	22.39	17.36	3.96	21.88	757	**Bs**			0.38	1.41	1.19	0.00	12.38	572
E			1.52	4.81	2.30	0.00	16.43	730	**Ah1**	**P198**		23.9	334.73	177.69	22.69	155.22	3257
Bs			1.15	3.05	0.38	0.57	15.98	830	**A2**		0.08	4.95	120.83	118.50	10.92	49.11	1371
A	**P148**	1.82	1.85	51.37	259.65	10.56			**BC**		0.36	8.85	263.97	186.80	6.80	34.08	1482
Montane soils																	
A	**P59**	1.59	28.11	106.54	47.52	8.32	9.80		**AC**	**P60**	0.62	9.5	107.65	27.88	2.53	10.23	
AC		0.80	11.77	129.22	47.53	2.62	12.69		**C**			2.66	130.8	37.42	11.57	28.35	
Ah	**P62**			0					**A**	**P82**	3.67	148.58	57.15	73.49	5.32	27.94	
C1			6.05	99.13	26.60	0.20	2.44		**BC1**		0.56	18.31	122.7	50.30	0.20	7.58	
C2		0.42	5.1	75.94	18.66	0.20	2.71		**BC2**		0.82	5.64	91.77	55.43	0.21	4.96	
A	**P99**	10.21	193.85	274.52	53.77	53.77	29.46		**A**	**P123**	0.64	10.78	211.27	127.41	39.80	32.78	
CB		2.68	12.42	131.23	48.36	4.06	13.93		**Bw1**		2.21	5.15	181.85	120.46	7.53	23.75	
A	**P124**	0.54	12.42	222.69	102.11	51.55	37.61		**Bw2**		1.67	6.32	228.18	166.90	7.98	28.41	
Bw		0.67	11.6	126.27	146.80	44.67	37.77										

Tab. 5.6: bioavailable metals (EDTA-extractable, mg kg^{-1}*) in the studied pedons. missing data are below the detection limit.*

		Cr$_{av}$	**Mn$_{av}$**	**Co$_{av}$**	**Ni$_{av}$**			**Cr$_{av}$**	**Mn$_{av}$**	**Co$_{av}$**	**Ni$_{av}$**
A1	**P37**		59.64	1.13	13.38	**A**	**P11**		2.28	1.00	98.5
AC1			54.29	0.62	12.25	**B**		0.15	1.12	0.27	52.6
CB1			351.85	2.19	17.08	**C**			1.53	0.00	38.66
CBn			453.98	7.54	64.66	**A**	**P12**		110.57	9.78	733.04
Bw			409.49	6.37	130.38	**BC**			58.96	5.17	546.22
A1	**P38**		74.39	0.92	65.31	**AC**	**P139**		16.62	1.38	129.89
AE			2.01	0.04	27.51	**C**			12.10	0.99	100.31
B						**C1**	**P140**		174.13	11.99	555.67
CB			13.63	0.02	26.29	**C2**			104.12	11.01	638.69
C			8.47	0.03	36.86	**A**	**P4**		3.81	0.00	33.81
A	**P52**		24.12	1.16	17.9	**Bw**			1.19	0.00	28.59
AC			15.45	0.51	9.55	**A**	**P141**		64.3	8.97	209.69
C			72.98	1.14	12.63	**AC**			41.10	5.78	337.2
A	**P56**		61.87	0.82	6.16	**C**			6.78	1.10	133.38
E			7.94	0.12	3.12	**A**	**P142**		10.14	1.16	16.38
B			4.94	0.03	2.70	**CA**			5.68	0.55	8.87
BC			2.60	0.00	21.81	**C**			3.14	0.18	82.68
C			2.48	0.00	21.88	**A**	**P143**	0.35	8.06	0.89	191.22
A	**P138**		0.00	14.80	321.65	**A**	**P144**		26.99	0.86	132.79
Bw			139.56	5.28	776.62	**A1**	**P145**	0.13	47.50	1.52	90.43
C			52.00	3.50	365.15	**A2**		0.59	3.33	0.43	81.40
A	**P10**		69.41	0.49	205.00	**AC1**	**P146**	0.05	109.57	10.94	1067.64
Bw		0.05	4.64	0.00	138.50	**AC2**		0.05	162.71	12.22	858.03
Subalpine soils											
E	**P1**	1.94	0.70	0.10	1.09	**A**	**P65**	0.95	11.49	3.40	28.02
Bs		2.24	0.80	0.05	2.14	**E**		1.29	0.35	0.05	4.75
A	**P135**	2.25	22.68	10.79	21.03	**Bsg**		0.55	1.04	0.25	10.44
E		3.14	11.20	1.64	8.26	**AE**	**P137**	2.83	0.25	0.20	2.59
Bs1		4.09	7.63	1.10	7.13	**E**		1.84	0.94	0.05	1.04
AE	**P134**	1.74	12.06	2.39	17.49	**Bs**		2.62	0.44	0.15	4.99
E		2.24	3.56	0.68	10.04	**Ah1**	**P198**	1.93	39.61	19.05	100.51
Bs		2.85	1.90	0.35	9.19	**Ah2**		1.30	4.04	0.40	30.40
A	**P148**	0.11	51.21	31.23	871.21	**BC**		0.60	23.03	4.30	20.28
Montane soils											
A	**P59**	0.2	50.34	19.51	28.49	**AC**	**P60**	0.00	37.01	9.84	33.46
AC		0.00	36.82	10.36	17.21	**C**		0.00	18.02	7.61	27.83
Ah	**P62**	0.30	31.21	12.21	41.21	**A**	**P82**	3.43	195.34	41.67	284.80
C1		2.59	22.11	9.56	27.89	**BC1**		0.00	43.03	13.11	44.06
C2		0.56	15.25	11.30	21.66	**BC2**		1.45	23.55	11.16	36.36
A	**P99**	0.00	201.41	29.81	98.69	**A**	**P123**	0.00	236.94	16.79	28.75
CB		0.93	45.08	17.81	57.51	**Bw1**		0.20	101.77	12.60	21.46
A	**P124**	0.83	349.17	13.69	10.58	**Bw2**		0.00	23.35	8.53	5.08
Bw		0.00	126.77	9.56	20.84						

6: Heavy Metals and Biological Properties of Subalpine Soils on Ophiolites

Adapted from:
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Abstract

Soils on ultramafic rocks are usually colonized by plant species and communities adapted to high heavy-metal content and low Ca/Mg ratio. However, the effects of metal speciation on microbial activity and arthropodal communities have scarcely been studied, especially under coniferous forests in boreal or subalpine areas. Six typical subalpine soils, in the ophiolitic area of Mont Avic Natural Park, located in the Western Italian Alps, were studied in order to verify the chemical speciation of Ni, Co, Mn, and Cr and their effects on soil biological properties and microbial activity. Five soils, developed from till composed of mafic and ultramafic materials, showed strong signs of podzolization, while the sixth was polluted by mine spoil. All the samples had high metal content, high acidity, and high metal mobility and bioavailability. These edaphic properties deeply influenced both arthropodal communities and microbial activity, all of which were strictly correlated with parent material and bioavailable Ni, Co, and Mn.

6.1 Introduction

Soils over ultramafic materials are characterized by the “serpentine factor:” low exchangeable Ca, low Ca/Mg ratio, low nutrients, and high Ni, Cr, Co, and Mn content. Such soils are of great ecological interest due to their unique chemical, physical, and biological characteristics (Brooks 1987). The “serpentine factor” makes these soils toxic for organisms that are not adapted to harsh conditions. For example, plant communities on serpentine are usually strikingly different from those on nearby areas on different substrata and are rich in endemic species (e.g., *Carex fimbriata* Schkuhr, *Thlaspi sylvium* Gaudin, and *Cardamine plumieri* Vill. in the European Western Alps) and in taxa tolerant to heavy metals (e.g., *Thlaspi caerulescens* J. and C., *T. sylvium*, *Cardamine plumieri* L., and *Biscutella laevigata* L. in the study area). Often, microbial communities are also different in these soils, displaying adaptations to edaphic stress caused by heavy metals (Amir and Pineau 2003, Mengoni et al. 2001); they are usually composed of a smaller number of taxa compared to nearby soils on other substrates (Oline 2006).

However, very few studies have been undertaken to determine the biological impacts of chemical speciation and the availability of metals, particularly in subalpine or boreal environments (Bulmer and Lavkulich 1994, Gasser et al. 1994, Roberts 1980). Many studies show how biological activity is broadly affected by heavy metals in recently contaminated soils. In particular, microbial biomass and respiration are normally reduced and the stress symptoms enhanced when metals are added to soils (Giller et al. 1998). This effect is often the result of heavy metal toxicity on microbial communities. The same result has been demonstrated on microarthropodal communities (Edwards 2002). Heavy metals added to the soil have effects at the population level (changes in the life cycle), community level (changes in species diversity and relationships among plants, between plants and microbial communities, and between plants and soil fauna) and ecosystem level (effects on primary and secondary productivity and rate of decomposition of organic matter).

The effects of heavy metals on biological activity are not clear in naturally metal-rich soils. Some studies show that on metal-rich, serpentinite-derived soils, microbial activity (biomass and respiration) is not reduced compared to nearby soils with a “typical” chemistry (Schipper and Lee 2004). This maintenance of microbial activity is due to specific adaptations of the microbes to edaphic stress. In contrast, other studies show that long-term metal contamination can lead to a permanently reduced microbial biomass (Giller et al. 1998).

The microarthropodal ecology and the microbial activity of soils formed from ophiolitic materials under subalpine or boreal vegetation are poorly studied, particularly on the Alps. In addition, only a few investigations deal with soils developed from ultramafic rocks in temperate climates (Mengoni et al. 2001, Schipper and Lee 2004). Nevertheless, this is an interesting subject, as subalpine environmental conditions (high acidity, humidity, and leaching) should enhance metal mobility and, perhaps, bioavailability and toxicity.

The goals of this study were to investigate heavy-metal speciation and bioavailability and assess whether heavy metals and their chemical forms can be considered toxic on microbial communities and on soil-dwelling arthropods. Biological soil quality index (BSQ; Parisi 2001) based on microarthopod communities, microbial activity (biomass and respiration), and stress indicators (i.e., metabolic quotient) were used as edaphic quality indices.

6.2 The Study Area

The six investigated soil pits were located in Mont Avic Natural Park, Valle d'Aosta, northwestern Italy. They were developed under subalpine *Pinus uncinata* Miller forest and ericaceous shrubs on glacial till composed of mafic and ultramafic rocks in different proportions (Table 3.3).

The soil pits were representative of the typical subalpine soils formed in the study area. They were selected among 87 previously observed and analyzed soil pits. One of the soils (P198) was polluted by mine debris (serpentinite with large amounts of magnetite and other metallic minerals). It was sampled in order to assess the differences in metal speciation and in biological activity between naturally metal-rich and polluted sites. Environmental properties of the sites are summarized in table 6.1.

The average yearly temperature is 2 °C and the precipitation is 1200 mm/y. The differences in vegetation cover are not important.

6.3 Materials and Methods

6.3.1 Sampling and chemical analysis

Soil sampling took place in late August 2006. Around 500 g of soil from each horizon were collected in order to make chemical analyses. Rock fragments were separated, cleaned (using a Calgon solution), observed, and divided according to the different lithologies. The fragments were weighed, in order to distinguish the proportions of the different rocks in the morainic parent material. The parent material was also characterized with the help of X-Ray diffractometry (XRD) analysis of the sandy textural fraction (D'Amico et al. 2008). The pedons were classified according to IUSS Working Group (2006).

The following chemical analyses were performed twice on each sample, after drying at air temperature and sieving at 2 mm: pH (in water and KCl, 1:2.5 solution), exchangeable bases extracted with $BaCl_2$ - TEA and ascertained using flame atomic absorption spectroscopy (FAAS), and total exchangeable acidity. Cation exchange capacity (CEC) was calculated with sum of exchangeable bases and acidity. Total organic carbon (TOC) and N were analyzed by CN elemental analyzer (Thermo Electron, NC Soil), and particle size distributions were determined by the pipette method and sieving. Spodic properties were determined through oxalate extractable Fe and Al. Total elemental composition was determined by X-ray fluorimetry (XRF).

"Available" Ni, Co, Cr, and Mn (Ni_{av}, Co_{av}, Cr_{av}, Mn_{av}) were extracted via ammonium acetate-EDTA (0.1M) (2.5 g of soil in 25 ml of solution, shaken for 30 min). Cr(VI) was measured using the diphenyl-carbazide method (Bartlett and James 1996) after 0.1M KH2PO4 extraction on field-humid samples. "Available" Cr(III) was extracted with 1M KCl.

The operationally defined fractionation of metals among the compartments of the soil solid phase was investigated by selective sequential extraction (SSE) methods. The SSE was performed on one g of soil. Ni, Co, Cr, Mn, and Fe were determined with FAAS. After each extraction, the samples were washed with 10 ml demineralised water, centrifuged, and dried at 60 °C.

A six-step scheme, modified from Tessier et al. (1979), was implemented (Table 5.1).

6.3.2 Biological soil quality

Soil quality is defined as the ability of soils to support healthy living communities and maintain biological productivity (Doran and Safley 1997). In particular, biological soil quality (BSQ) is related to the activity of soil dwelling communities, their biodiversity, the organic matter content, and its turnover rate.

Soil microorganisms and microarthropodes are strictly associated with the soil matrix throughout their life cycles and are sensitive to its chemical properties. We chose microbial parameters (biomass, respiration, and stress indexes) and microarthropodal communities (BSQ index; Parisi 2001) as indicators of biological quality.

Microbial properties change widely in space and time, and no threshold values for the identification of stress symptoms have been defined yet; the measured values must be compared in every study between soils with different properties (Nielsen and Winding 2002).

Microbial indicators alone can give incongruous results. For example, basal respiration can be reduced or increased in the presence of metals (Giller et al. 1998). They are better interpreted when related to each other as stress indices.

6.3.2.1 BSQ index

The BSQ index is based on the number of taxa of microarthropodal communities, the presence of sensitive genera, and the presence of taxonomic groups with soil-dwelling adaptations (Parisi 2001). The assumption is that the higher the soil quality, the greater the number of well-adapted microarthropod groups. Euedaphic biological forms (i.e., forms adapted to soil dwelling) are also known to be sensitive to metal toxicity (Fountain and Hopkin 2004).

Microarthropodes were collected from fresh soil samples (500 g, three samples for each soil pit at a depth of 0–10 cm) using Berlese-Tullgren selectors.

This method was based on soil fauna vertical tropism in relation to light and humidity (desiccation, due to an incandescence lamp lying overhead, pushes the soil organisms to escape to deeper horizons, thus falling into an underlying box, where they are fixed by a preservative solution [2 parts 75% ethanol and one part glycerol]). This extraction continued for seven days. After the extraction, the soil microarthropodes were observed with a binocular microscope (40X) and classed. Each taxon belonged to a biological form (BF), or ecotype. BFs are taxonomic groups (usually at the genera level) with similar body shapes, showing adaptive convergence to different degrees of soil dwelling (i.e., reduction or absence of visual apparatus, loss of pigmentation, reduced appendices, loss or reduction of flying organs). The BFs were classified according to an eco-morphological index (EMI; Parisi 2001), which gave scores to the different forms. Highest scores were given to the best-adapted, or euedaphic, forms. The BSQ score of the sample was the sum of its EMI scores. This score was then simplified according to an index (Parisi 2001), which produced the final seven quality classes (0–6) according to the complexity of soil arthropodal populations and soil dwelling adaptations.

6.3.2.2 Microbial activity and stress indicators

Microbial biomass (C_{mic}) and base respiration (Resp) were used as the main indicators of microbial activity.

Two samples (500 g) were collected for every pedogenetic horizon (A, AE, E, Bs). Microbial properties were analyzed on fresh, field-moist, mixed samples. Biomass was analyzed with the chloroform fumigation-extraction method (Vance 1987). Base respiration was measured according to the alkaline fixation method (Farini and Gigliotti 1989): the sample (equivalent to 20g dry weight) was placed in a hermetically sealed box and stored at 25°C for three days, the CO_2 produced by the soil microorganisms reacted with 10 ml of 0.5 N NaOH solution, the reaction was stopped by adding 10 ml of 1M $BaCl_2$, and the solution was titrated with 0.5 N HCl in order to quantify the amount of CO_2 reacted.

Cmic was measured after $CHCl_3$ fumigation (two days) and subsequent dissolution in K_2SO_4 (0.5 M, soil:solution ratio of 1:5) with the chemical oxygen demand method (COD; IRSA 1981). Labile carbon (C_{lab}), which was the readily available substrate for microbial growth, was extracted with a weak solubilizer (K_2SO_4; Hofman et al. 2002) on a non-fumigated sample treated as above.

The results of the previous analysis were used for the calculation of stress indices, such as the specific respiration rate (Resp/ Cmic, also called metabolic quotient or qCO_2), the C_{mic}/TOC ratio and the C_{lab}/C_{mic} ratio. Resp/C_{mic} (expressed in µg C-CO_2 d-1mg-1C-biomass) showed the presence of stress factors that increased the metabolic activity of the living microbial community without a growth of the dimension of the population. The qCO_2 is known to be a useful indicator of metal stress in soils (Giller et al. 1998); C_{mic}/TOC and C_{lab}/C_{mic} showed the existence of limiting factors (stress factors) to microbial growth in the presence of ample and immediately available growing substrate.

6.3.3 Statistical analyses

A correlation analysis and a principal component analysis (PCA) were performed on the log-transformed soil properties (pH was not transformed) and lithology of the parent material in order to recognize the main factors involved in the variability of the edaphic properties. The relationships with biological activity data were interpreted through correlation analysis and PCA. Some soil properties were excluded due to their high inter-correlation.

The program R 3.0 for Windows was used for all statistical analyses.

6.4 Results and Discussion

6.4.1 Soil chemistry

Profiles P1, P65, P135, P134, and P137 were characterized by the podzolization process (D’Amico et al. 2008). The P198 profile was less developed and had an important presence of technogenic materials (up to 65% of mine debris) in the top horizons. The content in available metals (Tables 3, 4, 5, 6) in the BC horizon of P198, which had no mining materials in the skeletal fraction, was much higher than in other similar horizons in the study area. This finding could be due to illuvial accumulation related to an incipient podzolization process.

Ecologically meaningful pH, exchangeable cations, and organic C and N varied widely between the six soils (Table 6.2). For example, serpentinite soils typically have a Ca/Mg ratio lower than one. Profiles P65, P135, and P134 fit this serpentinite characteristic, but the P198 profile had a Ca/Mg ratio well above one. This ratio was highest in some surface, organic matter-rich A and AE horizons, since Ca is readily utilized by plants and Mg is easily leached away from the profile (Rabenhorst et al. 1982).

6.4.2 Heavy metals

6.4.2.1 Generalities

The total content and the mobile and pedogenic forms of metals were most concentrated in the organic matter-rich A and AE horizons, and, to a lesser extent, in the spodic B horizon. This finding was due to the stabilizing effect of organic molecules. The high correlation values between these forms and TOC (Table 6.3) point to the same effect. The value of the $metal_{Mn+ox+d+org+ex}/metal_{tot}$ ratio was lowest in the E horizons because the pedogenic fraction is easily removed by the leaching related to the podzolization process.

All the pedogenic forms of Ni, Co, and Mn were significantly correlated, both among forms and among elements (Table 6.3), in agreement with the high geochemical affinity between these metals (Gasser et al. 1994, Jarvis 1984). The correlations with the respective Fe fractions were slightly lower. The correlation between these metals and Cr was low: only Cr_{org} was related with all the forms of Ni, Co, and Mn because of the affinity between organic matter and all metals.

Ni_{av}, Co_{av}, and Mn_{av} were strictly correlated with each other. Their highest correlations were with the respective Mn-associated form, followed by the oxalate-extractable fraction, as shown for Mn by Gambrell (1996). Organic forms and the ones associated with crystalline Fe oxides are less related with the so-called "bioavailable" fraction.

6.4.2.2 Iron

Mn oxide-associated Fe usually decreased with depth (Table 6.4), while all the other forms showed a strong podzolic depth trend, with lowest values in the bleached E horizons and higher ones in TOC-rich A and AE and in spodic B horizons. Pedon P198 did not show a similar trend, but the values in the non-polluted BC horizon, which were much higher than in other similar horizons in the study area, suggested illuviation from the upper horizons.

6.4.2.3 Chromium

Total Cr was highest on serpentinite (Table 5.3), but in soils formed from mainly mafic materials (P1, P137), Cr was much higher than usual (on mafic rocks it is usually around 200–300 mg kg^{-1} [Brooks 1987]), maybe because of the presence of Cr-rich chlorite in the parent material (D'Amico et al. 2008). In all the pedons, except P198, Cr_{tot} was lowest in the E and highest in the A, AE, and B horizons. This finding suggested unusual mobility of this element. In fact, chromium is usually residually accumulated in the most weathered pedogenic horizons in subalpine and alpine soils because of the high stability of Cr-bearing spinels (chromite and magnetite; Bulmer and Lavkulich 1994, Roberts 1980). Contrarily, Gasser et al. (1994) reported an increasing trend with depth due to aeolian inputs of Cr-poor, felsic minerals on the soil surface, that are here unlikely from P1 through P377 (D'Amico et al. 2008). The high Cr mobility is probably related to its high concentration in easily weatherable chlorites, and to subalpine climate and vegetation.

The low available Cr(III) values verified its low mobility. This value should increase at pH values below 3.5 (Oze et al. 2004), or below 4.5 (Cooper 2002). Cr_{org}, Cr_{d}, and Cr_{ox} values were significantly correlated with the respective Fe values, showing both the association of Cr with the respective Fe pedogenic oxi-hydroxides and a similar susceptibility to the cheluviation and illuviation processes of podzolization. The extremely low Cr_{Mn} values show the impossibility of Cr association with Mn: Cr is easily oxidized and solubilised in presence of Mn oxides (Fendorf 1995).

The toxic Cr(VI) was high in some B horizons, despite the low pH and the high organic matter content. This form should be readily reduced to Cr(III) in acidic conditions in the presence of Fe2+ and organic matter (Fendorf 1995), but the high levels of Mn oxidize Cr to the toxic forms. Temporary waterlogging at snowmelt, causing moderate reducing conditions, followed by drying, can favour the temporary reduction of Mn oxides and the simultaneous oxidation of Cr(III). During drying, Mn oxides can form again (Cooper 2002).

6.4.2.4 Nickel

The absolute values of Ni (Table 5.2) on serpentinite were similar to the normal contents in acidified "serpentine soils" formed in temperate climatic conditions (Chardot et al. 2007, Hseu 2006). "Available" nickel (Ni_{av}) was not as high as in many temperate or boreal, well-developed soils formed on ultramafic materials (Lombini et al. 1998, Slingsby and Brown 1977); weathering released Ni from parent minerals, but high acidity and temporary reductive conditions at snowmelt probably caused leaching of Ni_{av} away from the soil profile. Smaller concentrations of Ni_{av} were found in poorly developed soils (Roberts 1980, Sanchez-Marañon et al. 1999).
The Ni_{av} depth trend mainly followed TOC, a trend contrary to that of pH. This result is different from what was reported by Gasser et al. (1994) for subalpine soils on serpentinite in the Swiss Alps, where Niav values increased with depth because of higher pH causing the adsorption of metals onto phyllosilicates. Worldwide, Ni_{av} is negatively correlated with pH (Echevarria et al. 2006), but in the six soils assayed no significant relationship between these two properties was found.
The Niav toxicity level (around 6 mg kg^{-1}; Gasser et al. 1994, Proctor and Woodell 1975) was always reached in the investigated soils formed from a parent material containing more than 60–70% serpentinite (P65, P135, P134) and in the polluted P198 soil.

6.4.2.5 Cobalt

Total Co was similar on all the lithologies. It was quite low in comparison to other ultramafic soils (Roberts 1980). This finding may be due to the high leaching related with extreme acidity and podzolization. The Co_{av} values were nevertheless highest on ultramafic parent materials (Table 5.4).
Co_d and Co_{ox} (Table 5.4) were in the same order of magnitude as in the subalpine soils shown by Bulmer and Lavkulich (1994). The high weatherability of Co-bearing minerals was shown by the particularly high fraction of Co associated with pedogenic materials ($Co_{Mn+ox+org+d}/Co_{tot}$). Weatherability of primary minerals and leaching to the B horizons suggest high potential bioavailability of this metal in subalpine environments.

6.4.2.6 Manganese

Total Mn depended on serpentinite content in the parent material. It was highest in the polluted soil P198 (Table 5.5). The detected values were normal for serpentinite soils (Oze et al. 2004). Mn_d and Mn_o usually accumulated in the B horizons (due to the podzolization process). This accumulation was not the case with P134, where temporary waterlogging probably caused leaching (Table 5.5). These values were lower than in other subalpine, less acidic soils (Bulmer and Lavkulich 1994) because of the podzolization process, high acidity, and seasonal waterlogging, which favored strong leaching. The high values found in the BC horizon of P198 are presumably due to illuviation.

6.4.3 Biological soil quality

The highest BSQ value was two (Table 6.5), which corresponded to a low absolute value. Considering the high acidity and the low nutrient content of these soils, the poor biological activity of the mor or moder humus forms, and the harsh climatic condition, this value is actually relatively quite high. It is related to the profiles with the lowest metal content (P1, P137).
The BSQ value was slightly lower (1.6) in the A horizon of P65, where the parent material had a higher serpentinite content and the available metals were higher (particularly Co and Mn). Here, TOC and N were much higher, and the pH value was slightly higher, thus representing a

better habitat for soil dwelling fauna. High metal concentrations can cause stress, which reduces the diversity and the adaptation of micro-arthropodal communities.

Despite the higher organic matter content of these soils, high Mn, Co, and Ni contents seemed to be correlated with the low (1) BSQ index in serpentinite soils P135 and P134, and even more in the contaminated P198 (BSQ = 0.6). P198 also had the highest nutrient content and the highest pH value, but these positive properties were not able to counterbalance the extremely high available metals. In pedon P198, the arthropodal community was extremely poor, dominated by *Acari* (Table 6.5). The accumulation of organic matter on the top of this profile could be related with the low biological activity due to metal stress (as shown by Giller et al. 1998).

Statistical analysis (PCA) supports the hypothesis of an existing link between low soil arthropodal diversity and available and total metal content (Fig. 6.1). The first factor of the PCA biplot explains the highest variance of the data (60.58%), and it is strongly related to metal content, Ca/Mg ratio, N, and BSQ. Ca/Mg and N are, however, of little interest because they were highly intercorrelated with TOC and metals (P198 had the highest metal content, Ca/Mg, TOC, and N values). It was expected that biological activity and arthropodal diversity would be increased by these properties (N is a nutrient, and a high Ca/Mg value is optimal for plant life and for primary productivity of the habitat), but here the correlation was negative.

"Available" Co, Mn, and Ni had a strongly significant negative correlation with BSQ. Other edaphic and environmental properties (exchangeable bases, Cr, TOC, drainage, altitude, aspect, stoniness) were less important.

The "available" Cr_{av} and the toxic Cr(VI) were scarce in the organic-matter rich surface horizons, and were not related with the composition and the soil-dwelling adaptation of micro-arthropodal communities.

Differences in vegetation did not contribute to the explanation of BSQ values.

In the literature, there are many examples regarding all metals tested. For example, Co (Lock et al. 2004) and Mn (Phillips et al. 2002) toxicities were demonstrated for Collembola (*Folsomia candida*), and for animals in general (Lison et al. 2001). Kuperman et al. (2003) demonstrated growth inhibition for Collembola (*Folsomia candida*) and *Oligochaeta* due to Mn and Co. Ni toxicity was documented for a species of *Folsomia* (Scott Fordmands et al. 1999).

6.4.4 Microbial properties

Both Resp and C_{mic} followed more or less the TOC depth trend, but with significant differences among the different pedons (Table 6.6). Sometimes Cmic increased in B horizons, contrary to the results of Fritze et al. (2000). "Available" metals were not significantly related to Cmic or Resp (Table 6.7). The depth trend of stress indices is not easily interpretable. It seems that in most cases the B horizons had high C_{mic}/TOC values, but the qCO_2 and C_{lab}/C_{mic} did not show clear trends. C_{mic} was correlated with C_{lab}, showing adaptation of microbial communities to edaphic factors (Tab. 12).

The highest correlation values were between stress parameters and Mn_{av}, Co_{av}, and Ni_{av} (Table 6.7); Cr_{av} and Cr(VI) were not correlated with any microbial parameter. A graphical representation of the relationships between Co_{av} and qCO_2 and between Co_{av} and C_{mic}/TOC is shown in Figure 6.2 for A and B horizons. In the A horizons, the R^2 value was less significant than it was in the B horizons, probably because of the hidden effect of the different nutrient content: the positive effect of a high available substrate for growth (TOC, C_{lab}, N) neutralized the stress caused by metals. In B horizons, the nutrient content did not significantly change between the six soils, and the metal stress was clearer. A similar trend was evident for Ni_{av} (data not shown).

The statistical analyses confirmed the relationship between microbial activity and metals, even if the number of samples was too small to warrant statistical significance (Table 6.7). Omitting the polluted P198, the results were still confirmed. Some statistically significant results (P-value < 0.05) were found for qCO_2 and Ni_{av}, Mn_{av}, Co_{av}, and for C_{mic}/TOC and the same "available" metals. The C_{lab}/C_{mic} ratio was less strictly related with metals, but was significantly related with the other stress indices. The positive correlation between pH values and qCO_2 was not significant from an ecological point of view because higher soil pH should have positive effects on microbial activity (Pennanen 2001).

According to the PCA analysis (Fig. 6.3), nutrients are the best contributors to the second principal axis, which accounts for the 28.46% of the total variability. Resp and C_{mic} were similarly related with both axes. The first factor (which explained 57.20% of the total variability) was influenced by stress indices, available Co, Ni, Mn, and the autocorrelated pH and Ca/Mg.

6.5 Conclusions

In the six studied pedons, the total and "available" heavy metal content (Ni, Co, Mn, and Cr) were highly correlated with the serpentinite content in the parent material, as expected in soils on ophiolitic rocks (Brooks 1987). The chemical fractionation of the metals showed that weathering efficiently releases metal from the parent material, and the released forms are mobilized and redistributed in the profile by the podzolization process. This high mobility enhances bioavailability and toxicity: EDTA extractable ("bioavailable") Ni, Co, and Mn were significantly correlated with the redistribution of organic matter and iron oxides within the soil profiles, typical of podzolic soils. Toxic levels are reached on substrates dominated by serpentinite. Toxic Cr(VI) could have been a significant problem only in some B horizons.

In the six pedons, the micro-arthropodal communities were affected by metals as shown by the BSQ index and its strong, negative correlation with Ni_{av}, Co_{av}, and Mn_{av}. Where available metals were higher, the communities were simplified and the number of soil-dwelling adapted forms decreased.

Cr had no visible effects within the surface horizons, probably because of the low content of the toxic Cr(VI) due to the high TOC amount. In fact, organic matter and ferrous iron (Fe^{2+}) are the main reducing factors for Cr(VI) in soils (Fendorf 1995).

The proposed strong effects of natural loads of heavy metals on arthropods was supported: the simplified communities in metal-rich soils were probably the result of toxicity at the organism level (changes in life cycle and reproductive efficiency), at the population level, and at the community level (different reactions of different species to the same ecological factors) (Edwards 2002). However, it was not clear if all the considered metals had effects on microarthropodal ecology or just one or few of them; the metals are highly intercorrelated.

Microbial activity indices (base respiration and biomass) were not clearly related to the soil metal contents because of the masking effect of nutrients; stress indices (qCO_2, TOC/C_{mic}, C_{lab}/C_{mic}) were related to "available" Ni, Co, Mn, pH values, Ca/Mg, TOC, and C_{lab}. Metals were, however, the only significant parameters from an ecological point of view. In fact, TOC and C_{lab} are nutrients, and high nutrient content should decrease the stress in the soil living communities. Higher pH values usually support microbial activity, while the Ca/Mg ratio is normally strongly related with the primary productivity of the habitat and higher values should have positive effects on the soil dwelling communities. These properties are positively related with enhanced stress symptoms in microbial communities because of the strong intercorrelation with all the forms of metals.

Metal stress on microbial communities was evident in the additional amount of energy required by the microorganisms to support metal tolerance mechanisms. In turn, this energy could not be used for growth. Contrary to common belief (Schipper and Lee 2004), there are limits to the evolution of metal-resistant microbial strains.

The thick organic layer on the top of the heavily polluted P198 could be related to the slow decomposition rate caused by low arthropodal and microbial activity, which was probably an effect of the extremely high metal content of anthropic input. Further studies on the different composition of the microbial communities in soils with different metal content could reveal more information regarding their adaptive mechanisms.

All the results demonstrated the existence of metal stress, on both microbial communities and micro-arthropodal populations, and can therefore be considered ecologically meaningful. A secondary conclusion is that both BSQ (Parisi 2001) and microbial stress indices seemed to be useful in indicating metal toxicity in natural or polluted soils on ophiolitic parent material.

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Figure 6.1. Biplot of the PCA analysis between the main edaphic factors and the BSQ.

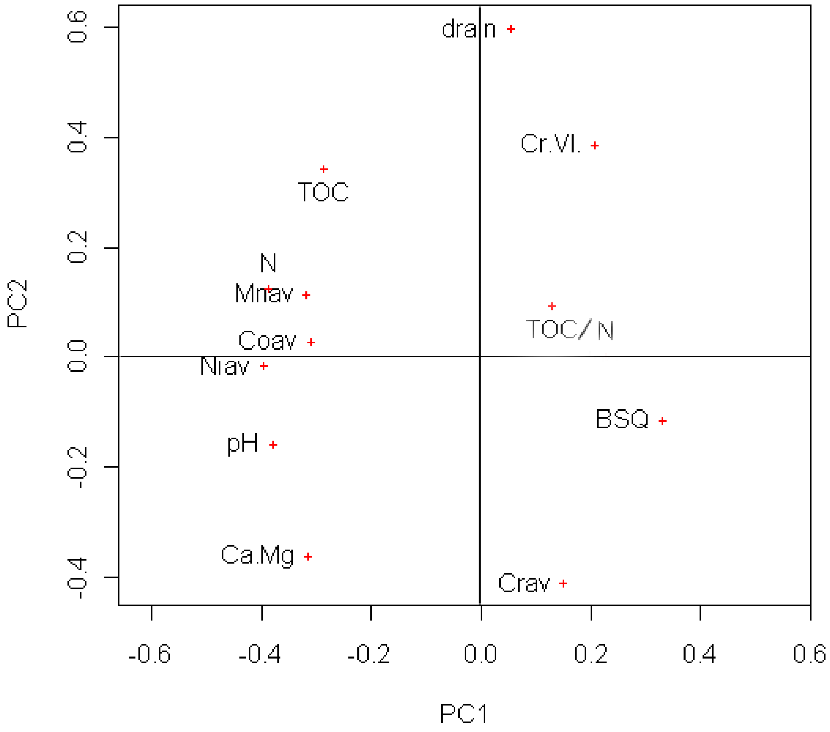

Figure 6.2. Relationship between qCO_2, C_{mic}/TOC, and available Co in A and B horizons. The correlation is particularly evident in the B horizons.

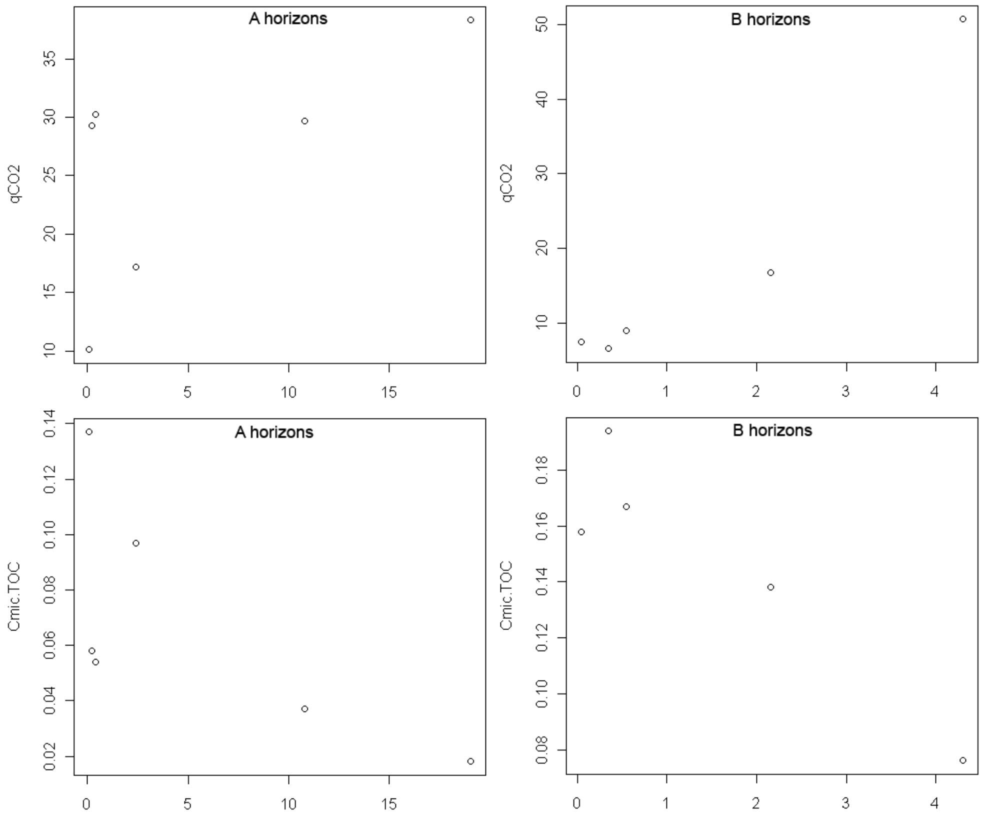

Figure 6.3. Biplot of the PCA analysis performed on the microbial MDS on available metals and on the main soil properties (B horizons).

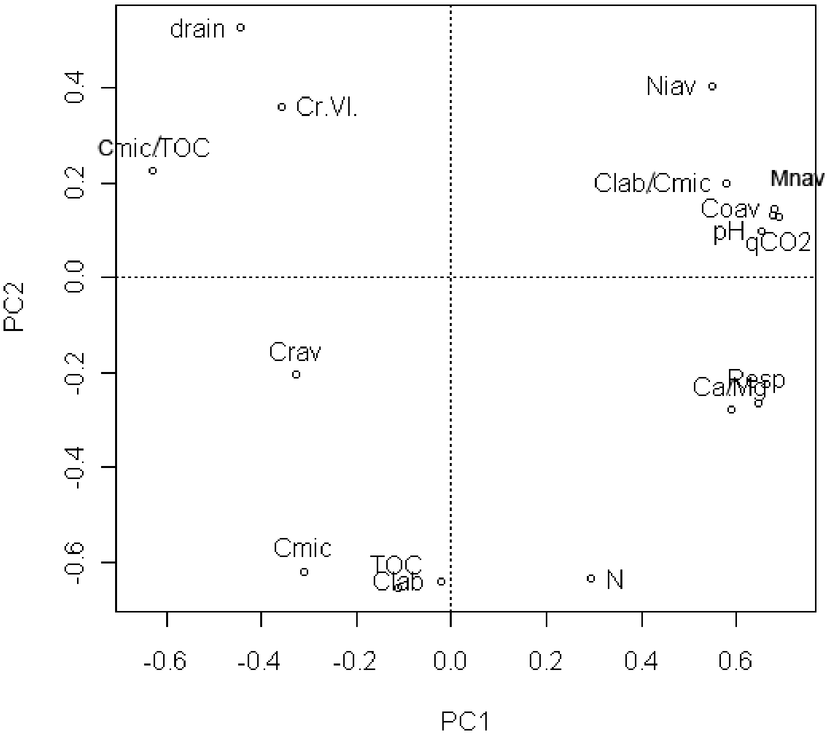

Table 6.1: general information about the pedons and composition (%) of the parent material, according to the lithology of the coarse fraction (BC, CB or C horizons).

Pedon	Altitude	Aspect	Slope	Soil type (WRB)	Main tree species	Tree cover (%)
P1	1830	340°	12°	Ortsteinic Podzol	Pinus uncinata	80
P65	1795	5°	1°	Epistagnic Podzol	Pinus uncinata	50
P135	1975	350°	14°	Haplic Podzol	Pinus uncinata, Larix decidua	50
P134	2117	30°	10°	Haplic Podzol	Pinus uncinata, Larix decidua	50
P137	1865	0°	12°	Ortsteinic Podzol	Pinus uncinata	70
P198	1685	80°	5°	Spolic Technosol	Pinus uncinata	60
Pedon	**Serpentinite**	**Metagabbro**	**Prasinite**	**Amphibolite**	**Chlorite schist**	**Mine debris**
P1	20	70	7	2	1	0
P65	50	38	4	4	4	0
P135	90	0.5	1	3	5.5	0
P134	95	0	4	0	1	0
P137	48	37	3	3	6	0
P198	30	5	0	0	0	65

Table 6.2: Selected chemical properties of the six soils.

Pedon	Depth	Horizon	pH H_2O	pH KCl	TOC	N	Ca	Mg	Na	K	Ca/Mg	Exch. Acidity
	cm				g kg^{-1}	g kg^{-}	Cmol kg^{-1}	Cmol kg^{-1}	Cmol kg^{-1}	Cmol kg^{-1}		Cmol kg^{-1}
P1	0-5	OF-OH	3.7	2.9	191		4.36	1.33	0.48	0.37	3.28	-
	5-15	E	4.4	3.7	14	0.8	0.58	0.36	0.41	0.11	1.61	9.07
	15-27	Bs	4.7	4.2	52	1.2	0.62	0.38	0.43	0.11	1.63	14.99
	27-34	Bsm	4.7	4.3	17		0.42	0.24	0.41	0.20	1.75	19.38
	34-42+	Cm	4.8	4.5	8		0.41	0.29	0.45	0.16	1.41	8.11
P65	0-10	Ah	4.8	4.2	70	2.2	1.30	1.44	0.50	0.14	0.90	6.87
	10-20	Eg	5.0	4.2	7	0.6	0.46	0.65	0.37	0.16	0.71	5.61
	20-31	Bsg	5.4	4.4	9	0.5	0.68	0.92	0.40	0.09	0.74	5.94
	31-50+	Cg	5.3	4.7	4		0.58	0.48	0.49	0.15	1.21	4.06
P135	4-13	A	4.9	4.0	23	2.4	1.18	1.91	0.32	0.19	0.62	11.88
	13-27	E	4.6	3.5	23	0.8	1.43	2.21	0.38	0.10	0.65	3.75
	27-37	Bs1	4.9	3.9	9	0.8	1.19	1.86	0.40	0.10	0.64	9.70
	27-53	Bs2	5.3	4.2	4		0.89	1.25	0.41	0.10	0.71	6.56
P134	3-10	AE	4.7	3.4	31	1.1	1.24	1.85	0.43	0.35	0.67	9.06
	10-22	E	4.7	3.3	17	0.8	0.66	1.15	0.39	0.15	0.57	9.07
	22-42	Bs	4.8	3.7	11	0.8	0.18	1.36	0.44	0.10	0.13	9.05
	42-51	Bshg	4.8	3.8	18		1.26	1.54	0.01	0.03	0.82	10.92
P137	3-10	AE1-AE2	3.9	3.9	13	0.8	1.20	0.74	0.64	0.29	1.62	2.5
	10-24	E	3.8	4.0	7	0.5	1.34	0.54	0.75	0.29	2.48	2.19
	24-48	Bs	4.7	4.7	5	0.5	1.01	0.74	0.62	0.11	1.36	1.87
	48-70+	Cm	5.2	5.0								
P198	1-10	Ah1	5.4	5.3	51	3.0	5.63	1.54	0.57	0.22	3.5	3.3
	10-21	Ah2	5.5	5.5	50	3.0	5.63	1.54	0.57	0.22	3.6	3.44
	21-42	BC	5.6	5.5	8.1	1.0	3.24	1.54	0.68	0.12	2.1	1.87

Table 6.3: Correlation analysis between the main chemical properties and metal speciation of the six soils. Significant results (p-value > 0.05) are above 0.49. Cr(VI), Cr_{av}, Cr_{o}, Cr_{mn}, Cr_{d}, Co_{org}, Mg_{ex} and drainage are omitted, as they are never significantly correlated with any other.

	Mn_{av}	**Mn_{mn}**	**Mn_{ox}**	**Mn_{org}**	**Mn_{d}**	**Co_{av}**	**Co_{mn}**	**Co_{ox}**	**Co_{d}**	**Ni_{mn}**	**Ni_{o}**	**Ni_{org}**	**Ni_{d}**	**Ni_{av}**	**pH**	**CO**	**Ca.ex**
Mn_{av}	1.00																
Mn_{mn}	0.92	1.00															
Mn_{ox}	0.79	0.91	1.00														
Mn_{org}	0.80	0.81	0.82	1.00													
Mn_{d}	0.80	0.77	0.74	0.94	1.00												
Co_{av}	0.94	0.88	0.66	0.81	0.84	1.00											
Co_{mn}	0.91	0.99	0.93	0.81	0.73	0.82	1.00										
Co_{ox}	0.70	0.78	0.84	0.96	0.90	0.73	0.76	1.00									
Co_{d}	0.64	0.61	0.47	0.65	0.70	0.72	0.59	0.54	1.00								
Ni_{mn}	0.80	0.80	0.77	0.98	0.95	0.86	0.77	0.96	0.66	1.00							
Ni_{o}	0.73	0.71	0.68	0.92	0.96	0.82	0.65	0.93	0.64	0.97	1.00						
Ni_{org}	0.83	0.82	0.80	0.90	0.86	0.83	0.82	0.84	0.74	0.89	0.85	1.00					
Ni_{d}	0.79	0.82	0.71	0.89	0.93	0.89	0.75	0.89	0.70	0.93	0.92	0.81	1.00				
Ni_{av}	0.84	0.80	0.74	0.97	0.95	0.89	0.77	0.92	0.71	0.99	0.96	0.92	0.92	1.00			
Cr_{org}	0.75	0.60	0.51	0.73	0.79	0.71	0.59	0.62	0.55	0.73	0.67	0.65	0.73	0.77			
pH	0.44	0.66	0.81	0.68	0.56	0.40	0.68	0.73	0.48	0.61	0.56	0.72	0.55	0.56	1.00		
CO	0.52	0.50	0.51	0.82	0.70	0.59	0.50	0.78	0.52	0.81	0.75	0.64	0.68	0.78	0.50	1.00	
Ca.ex	0.62	0.74	0.87	0.88	0.78	0.58	0.75	0.93	0.48	0.84	0.77	0.71	0.77	0.78	0.78	0.71	1.00
Ca/Mg	0.42	0.58	0.72	0.74	0.64	0.43	0.57	0.82	0.42	0.71	0.69	0.58	0.63	0.63	0.77	0.62	0.91

Table 6.4: Chemical speciation, or extractability, of Iron. Fe_{Mn} is hydroxylamine-extractable Fe.

		Fe_{Mn}	Fe_{ox}	Fe_{org}	Fe_{d}
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
P1	E	355	5217	4027	10291
	Bs	260	10175	4611	42202
P65	A	458	9273	10774	37699
	E	95	2638	4233	24224
	Bsg	167	8650	9310	42758
P135	A	568	8334	8418	45549
	E	272	6029	4506	30381
	Bs1	200	8090	9587	46734
P134	AE	342	6581	7119	33998
	E	231	3931	4777	24183
	Bs	169	7782	6989	42481
P137	A	436	6933	6100	32298
	E	125	2251	2806	26072
	Bs	118	7694	3528	40887
P198	A1	203	10490	18932	58973
	A2	785	11895	7537	54665
	BC	171	7759	4988	34239

Table 6.5: Microarthopodal forms and BSQ values in the samples of the six pedons. Avg. P is the average value for the profile.

	Collembola Orchesella	Collembola Folsomia	Collembola Neanura	Collembola Euedaphic (others)	Collembola Onichiurides	Protura	Arachnida	Total score	QBS index
P1a		1	2					39	1
P1b		4	10					58	1
P1c	2	12	16		1			70	4
Avg. P1								56.7	2
P65a			1	1				40	1
P65b	1	4	2					48	1
P65c	2	6	6		2		1	51	3
Avg. P65								46.3	1.6
P135a		7	8					38	1
P135b	1	25	30	10				40	1
P135c		9						36	1
Avg. P135								38	1
P134a	2	14	15	1				41	1
P134b	2	17	6					38	1
P134c		12	4	1				51	1
Avg. P134									1
P137a		2				1		56	4
P137b	2	15						46	1
P137c		2	1					38	1
Avg. P137									2
P198a								20	0
P198b	1	8		1				35	1
P198c		7						36	1
Avg. P198									0.6

Table 6.6. Microbial characterization of the six soils. Results from the B horizon of profile P7 and from the A horizon of profile P3 are omitted because of analytical problems.

		TOC (g/kg)	C_{lab} (g C-CO2/ kg dry soil)	Resp (µg C-CO2/ g dry soil)	C_{mic} (µg C_{mic}/ g dry soil)	qCO_2 (µg C-CO2 $d^{-1}mg^{-1}C_{mic}$)	C_{mic}/TOC -	C_{lab}/C_{mic} -	BSQ
P1	E	17.2	0.066	46.5	2356.52	10.1	0.137	0.028	2
	BS1	21.1	0.083	36.0	2479.28	7.4	0.118	0.033	
P65	A	70.0	nd	nd	Nd	nd	Nd	nd	1.6
	E	4.1	0.030	18.0	977.96	9.4	0.239	0.031	
	Bsg	4.6	0.031	13.5	768.40	9.0	0.167	0.041	
P135	A	37.4	0.116	82.5	1390.44	29.7	0.037	0.083	1
	E	16.8	0.062	24.0	1308.54	9.4	0.078	0.048	
	Bs1	6.7	0.067	30.0	922.68	16.7	0.138	0.073	
P134	AE	26.1	0.087	87.0	2523.63	17.2	0.097	0.035	1
	E	12.7	0.055	28.5	872.63	16.7	0.069	0.063	
	Bs	7.9	0.048	19.5	1532.36	6.5	0.194	0.032	
P137	AE	13.2	0.061	43.5	760.08	29.3	0.058	0.080	2
	E	7.0	0.070	46.5	833.82	27.8	0.119	0.084	
P198	Ah1	49.8	0.060	67.5	880.39	38.3	0.018	0.068	0.6
	Ah2	49.8	0.117	163.5	2705.47	30.2	0.054	0.043	0.6
	BC	7.0	0.048	54.0	532.22	50.7	0.076	0.090	

Table 6.7. Correlations between microbial properties and the main soil parameters.

	Cr_{av}	Mn_{av}	Co_{av}	Ni_{av}	Cr(VI)	N	TOC	pH	resp	C_{mic}	qCO_2	C_{lab}	C_{mic}/TOC	C_{lab}/C_{mic}
Cr_{av}	1	-0.08	-0.05	-0.16	0.28	-0.11	-0.08	-0.54	-0.24	-0.01	-0.3	0.15	-0.07	0.11
Mn_{av}		1	0.94	0.84	-0.14	0.64	0.57	0.49	0.27	-0.22	0.65	0.17	-0.61	0.45
Co_{av}			1	0.89	-0.17	0.7	0.65	0.43	0.25	-0.2	0.54	0.19	-0.58	0.38
Ni_{av}				1	-0.18	0.75	0.72	0.6	0.38	-0.09	0.51	0.11	-0.53	0.19
Cr(VI)					1	-0.26	-0.33	-0.16	-0.3	-0.21	-0.33	-0.19	0.32	-0.03
N						1	0.97	0.49	0.81	0.34	0.46	0.68	-0.68	0.12
TOC							1	0.44	0.8	0.47	0.38	0.72	-0.69	0.02
pH								1	0.48	-0.09	0.69	0.08	-0.29	0.26
resp									1	0.54	0.49	0.8	-0.56	0.08
C_{mic}										1	-0.33	0.63	-0.02	-0.64
qCO_2											1	0.23	-0.6	0.78
C_{lab}												1	-0.57	0.12
C_{mic}/TOC													1	-0.56

7. Biological properties of alpine soils.

Abstract

Soils on ultramafic rocks are usually colonized by plant species and communities adapted to high heavy-metal content and low Ca/Mg ratio. However, the effects of metal speciation on microbial activity and arthropodal communities have scarcely been studied, especially under coniferous forests in boreal or subalpine areas. Seventeen typical alpine soils (i.e., above present day treeline), in the ophiolitic area of Mont Avic Natural Park, located in the Western Italian Alps, were studied in order to verify the effect of Ni, Co, Mn, and Cr and of their speciation and mobility and their effects on soil biological properties and microbial activity. The soil-forming processes are dominated by climatic and topographical factors, and soil properties are usually well correlated with the parent materials. Metal content and bioavailability are highest on serpentinite, but huge differences are visible among different soils on the different rock types. However, differently from what happens under subalpine forests, these edaphic properties don't deeply influence arthropodal communities or microbial activity, all of which were not correlated with parent material or bioavailable Ni, Co, and Mn.

7.1 Introduction

Despite the interest in heavy metal soil ecology, very few studies have been undertaken to determine the biological impacts of chemical speciation and the availability of metals, particularly in alpine or boreal environments. Many studies show how biological activity and biodiversity are broadly affected by heavy metals in recently contaminated soils (e.g. Giller et al. 1998, Scott Fordmands et al. 1999, Chander et al. 2001), but only a small number deal with the same subject on naturally metal-rich soils (e.g., Amir and Pineau 2003, Mengoni et al. 2001, Schipper and Lee 2004).

The goals of this study were to assess whether heavy metals and their chemical forms and bioavailability can be considered toxic on microbial communities and on soil-dwelling arthropods in high altitude soils. Biological soil quality index (BSQ; Parisi 2001) based on microarthopod communities, microbial activity (biomass and respiration), and stress indicators (i.e., metabolic quotient) were used as edaphic quality indices.

7.2 The Study Area

The seventeen investigated soil pits were located above the present-day tree-line in Mont Avic Natural Park, Valle d'Aosta, northwestern Italy. Plant community composition changed widely according to the substrate (chapter 2).

The soil pits were representative of the typical alpine soils formed in the study area. They were selected among 102 previously observed and analyzed soil pits. Environmental properties of the sites are summarized in table 7.1. The average yearly temperature is below 2 °C and the precipitation is between 1200 and 1500 mm/y (Mercalli 2003).

7.3 Materials and Methods

Soil sampling took place in August 2008. The sampling and laboratory analytical methods are described in chapter 6.3.

During late summer 2009, three heavily cryoturbated soils (1-1.5 m wide rock circles and stripes, P52 on calcschists, P141 on serpentinite and P142 on metagabbros and amphibolites) where sampled in order to better characterize their micro-scale variability, with the aim of recognizing ecologically significant relationships between cryoturbation, edaphic properties, metal speciation and bioavailability, microbial activity and stress symptoms.

The whole soil pattern (rock circle or stripe) was sampled along complete horizontal transects (five samples for each pedon, at a depth between 1 and 10 cm). The same chemical and microbial analysis were performed on the soil samples (chapter 6.3); microarthropodal communities were not observed. Only the most labile and bioavailable forms of metals were analyzed (soluble, exchangeable, associated with Mn oxides, amorphous Fe-oxides and organic matter, tab. 5.1).

As these soils were developed in cold, high altitude regions, base respiration (chapter 6.3.2.2) was measured at 25°C (standard temperature) and at 10°C, which is probably closer to the summer temperature of the surface layers, and to which microbial populations are possibly better adapted.

7.4 Results and Discussion

7.4.1 Soil properties and heavy metals speciation and availability

A general description of soils and pedogenic processes active above the treeline in Mont Avic Natural Park are in chapter 2. A great pedogenic and chemical variability related to substrate and topography/microclimate is visible in table 7.1 and 7.2. Slope stability, snow and vegetation cover were in favor of pedogenic evolution and acidification. On serpentinite, for example, pH values were close to 6 in eroded and cryoturbated soils, and they became extremely acidic in stable soils. Here, the organic acids produced by vegetation (in particular by ericaceous dwarf shrubs) were added to the surface horizons, and leaching was increased by the waterlogging caused by the melt of the deep snow cover.

Metal speciation and bioavailability of the studied alpine soils are described and commented in chapter 5.

7.4.2 Biological soil quality

The comparison between the results shown in chapter 5 and in table 7.3 shows that heavy metal content, availability and speciation didn’t have an ecological influence on micro-arthropodal communities in the studied high-altitude soils. This was different from what happened in subalpine forests (chapter 6), where available heavy metals had a strong ecological effect on micro-fauna.

In particular, the soils which possessed the (commonly considered) positive properties (favorable Ca/Mg ratio and high N content), the ones that supported a high plant biodiversity and the most stable ones, on calcschists or gabbros, had an extremely low micro-arthropodal biodiversity and low number of species adapted to soil dwelling (euedaphic genera). A stable, biologically active soil should be colonized by genera well adapted to the soil environmente (Parisi 2001).

In fact, the lowest BSQ values were obtained in P38, P52 and P56 (tab. 7.3), which were developed on calcschist. P38 and P56, in particular, supported a rich and diverse vegetation, while P52 was a heavily cryoturbated, high altitude sorted circle.

The analyzed soils developed on serpentinite in similar landscape positions were usually more stony, eroded, sparsely vegetated, were characterized by a lower Ca/Mg ratio, TOC and nutrient content. However, their BSQ index values were usually higher. In particular, P12 and P139 seemed to have a high biological quality (average BSQ index values were above 3). P140 was extremely disturbed by erosion, almost devoid of vegetation and the few plants growing on it belonged to heavy metals-adapted serpentine species. Available Ni was extremely high in this soil (chapter 5). The BSQ index was quite low (1.3), but one sample had a high micro-arthropodal biodiversity, including many euedaphic species and some which are known to be sensitive to metal contamination (*Folsomia*, according to Scott Fordmans et al. 1999, Phillips et al. 2002, Fountain and Hopkin 2003, Kuperman et al. 2003, Lock et al. 2004).

Comparing P10, P11 and P12 (very close to each other but with different metal contents and availability), we see that there was no decrease in the soil quality (biodiversity and soil-dwelling adaptation) with increasing total and available metal contents.
The correlation analysis (tab. 7.4) and the PCA (fig. 7.1) between the BSQ values and other edaphic and environmental parameters showed that only Mn and Co_{org} were able to negatively influence microarthropodal biodiversity. This is in agreement with the results obtained in subalpine soils, where BSQ values were influenced by Mn, Co and Ni (in order of importance). It seems however ecologically unlikely that the most fertile soils, supporting a rich and diverse vegetation, are the most toxic for micro-arthropodes. Statistical significance of these results was inexistent, because of the low number if samples.
Humidity, organic matter, pH values were not correlated with BSQ values as well.

7.4.3 Microbial properties

Microbial parameters are shown in tab. 7.5.
C_{mic} followed more or less the TOC depth trend (tab. 7.5). Basal respiration seemed related to C_{lab}, as their trend was similar and the decrease with depth less marked than the one of TOC and C_{mic}.
The comparison between microbial parameters in analogous soils developed on different materials showed that there were scarce relationships between parent material, metal content and speciation and stress for microbial communities. P12, for example, had a higher microbial biomass and respiration (particularly in subsurface horizons) than P11; these two profiles were 50 m far from each other, but were developed respectively on serpentinite and on metagabbros. Cryoturbation and erosion were in favor of high available metal contents on serpentinite (chapter 5): in fact, P12, supported a sparse vegetation, rich in Ni hyperaccumulators and other serpentinite-endemic species. Stress indices were uncorrelated with every parameters.
The correlation analysis between microbial parameters and soil properties didn't give any significant results in either A (not shown) or subsurface horizons (tab. 7.6). A negative correlation was visible between respiration and some forms of Ni, Cr and Mn, while biomass was positively related with Mn. The ecological and statistical significance were extremely scarce. Considering the stress indices, only TOC/C_{mic} had some nearly-significant statistical correlation values with some edaphic properties (some forms of Mn, Co and Ni). In subsurface horizons, respiration was inhibited by some Co and Ni forms, while biomass was uncorrelated with any chemical property.
No clear relation was visible in the dispersion graphics (fig. 7.2, 7.3, 7.4) as well. Weak relationships between some microbial stress indices and easily reducible metals emerged in A horizons, while in subsurface horizons microbial stress was completely uncorrelated. In subalpine soils (chapter 6), the ecological effect of heavy metals was more visible in deep B horizons than in surface A or AE ones.
No clear relationships between microbial activity, stress indices and edaphic properties emerged from the PCA analysis as well (for horizons A, see picture 7.6, tab. 7.7).

7.4.4 Patterned ground transects

To reduce the confusing effect of the great environmental and pedological variability on the relationships between heavy metals and microbial activity and stress, 3 analogous soils were chosen on serpentinite (P141, fig. 7.6), mafic rocks (P142, fig. 7.7) and calcschists (P52, fig. 7.8). They were active, heavily cryoturbated (sorted ground, rock circles) and they had many environmental and pedological properties in common. TOC and exchangeable acidity decreased from the stable, stone-rich borders to the cryoturbated centers, as normally happens in such soils (Ugolini et al. 2006, tab 7.8). Correlated with the higher organic matter content and the higher stability (which favored leaching), pH values decreased of more than 1 point from the stony borders to the disturbed, cryoturbated centers (tab 7.8). Exchangeable bases as well decreased from the borders to the center, because of the higher CEC values characterizing organic matter-rich sectors. The Ca/Mg ratio changed only slightly, between the different substrates and along the transects (tab. 7.8). Labile forms of metals (tab. 7.9) changed weakly along the transects, evidencing a high lateral mobility of them and a weak dependence on the CEC of the organic matter; an early weathering of the parent material was demonstrated by the higher level of metals associated with Mn and amorphous Fe oxides in the less weathered central parts of the soil patterns, in comparison with the more stable and acidified, TOC-rich borders. The fast weathering was probably caused by the cryo-fracturation of the material, which increased the silty textural fraction and the surface/volume ratio, rendering the material susceptible to weathering.

C_{lab} (tab 7.10) was uncorrelated with TOC, evidencing a movement of labile organic matter in solution.

No clear trend across the transects was also visible for microbial biomass, while respiration was usually higher in TOC-rich regions of the sorted soil pattern. Soil base respiration was better related with TOC content, with a clearer trend when measured at 25°C (tab. 7.10).

Stress indices were usually uncorrelated with TOC along the transects. Only Q_{met} showed a visible correlation with some forms of labile Ni (tab. 7.10).

7.5 Conclusions

Metal speciation and bioavailability above the treeline were influenced by pedological and geomorphological processes (chapter 5). An early weathering of “fresh” materials and an easy release into labile, pedogenic forms was demonstrated by the patterned ground transects: the central, least developed sectors had a high pedogenic oxide content, which were later dissolved by organic acids and by anoxic conditions at snowmelt. The strong decrease in metal content in the TOC-rich sections was probably caused by the dissolution of labile pedogenic materials followed by solubilization. Heavy metals could thus be transported for long distances in the soils with pore water (abundant at snowmelt), and could cause the observed enrichment in the deep horizons of the soils developed on metal-poor substrata (for example, in downslope calcschist soils, chapter 5). The strong mobilization and bioavailability of metals had strong, statistically significant effects on vegetation (chapter 2), but not on soil micro-fauna and microbial communities.

In the studied alpine pedons, the micro-arthropodal communities were not significantly affected by heavy metals, as shown by the absence of statistically or ecologically significant correlations between BSQ index and most heavy metal “species”. A weak effect could be observed for Mn, as the most Mn-rich calcschist soils showed the lowest Biological Soil Quality index values. However, these soils were the most favorable for vegetation: they supported the richest and most diverse plant communities, they had a high Ca/Mg ratio, a high stability and development degree.

The ecological effect of heavy metals was, thus, less visible in high altitude soils than in subalpine forests. This could be due to other, unknown but more important ecological or edaphic factors. Soil compaction could be an important factor, as the unstable, eroded and cryoturbated soils were probably the most aerated. At snowmelt, compacted stable soils could easily suffer anoxic conditions, possibly affecting soil micro-fauna. Waterlogging in stable calcschist soils was demonstrated by the bleached subsurface AE horizons (chapter 2 and 5).

Microbial activity (base respiration and biomass) and stress indices were not clearly related to the soil metal contents and speciation as well. These results were very different from what observed in subalpine soils: there, microbial communities were strongly influenced by heavy metals. A shift towards catabolic processes with increasing available metals was there demonstrated by the increased qCO_2, TOC/C_{mic} and C_{lab}/C_{mic} (chapter 6).

The lack of correlation between microbial stress and heavy metals could be due to many hypothesis. It could be caused by adaptation of microbial communities to heavy metals-rich soils: similar adaptation processes were observed in ophiolitic soils in New Zealand by Shipper and Lee (2001). The large temporal variability (Nemergut et al. 2005) can be an example of how high altitude microbial communities quickly react to environmental changes and variability.

Other reasons could be found in the different carbon sources in the different soils, caused by the different weatherability of the humic substances produced by the different plant species (Grayston et al. 2001). Some microclimatic or topographic differences could have been omitted. Different microbial community composition could be another explanation. It is known that heavy metal pollution (Chander et al. 2001) and low fertility (Grayston et al. 2001) cause a shift in the microbial community structure towards fungi. Fungi-dominated communities are characterized by higher metabolic quotient values than bacteria-dominated ones (Anderson and Domsch 1975).

In addition, according to Chander et al (2001), a large part of microbial biomass is inactive in heavy-metals polluted soils, thus decreasing the observed stress indices. In fact, the chloroform fumigation extraction technique (used in this study) is not able to distinguish between active and inactive biomass (Grayston et al. 2001).

The study along transects on analogous soils on different parent materials gave slightly better results, but the only stress index related with some metals (labile forms of Ni) in an ecologically significant way was the metabolic quotient.

A deeper knowledge in mineral weathering and a better characterization of organic substances should be performed in order to better understand metal ecology in these high-altitude ophiolitic soils. It should be also necessary to distinguish bacterial and fungal biomass and respiration, in order to better observe a possible ecological effect of natural high heavy metal contents.

The methods used in this study are, therefore, inefficient in detecting metal stress in so diverse edaphic and environmental conditions.

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Figure 7.1. Biplot of the PCA analysis between the main edaphic factors and the BSQ index.

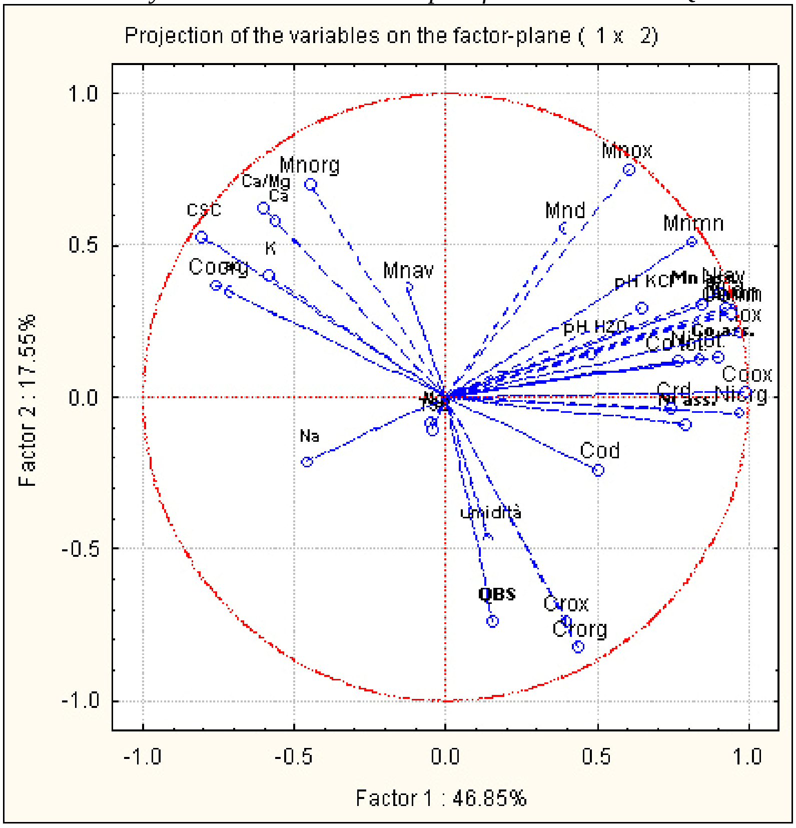

Figure 7.2. Relationship between Ni_{mn} and C_{mic}/TOC in surface (left) and subsurface horizons (right).

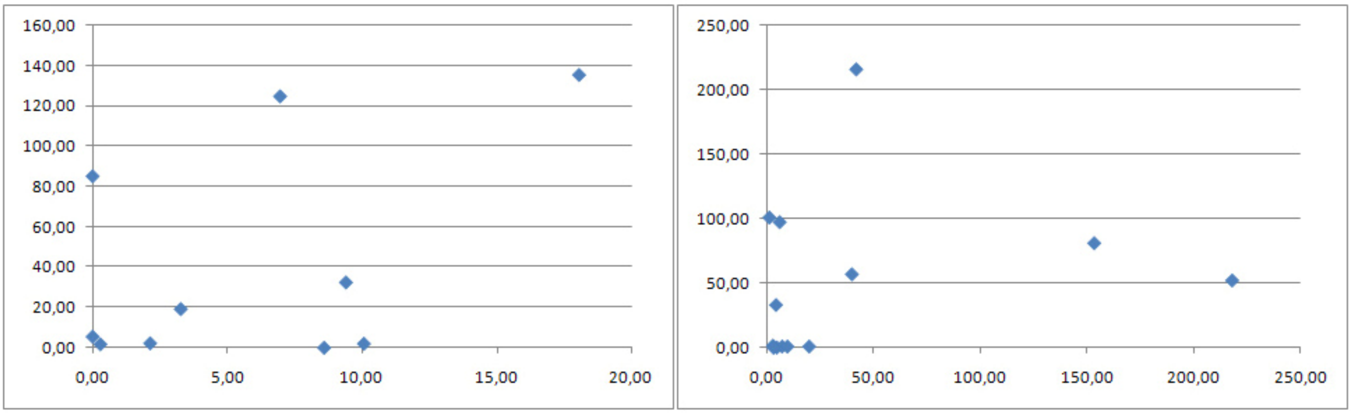

Figure 7.3. Relationship between Co_{mn} and qCO_2 in A (left) and subsurface horizons)

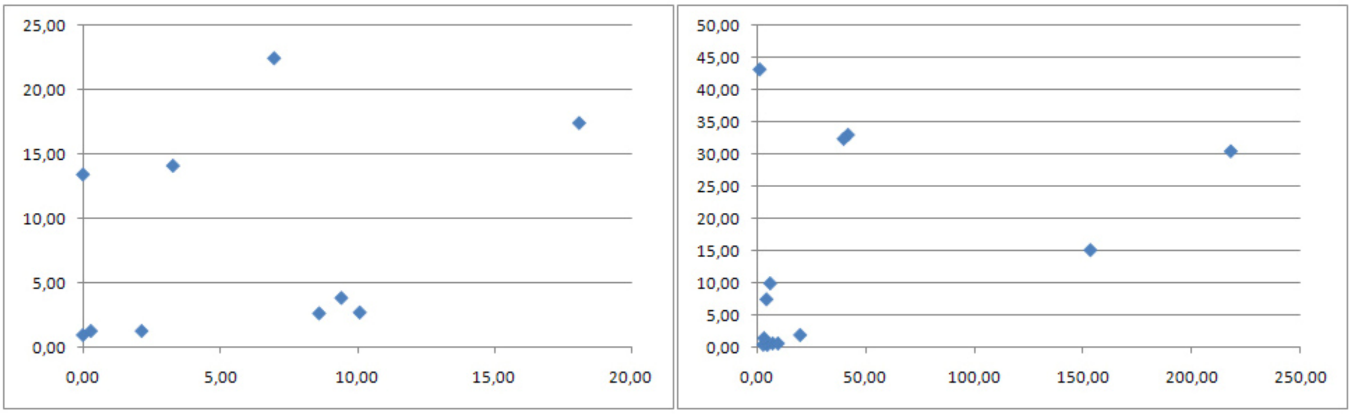

Figure 7.4. Relationship between NI_{mn} and TOC/C_{mic} in A (left) and subsurface horizons.

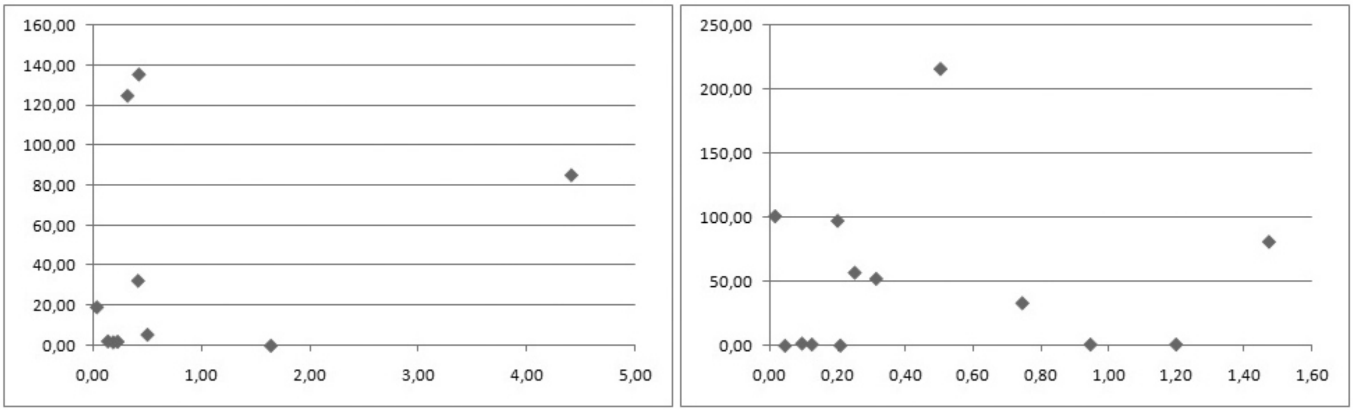

Figure 7.5. Biplot of the PCA analysis performed on the microbial and edaphic factors in A horizons).

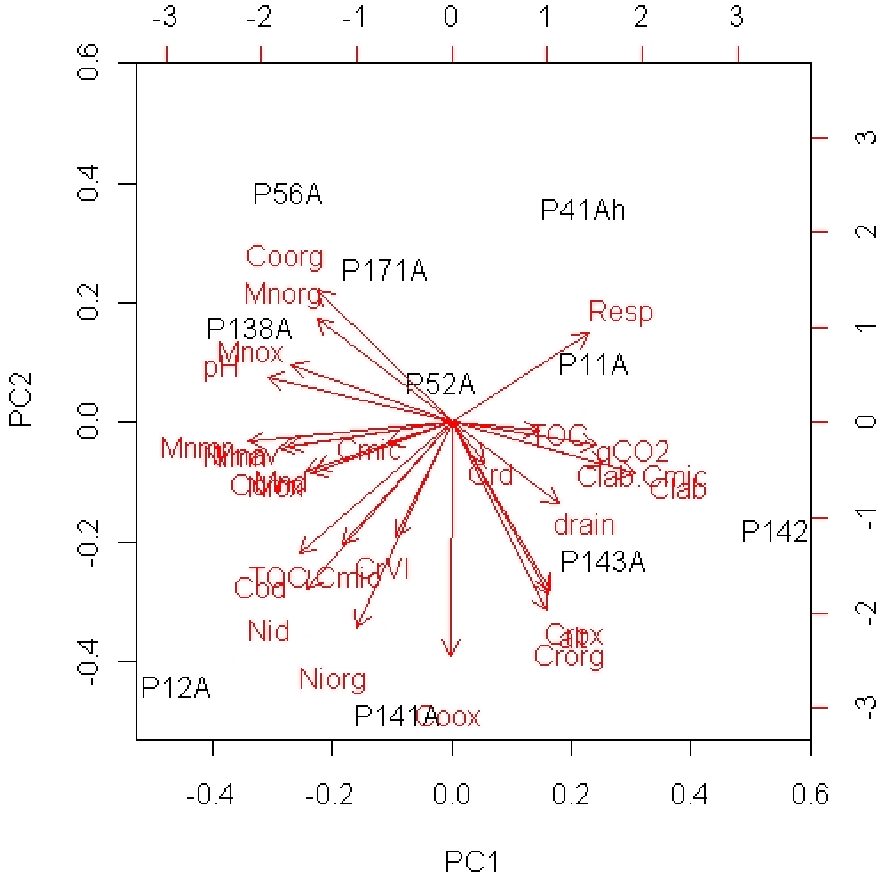

Fig. 7.6: P141, transect across a serpentinic rock circle

Fig, 7.7: P142, transect across a mafic rock circle

Fig. 7.8: P52, transect across a calcschist rock circle/earth hummock.

Table 7.1: general information about the pedons and composition (%) of the calcschists (for other rock types, see lithology tab. 2.3). Soil type is the WRB classification (IUSS Working Group 2006)

Pedon	Altitude	Aspect	Slope	Soil type	Plant community	Plant cover (%)
P37	2480	70°	20°	Haplic Cambisol (Eutric, Turbic).	Basophilous prairie	100
P38	2590	0	5°	Gelistagnic Cambisol (Hyperdystric, Skeletic, Protospodic)	Caricetum curvulae	100
P41	2565	320°	10°	Humic Podzol	Caricetum curvulae, Vaccinium ssp.	70
P52	2705	45°	1°	Turbic Cryosol (Eutric) – hummocks, rock circle	Salicetum herbaceae	30
P56	2535	30°	7°	Haplic Cambisol (Protospodic)	Caricetum curvulae	100
P138	2417		1°	Leptic Cambisol (Eutric,	Caricetum curvulae, Vaccinium	30

				Chromic)	ul.	
P10	2425	180°	10°	Leptic Cambisol (Dystric)	Caricetum fimbriatae, ericaceae	70
P11	2625	220°	15°	Epileptic Cambisol (Dystric, Hyperskeletic, Turbic)	Caricetum curvulae	70
P12	2600	180°	25°	Haplic Regosol (Skeletic, Eutric)	Caricetum fimbriatae, serpentine species	50
P139	2260	160°	5°	Haplic Regosol (Turbic, Eutric, Skeletic), Solifluction lob	Caricetum fimbriatae, calcophilous species	70
P140	2310	260°	30°	Haplic Regosol (Eutric, Hyperskeletic), debris	Serpentine species	5
P4	2240	180°	3°	Cambic Leptosol (Dystric)	Caricetum fimbriatae, Carcicetum curvulae	30
P141	2680	90°	2°	Turbic Cryosol (Eutric, Hyperskeletic); rock stripe	Thlaspietum rotundifolii	15
P142	2775	90°	1°	Turbic Cryosol (Dystric, Hyperskeletic); rock circe	Vaccinium uliginosum, Salix herbaceae	15
P143	2545	270°	10°	Umbric Leptosol (Humic) (rock crevice)	Caricetum fimbriatae	90
P144	2420	0°	5°	Leptic Umbrisol (Hyperskeletic)	Caricetum curvulae	70
P145	2425	0°	5°	Leptic Umbrisol (Hyperskeletic)	Caricetum fimbriatae	60
P146	2130	180°	20°	Haplic Regosol (Eutric, Hyperskeletic); debris	Serpentine species	30
P171	2420	0°	20°	Leptic Regosol (Dystric, Skeletic)	Caricetum fimbriatae	70

Pedon	Serpentinite	Metagabbro	Prasinite	Amphibolite	Chlorite schist	Calcschist
P37	0	0	0	0	0	100
P38	5	0	0	0	0	95
P41	0	100	0	0	0	0
P52	5	0	0	0	0	95
P56	0	0	0	0	0	100
P138	100	0	0	0	0	0
P10	100	0	0	0	0	0
P11	10	90	0	0	0	0
P12	100	0	0	0	0	0
P139	100	0	0	0	0	0
P140	100	0	0	0	0	0
P4	10	60	30	0	0	0
P141	100	0	0	0	0	0
P142	10	50	0	40	0	0
P143	100	0	0	0	0	0
P144	2.5	97.5	0	0	0	0
P145	2.5	97.5	0	0	0	0
P146	98	0	0	0	0	2
P171	100	0	0	0	0	0

Table 7.2: Selected chemical properties of the selected soils. TOC and BS are %, CEC, Ca, Mg, Na, K and Ac (exchangeable acidity) are in cmol/kg.

		pH H_2O	**pH KCl**	**TOC**	**CEC**	**Ca**	**Mg**	**Na**	**K**	**Ac**	**BS**	**Ca/Mg**	**TXT**
A1	**P37**	6.5	5.7	4.2	66.69	52.23	1.05	0.36	0.22	12.83	80.76	49.74	SF
AC1		6.9	5.9	1.8	36.98	26.92	0.98	0.30	0.17	8.61	76.72	27.47	FS
CB1		7.2	6.1	1.4	12.99	8.78	0.14	0.00	0.08	3.99	69.28	62.71	FS
CBn		7.2	6.1	0.5	5.63	4.54	0.10	0.00	0.09	0.9	84.01	45.40	SF
Bw		7.2	6.5	1.4	10.64	6.36	0.12	0.00	0.09	4.07	61.75	53.00	SF
A1	**P38**	4.7	3.4	2.7	43.5	10.22	1.1	0.33	0.26	31.59	27.38	9.29	SF
AE		4.4	3.5	1.0	8.87	1.36	0.09	0.02	0.09	7.31	17.59	15.11	FS
B		4.2	3.9	0.7	6.94	0.51	0.18	0.00	0.00	6.25	9.94	2.83	FS
CB		5.7	4.5	0.6	11.28	0.9	0.04	0.01	0.02	10.31	8.60	22.50	S
C		5.4	4.1	0.4	5.22	0.47	0.1	0.00	0.06	4.59	12.07	4.70	FS
A	**P52**	5.5	4.9	1.3	20.5	9.1	1.54	0.00	0.17	9.69	52.73	5.91	FS
AC		5.5	5.1	0.8	13.58	8.08	1.22	0.00	0.07	4.21	69.00	6.62	FS
C		6.5	4.7	0.7	6.01	3.91	0.58	0.00	0.00	1.52	74.71	6.74	SF
A	**P56**	6.1	5.6	1.9	58.75	25.43	1.22	0.3	0.4	31.4	46.55	20.84	SF
E		5.8	5.5	0.9	25.15	10.22	0.36	0.29	0.07	14.21	43.50	28.39	FS
B		6.3	5.6	0.8	12.9	4.48	0.05	0.00	0.06	8.31	35.58	89.60	S
BC		6.7	5.1	0.6	4.16	0.75	0.03	0.01	0.18	3.19	23.32	25.00	S
C		6.5	4.7	0.4	2.23	0.65	0.03	0.01	0.05	1.49	33.18	21.67	SF
A	**P138**	5.8	4.8	1.8	26.69	2.39	7.99	0.00	0.1	16.21	39.27	0.30	FS
Bw		6.5	5.7	0.8	15.92	1.7	8.79	0.02	0.12	5.29	66.77	0.19	FS
C		7.3	5.6	0.5	12.58	0.56	8.49	0.00	0.15	3.38	73.13	0.07	FS
A	**P10**	4.6	3.7	3.3	37.27	3.8	1.62	0.49	0.26	31.1	16.55	2.35	FS
Bw		4.7	4	1.5	16.24	2.26	0.99	0.36	0.13	12.5	23.03	2.28	FS
A	**P11**	4.5	4.3	2.1	28.81	1.12	0.32	0.15	0.01	27.21	5.55	3.50	SF
B		4.6	4.5	1.6	18.57	0.95	0.26	0.14	0.01	17.21	7.32	3.65	FS
C		5.8	4.4	0.6	7.23	0.78	0.09	0.00	0.00	6.36	12.03	8.67	FS
A	**P12**	5.6	5.2	1.4	18.99	2.48	1.73	0.15	0.02	14.61	23.06	1.43	FS
BC		5.9	5.5	0.7	10.04	1.98	1.81	0.03	0.01	6.21	38.15	1.09	FS
AC	**P139**	6.3	5.4	1.8	14.43	10.26	1.74	0.6	0.31	1.52	89.47	5.90	FS
C		6.6	5.5	0.9	5.76	3.61	0.41	0.02	0.13	1.59	72.40	8.80	FS
C1	**P140**	6.8	5.5	0.6	5.35	0.58	0.84	0.00	0.04	3.89	27.29	0.69	FS
C2		6.9	5.8	0.5	4.6	0.7	1.68	0.00	0.04	2.18	52.61	0.42	FS
A	**P4**	4.8	3.9	1.2	4.53	0.28	0.19	0.00	0.09	3.97	12.36	1.47	FS
Bw		5.8	4.3	0.8	4.4	0.16	0.15	0.00	0.05	4.04	8.18	1.07	FS
A	**P141**	6.2	4.7	0.5	4.32	0.61	0.78	0.00	0.11	2.82	34.72	0.78	FS
AC		6.1	5.2	0.4	5.13	0.97	1.22	0.00	0.13	2.81	45.22	0.80	FS
C		6.6	5.3	0.1	1.31	0.33	0.62	0.00	0.05	0.31	76.34	0.53	FS
A	**P142**	5.7	4.3	1.7	10.44	3.47	1.67	0.43	0.18	4.69	55.08	2.08	FS
CA		6.1	4.6	0.4	3	0.95	0.76	0.00	0.07	1.22	59.33	1.25	FS
C		6.4	4.7	0.5	3.85	1.39	0.89	0.00	0.06	1.51	60.78	1.56	FS
A	**P143**	4.7	3.7	5.2	21.58	1.63	0.87	0.36	0.18	18.54	14.09	1.87	FS
A	**P144**	4.5	3.3	2.2	36.57	5.23	2.03	0.32	0.4	28.59	21.82	2.58	FS
A1	**P145**	4.7	3.6	2.3	37.92	4.42	2.16	0.25	0.35	30.74	18.93	2.05	FS
A2		4.6	3.5	1.5	33.91	2.79	1.2	0.41	0.14	29.37	13.39	2.33	FL
AC1	**P146**	7.1	6.5	1.2	16.38	11.71	1.17	0.3	0.22	2.98	81.81	10.01	FS
AC2		7.8	6.8	0.9	7.17	5.22	0.28	0.00	0.21	1.46	79.64	18.64	FS
A	**P41**	4.6	4.0	2.0	33.47	2.68	0.82	0.33	0.10	29.54	11.74	3.27	FS
AE		4.8	3.9	3.1	27.18	2.10	0.61	0.25	0.05	24.17	11.07	3.44	FS
Bhs		4.8	4.4	2.8	24.31	1.91	0.75	0.24	0.03	23.21	12.21	3.21	FS
A	**P171**	6.5	5.8	0.7	8.80	1.40	1.36	0.22	0.04	5.78	34.32	1.03	SF

BC	6.0	5.4	0.3	8.66	1.22	1.11	0.20	0.03	6.10	29.56	1.10	FS

Tab. 7.3: micro-arthropodal genera found in the samples.

Campione	Collembola (Orchesella)	Collembola (Folsomia)	Collembola (Neanura)	Collembola (Onichiuride)	Collembola (Sminturidae)	Coleottera (larvae)	Protura
P38a							
P38b		4					
P38c							
P52a		1					
P52b		1					
P52c		3					
P56a		2					
P56b							
P56c							
P10a		3	3				
P10b		9	12	3			
P10c		2	12	2	1		
P11a		3		1			
P11b							
P11c		13	4	1	1	1	
P12a		2				2	2
P12b		10	12	1			
P12c	1	5	3			3	
P139a	3	4	19		1		
P139b			4				
P139c		2	10			2	
P140a	1	1					
P140b	1	1					
P140c							

Sample	Araneides	Acarae	Dittera	Sinphila	Chilopodes	QBS scores	Quality class	Average Profile
P38a		6	6			21	1	1
P38b		4	5			27	1	
P38c		2	2			21	1	
P52a		7	3			27	1	1
P52b		1	2			27	1	
P52c		8	8			27	1	
P56a		4	5			27	1	1
P56b		5	10			21	1	
P56c		3	1			21	1	
P10a		55	4			39	1	2.2
P10b		200	3			41	2.5	
P10c		28	6			51	3	
P11a		33	3			51	3	2.3
P11b		30	6			31	1	
P11c		208	6			61	3	
P12a	9	75	28			72	4	3.6
P12b	3	270	33	2		76	4	
P12c	4	120	2			54	3	
P139a	4	54	7	1		74	4	3.3
P139b		22	5	1		59	3	
P139c		45	8		1	59	3	
P140a	2	4	2			52	2	1.3
P140b		3				27	1	
P140c		5				20	1	

Table 7.4. correlation coefficients between BSQ values and edaphic parameters

	$Mn_{ass.}$	$Co_{ass.}$	$Ni_{ass.}$	Ni_{av}	Ni_{mn}	Ni_{ox}	Ni_{org}	$Ni_{tot.}$
QBS	-0.11	0.21	0.50	-0.21	-0.16	-0.01	0.33	-0.11
	Mn_{org}	**Mn_{d}**	**Cr_{ox}**	**Cr_{org}**	**Cr_{d}**	**pH KCl**	**pH H2O**	**CSC**
QBS	-0.26	-0.14	0.59	0.78	0.09	0.00	0.17	-0.41
	Co_{org}	**$Co_{tot.}$**	**Mn_{av}**	**Mn_{mn}**	**Mn_{ox}**	**Co_{mn}**	**Co_{ox}**	**Co_{d}**
QBS	-0.41	-0.20	-0.47	-0.11	-0.45	-0.13	0.23	0.70
	ac	**TSB**	**Ca/Mg**	**umidità**	**Ca**	**Mg**	**Na**	**K**
QBS	-0.31	0.12	-0.48	0.10	-0.40	0.37	0.38	-0.29

Table 7.5. microbial parameters for the analyzed soils. qCO_2=resp/Cmic.

Codice	**TOC**	**C_{lab}**	**Resp**	**C_{mic}**	**qCO_2**	**TOC/C_{mic}**	**C_{lab}/C_{mic}**
	(%)	(g C_{lab}/ Kg suolo)	. µg C-CO2/ g suolo)	(µg C_{mic}/ g suolo)	(µg C-CO2 $d^{-1}mg^{-1}C_{mic}$)	*100	
P141A	0.5	1.85	3.30	11404.8	0.30	0.03	0.16
P141AC	0.4	1.32	11.31	1584.0	7.14	0.25	0.83
P141C	0.1	1.32	0.00	316.8	0.00	0.32	4.17
P142A	1.7	8.98	72.94	475.2	153.49	0.22	18.89
P142AC	0.4	7.79	77.37	4276.8	18.09	0.13	1.82
P142C	0.5	7.52	66.31	1584.0	41.86	0.05	4.75
P143Ah	5.2	8.32	49.85	15206.4	3.28	1.64	0.55
P171A	0.7	2.51	63.13	1584.0	39.85	0.32	1.58
P171BC	0.3	2.51	69.12	316.8	218.18	0.02	5.00
P41Ah	2.0	5.68	76.74	7632.2	10.09	0.13	0.75
P41Eh	3.1	6.10	62.67	3168.0	19.82	0.95	1.92
P52A	1.3	2.24	32.30	10612.8	3.14	0.41	0.21
P52AC	0.8	1.85	27.26	3168.0	8.61	0.75	0.58
P52C	0.7	0.26	15.45	2217.6	6.97	0.20	0.12
P56A	1.9	2.24	19.15	16790.4	1.14	0.50	0.13
P56AE	0.9	3.83	31.79	14889.6	2.13	0.21	0.26
P56B	0.8	3.30	30.46	3168.0	9.61	0.10	1.04
P138A	1.8	2.24	38.80	4118.4	9.42	0.42	0.54
P138B	0.8	2.24	7.45	1742.4	4.18	0.51	1.29
P11A	2.1	3.17	23.76	3960.0	6.00	0.18	0.80
P11B	1.6	3.04	0.00	3801.6	0.00	1.20	0.80
P12A	1.4	3.56	23.27	8236.8	2.83	4.42	0.43
P12BC	0.7	2.38	19.96	4278.8	4.67	1.47	0.56

Table 7.6: correlation matrix between microbial parameters and metal speciation

	alt	*drain*	*TOC*	C_{lab}	*Resp*	C_{mic}	qCO_2	TOC/C_{mic}	C_{lab}/C_{mic}
Resp	-0.24	0.08	0.22	0.66	1.00				
C_{mic}	-0.03	0.45	0.40	-0.11	-0.49	1.00			
qCO_2	0.45	0.16	-0.11	0.61	0.58	-0.61	1.00		
TOC/C_{mic}	-0.02	-0.21	0.18	0.09	-0.20	0.18	-0.21	1.00	
C_{lab}/C_{mic}	0.55	0.24	-0.05	0.65	0.51	-0.52	0.98	-0.17	1.00
Mn_{av}	-0.07	0.01	-0.19	-0.50	-0.43	0.06	-0.27	0.09	-0.27
Mn_{mn}	-0.24	-0.42	-0.27	-0.45	-0.47	0.30	-0.29	0.64	-0.29
Mn_{ox}	-0.23	-0.04	-0.07	-0.45	-0.44	0.61	-0.37	0.25	-0.35
Mn_{org}	-0.50	-0.35	-0.05	-0.36	-0.27	0.44	-0.27	0.20	-0.29
Mn_d	-0.10	0.11	0.21	-0.13	-0.38	0.71	-0.36	0.64	-0.34
Co_{mn}	-0.23	-0.28	-0.43	-0.43	-0.12	-0.30	-0.19	0.18	-0.26
Co_{ox}	0.63	0.27	0.04	0.30	-0.25	0.08	0.17	0.60	0.24
Co_{org}	-0.60	-0.35	-0.17	-0.49	0.03	-0.19	-0.27	-0.12	-0.34
Co_d	-0.03	-0.32	-0.31	-0.29	-0.30	0.04	-0.25	0.75	-0.29
Ni_{mn}	-0.25	-0.33	-0.25	-0.41	-0.17	-0.24	-0.22	0.41	-0.25
Ni_{ox}	-0.23	-0.16	-0.03	-0.22	-0.10	-0.22	-0.16	0.38	-0.19
Ni_{org}	0.34	0.14	0.10	-0.03	-0.48	0.13	-0.20	0.65	-0.14
Ni_d	0.22	-0.19	-0.47	-0.42	-0.58	0.08	-0.28	0.51	-0.26
Cr_{ox}	0.65	0.26	0.19	0.29	-0.26	-0.19	0.24	0.00	0.30
Cr_{org}	0.82	0.46	0.34	0.46	-0.27	0.11	0.31	0.29	0.41
Cr_d	0.07	0.18	-0.20	0.28	0.56	-0.31	0.26	0.06	0.23
CrVI	0.42	0.24	-0.46	-0.40	-0.55	0.36	-0.33	-0.04	-0.28

Table 7.7: variable contribution to the first two PCA axes.

Variable contribution	**factor 1**	**factor 2**	**Variable contribution**	**factor 1**	**factor 2**
% variance	31.72	21.07	**% variance**	31.72	21.07
TOC	0.11	0.03	**Comn**	-0.24	-0.15
Clab	0.25	-0.16	**Coox**	-0.08	-0.40
Resp	0.25	0.00	**Coorg**	-0.16	0.22
Cmic	-0.13	0.17	**Cod**	-0.27	-0.23
qCO2	0.22	-0.16	**Nimn**	-0.26	-0.06
TOC/Cmic	-0.20	-0.17	**Niox**	-0.23	-0.12
Clab/Cmic	0.22	-0.17	**Niorg**	-0.22	-0.32
Mnav	-0.26	0.01	**Nid**	-0.27	-0.25
Mnmn	-0.29	0.07	**Crox**	0.09	-0.32
Mnox	-0.22	0.26	**Crorg**	0.08	-0.31
Mnorg	-0.15	0.28	**Crd**	0.03	-0.17
Mnd	-0.22	0.07	**Cr(VI)**	-0.13	-0.12
Alt	0.14	-0.30	**pH**	-0.27	0.08
drain	0.16	-0.14			

Table 7.8: chemical properties along the transects of the three Turbic Regosol / Turbic Crysols..

	pH	pH_{aq}	TOC	Ca	Mg	Na	K	Ca/Mg	Ac
P141-1	5.1	6.1	8.2	4.51	2.08	0.22	0.07	2.17	8.25
P141-2	5.4	6.4	3.6	4.34	1.37	0.26	0.07	3.17	5.71
P141-3	5.3	6.4	2.8	3.76	1.44	0.18	0.07	2.61	8.7
P141-4	5.1	6.3	3.2	4.13	1.55	0.19	0.05	2.66	10.93
P141-5	4.8	5.9	21.1	5.57	2.16	0.14	0.12	2.58	17.47
P142-1	4.1	5.4	4.6	4.92	1.34	0.22	0.05	3.67	22.37
P142-2	4.4	5.7	3.8	5.27	1.58	0.15	0.05	3.34	23.88
P142-3	4.6	6.1	4.9	5.18	1.46	0.16	0.04	3.55	24.38

P142-4	4.5	5.7	9.2	3.95	1.25	0.25	0.04	3.16	27.2
P142-5	4.5	5.7	16.2	4.55	1.15	0.26	0.06	3.96	22.51
P52-1	3.7	5.1	41.3	13.32	2.84	0.29	0.06	4.69	34.83
P52-2	3.7	5.2	14.5	8.32	1.74	0.18	0.03	4.78	29.56
P52-3	4.7	6	8.5	4.97	1.38	0.28	0.03	3.60	26.62
P52-4	4.1	5.6	10.8	6.4	1.52	0.44	0.05	4.21	34.79
P52-5	4	5.2	29.7	11	1.95	0.22	0.06	5.64	35.95

Table 7.9: labile forms of metals along the transects of the three Turbic Regosol / Turbic Crysols..

	Ni_{aq}	Mn_{aq}	Cr_{aq}	Ni_{ex}	Mn_{ex}	Cr_{ex}	Ni_{mn}	Mn_{mn}	Cr_{mn}	Ni_{ox}	Mn
P141-1	4.23	0.6	0.72	20.27	2.11	7.51	30.71	91.14	11.02	272.05	47.
P141-2	5.27	0.55	1.06	18.82	1.83	4.36	51.76	139.61	8.82	278.43	58.
P141-3	5.26	0.45	0.78	17.57	0.82	6.19	47.75	103.50	9.19	264.54	61.
P141-4	4.2	0.51	0.99	17.47	1.3	8.51	35.08	88.40	10.70	288.60	64.
P141-5	5.15	0.51	0.94	20.55	3.04	6.2	17.50	90.06	11.73	144.73	70.
P142-1	0.38	0.08	1.44	2.47	0.46	9.02	3.77	14.07	10.31	14.67	16.
P142-2	0.19	0.11	1.47	0.76	0.86	6.94	2.80	21.40	14.40	17.40	17.
P142-3	0.16	0.08	0.55	1.14	0.08	4.48	1.57	26.72	9.23	19.65	19.
P142-4	0	0.2	1.49	3.13	0.4	8.72	0.79	22.99	10.11	11.89	20.
P142-5	0.15	0.15	1.51	1.12	0.54	3.44	1.99	23.26	11.33	16.90	21.
P52-1	0	0.12	0.87	1.58	2.5	7.6	2.52	18.20	10.26	18.59	25.
P52-2	0.04	0.12	1.54	3.59	0.32	4.89	4.49	34.73	10.73	18.93	39.
P52-3	0.28	1.1	0.9	4.21	2.28	4.63	48.65	509.07	10.77	86.14	296.
P52-4	0.11	0.72	1.69	5.57	2.98	5.08	51.30	496.05	11.57	73.67	212.
P52-5	0	0.31	1.52	3.89	3.81	5.02	2.57	77.62	9.90	43.17	126.

Table 7.10: microbial indices along the transects of the three Turbic Regosol / Turbic Crysols. The numbers 10 and 25 are the temperatures at which the analysis were performed.

	C_{mic}	C_{lab}	resp10	resp25	Clab/C_{mic}	qmet10	qmet25	TOC/C_{mic}	Resp/TOC1
P141-1	12.89	11.47	6.52	13.47	0.89	0.51	1.04	0.64	0.7
P141-2	14.22	50.62	7.18	13.81	3.56	0.50	0.97	0.25	1.9
P141-3	33.56	12.77	6.93	9.90	0.38	0.21	0.29	0.08	2.4
P141-4	37.38	38.84	9.32	8.78	1.04	0.25	0.23	0.09	2.9
P141-5	140.38	115.17	10.10	31.90	0.82	0.07	0.23	0.15	0.4
P142-1	100.04	36.80	14.03	15.15	0.37	0.14	0.15	0.05	3.0
P142-2	35.62	48.15	4.93	10.95	1.35	0.14	0.31	0.11	1.3
P142-3	110.09	60.57	4.46	11.71	0.55	0.04	0.11	0.04	0.9
P142-4	53.99	67.53	7.72	13.78	1.25	0.14	0.25	0.17	0.8
P142-5	32.90	47.44	5.98	17.93	1.44	0.18	0.54	0.49	0.3
P52-1	201.43	54.90	22.05	46.39	0.27	0.11	0.23	0.20	0.5
P52-2	225.33	70.46	10.04	24.77	0.31	0.04	0.11	0.06	0.6
P52-3	135.62	63.68	9.99	15.86	0.47	0.07	0.12	0.06	1.1
P52-4	158.01	47.63	7.38	17.83	0.30	0.05	0.11	0.07	0.6
P52-5	200.69	177.17	14.62	49.17	0.88	0.07	0.24	0.15	0.4

8. Overall conclusions.

Climate, altitude, slope aspect and vegetation are the main factors influencing pedogenesis on ultramafic and mafic materials in Mont Avic Natural Park. At the subalpine altitudinal level, particularly on north-facing slopes, the soils are the most weathered and evolved: the process of podzolization is active on all substrates, also on base-rich serpentinites. Acidification is extreme, probably due to acidifying vegetation (coniferous forest and ericaceous shrubs) and deep snow cover, which helps the presence of percolating water through the profile for many months every year (chapter 3) at melting. At lower altitudes and on xeric, southward slopes, less developed and slightly less acidified Cambisols or Regosols developed.

Above the present day timberline, soil properties were strongly related with the lithology of the parent material, particularly in the most disturbed sites (by cryoturbation or erosion-deposition processes). Montane and subalpine soils were less differentiated in response to parent material variability: pH values and base status were always low, while the ecologically important Ca/Mg values in biologically-active horizons were similar on all substrates. Only seldom the Ca/Mg values were below 1 on serpentinite (chapter 2). Heavy metal content and speciation (chapter 2, 5) were the main chemical factors differentiating the soils developed on mafic and ultramafic parent materials. At the alpine level, these differences became deeper (pH values were very low on mafic rocks, low on serpentinite and strongly changing with depth on calcschists). Heavy metal contents were sometimes extremely high on serpentinite, particularly in the most eroded and cryoturbated sites.

One of the most interesting pedogenic features in the study area is the podzolization process, active on serpentinite under subalpine *Pinus uncinata* and *Larix decidua* forest (chapter 3). Weathering, as demonstrated by mass balance calculations and clay mineralogy, verified the activity of a particularly “aggressive” environment (chapter 4): a high Mg and Ni leaching was associated with an almost complete dissolution of serpentine minerals and with chlorite transformation into smectites and vermiculites, via hydroxy-interlayered minerals. Cr and Fe, which are usually considered stable in soils developed on ultramafic substrates, were mobilized, in response to an important and unusual dissolution of chemically resistant spinels. This process of dissolution needs deeper studies, as in literature nothing has been found regarding magnetite weathering in soils caused by strong acidity and/or organic complexation.

Under subalpine forests, clay minerals evolution depended mostly on Al-bearing minerals, particularly chlorite. This mineral weathered very early: only in unweathered C horizons it was chemically similar to the primary Mg-rich chlorite (chlinochlore), while in BC horizons it was transformed into a Fe-rich chlorite. The first step is, thus, the substitution of Mg by Fe in the octahedral sheet, followed by the transformation of chlorite to trioctahedral HIV and HIS. In E horizons, trioctahedral occupations are partially replaced by dioctahedral ones, and a large quantity of high-charge smectites and vermiculites appear. The increase in dioctahedral occupancies, and the residual accumulation of Al indicate that the smectites have a large component of Al-rich beidellites. The last step is the transformation of smectite into kaolinite.

The weathering trend of clay minerals is important, because chlorites are rich in heavy metals (Cr and Ni), which are probably included mostly in the octahedral layer, substituting Mg.

Ni was mostly included in unstable serpentine minerals: Ni and Mg are, thus, the most easily mobilized and leached elements. Under the extremely acidic subalpine soil conditions, Ni was depleted, but its toxicity was probably higher than in other, less acidic soils with the same Ni content: serpentine-endemic species (*Thlaspi sylvium, Cardamine plumieri*), statistically correlated with available Ni, grew in these soils at much lower available Ni levels than in alpine habitats (chapter 2).

Metals released by subalpine soils are accumulated along stream banks or in weakly developed, organic matter-rich soils in rock crevices. In these cases, the available Ni reaches extremely high values, seldom found on a worldwide base (chapter 5). A large number of serpentine endemic species were found in these particular metal-rich habitats.

The high weatherability of serpentine minerals was evidenced also by metal speciation in weakly developed high altitude soils: despite the young age and strength of geomorphological disturbances (caused by cryoturbation, erosion and deposition), large proportions of heavy metals were included in “labile” forms, such as the water-soluble, exchangeable, or associated to Mn-oxides. Therefore, there is an actual risk of contamination for surface water.

The highly mobile and toxic form of Cr (CrVI) was sometimes extremely high, particularly in spodic horizons of soils developed from ultramafic rocks, or in alpine soils (chapter 5). Above the treeline, high Cr(VI) levels were found also on Cr-poor substrates, probably because of solute transportation with pore water flowing on the interface between the soil and the hard rock or subsurface frozen layers.

The most important ecological edaphic factor seemed to be represented by heavy metals (particularly Ni). Plants communities at the montane and subalpine altitudes were enriched in Ni-adapted species (with significant statistical meaning), while toxic effects were not visible. Above the timberline, some species were excluded from Ni-rich serpentine sites. The correlation between plant communities and species, low Ca/Mg values, or nutrient deficiency, were not significant. The “serpentine factor”, in the studied soils, seemed mostly related with high available Ni (chapter 2).

In subalpine soils, microbial and microarthropodal communities were influenced by the stress caused by bioavailable metals (chapter 6): the biodiversity of microarthropodal communities were strongly related with bioavailable Ni, Co and Mn. The microbial stress indicators (metabolic quotient, TOC/C_{mic} and C_{lab}/C_{mic}) were similarly well correlated with available metals.

This situation was different at the alpine level: no effect on biodiversity was visible on microarthropodal communities, and no microbial stress indicators were correlated with any metal form (chapter 7). This could be due to other, stronger ecological constraints in these “cold” and disturbed soils, or to a good adaptation of microbial communities, or even to a low degree of organic matter degradation, which reduces the bioavailable fraction of organic matter reducing the meaning of some stress indices.

A more detailed characterization of the weathering status of high altitude soils, of the humic materials produced by the different plant communities and a discrimination between bacterial and fungal activity could improve the interpretation of heavy metal ecology of alpine soils on ophiolites.