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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/77626> since

Published version:

DOI:10.1007/s11368.010.0244.0

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UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

Bonifacio E., Falzone G., Piazza S. 2010. Linking Ni and Cr concentrations to soil mineralogy: does it help to assess metal contamination when the natural background is high? Journal of Soils and Sediments, 10, 1475–1486. DOI: 10.1007/s11368-010-0244-0.

The definitive version is available at:

La versione definitiva è disponibile alla URL:

<http://www.springer.com/environment/soil+science/journal/11368>

Linking Ni and Cr concentration to soil mineralogy: does it help to assess metal contamination when the natural background is high?

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Abstract

Purpose In soils from serpentinitic areas the natural background of Ni and Cr is so high that the assessment of contamination by comparing metal concentrations with some fixed thresholds may give unreliable results. We therefore sought a quantitative relation between serpentines and Ni and Cr concentration in uncontaminated soils, evaluated if the approach may help in establishing a baseline, and discussed if additional anthropogenic inputs of Ni and Cr can be realistically individuated in these areas.

Materials and methods We analysed the total, acid-extractable and exchangeable concentrations of Ni and the total and acid-extractable concentrations of Cr in 66 soil horizons, belonging to 19 poorly developed and uncontaminated Alpine soils. The soils had different amounts of serpentines, depending on the abundance of these minerals in the parent material. We calculated an index of abundance of serpentines in the clay fraction by XRD and related total metal contents to the mineralogical index. We then tested the regressions on potentially contaminated soils, developed on the alluvial plain of the same watershed.

Results and discussion We found extremely high total concentrations of Ni (up to 1,887 mg kg⁻¹) and Cr (up to 2,218 mg kg⁻¹) in the uncontaminated soils, but only a small proportion was extractable. Total Ni and Cr contents were significantly related to serpentine abundance ($r^2=0.86$ and 0.74, respectively). The regressions indicated that even small amounts of serpentines induced metal contents above 200 mg kg⁻¹, and the 95% confidence limits were 75 and 111 mg kg⁻¹ of Ni and Cr, respectively. When the regressions were tested on the potentially contaminated soils, a good estimate was obtained for Cr, while the Ni concentration was overestimated, probably because of some leaching of this element.

Conclusions The concentrations of Ni and Cr that can be expected in soils because of the presence of small amounts of serpentines are comparable to the amounts accumulated in the soil because of diffuse contamination and potentially contaminated soils had metal concentrations falling in the range expected from the presence of natural sources. Only in the case of very severe contamination events, the identification of anthropogenic sources adding to the natural background would be feasible.

Keywords Alpine areas • Heavy metals • Soil development • Uncontaminated soils • Ultramafic rocks

1 Introduction

Ni and Cr are among the most widespread heavy metals in contaminated areas because they may arise from a number of sources (Bodek et al. 1988), and their content in soils may be as high as 20,000 mg kg⁻¹ in some highly industrialised areas (Kabata-Pendias and Pendias 1992). To assess soil contamination, the total heavy metal concentration is often compared with some threshold limits, which are representative of unpolluted sites, but the evaluation of background levels for Ni and Cr may be problematic where natural sources, such as ultramafic rocks, add to anthropogenic contamination.

Among ultramafic rocks, serpentinites are widely diffused in the Alps of industrialised countries such as Italy, France and Switzerland. The high Cr contents are related to the presence in serpentinites of Cr-spinels, such as chromites, magnesium chromites and Cr-magnetite (Oze et al. 2004a), but Cr is also found in chlorites (Caillaud et al. 2009) and in Fe oxides and hydroxides (Gasser et al. 1995). The high resistance to weathering of spinels and the low geochemical mobility of Cr(III), the most abundant form of chromium in serpentinites (Oze et al. 2004a), lead to its residual accumulation during pedogenesis. Ni is mainly present in primary silicates, but it may progressively become sorpted onto secondary smectites and iron oxides when weathering is more pronounced, or incorporated into these pedogenic minerals (Schwertmann and Pfab 1996). The high susceptibility to weathering of primary Ni-bearing silicates and the charge density of nickel favour its leaching to the soil C horizons or out of the profile (Bulmer and Lavkulich 1994), when secondary mineral phases with high Ni affinity have not yet formed. When pedogenic processes have proceeded enough to lead to an appreciable soil development, the Ni and Cr contents will depart from the initial concentration in the parent material, and the ratio between these two elements is expected to change because of the differences in their chemical behaviour.

Soils are poorly developed in Alpine serpentinitic areas (Legros 1992); the intrinsic low fertility does not allow the development of a thick vegetation cover, and the steep slopes limit pedogenic processes. Erosion and mass wasting is common. The plains located at the bottom of Alpine valleys, originated during past fluvio-glacial events, are therefore made by sediments, which, among others, derive from the upland serpentinitic areas. These plains are often urbanised and anthropogenic soil contamination is thus superimposed on a natural high background for Cr and Ni, making the evaluation of effective contamination rarely feasible. This issue was recently studied in North-western Italy by Biasioli et al. (2006) who evaluated the effect of a large city on heavy metal contents in soils. These Authors could clearly identify the effect of anthropogenic contamination on Pb, Zn and Cu, but failed in recognising any

trend for Cr and Ni. Similar results were found in other ophiolitic areas, from Spain (Paz-Gonzalez et al. 2000), to Australia (Ashley and Napier 2005), where either agricultural or industrial contamination adds to the natural baseline.

Several attempts have been made to separate between anthropogenic and natural contributions on metal contents in soils. They range from the statistic evaluation of the outliers, as reviewed by Reinmann et al. (2005), to regressions between metals and Al and Fe (Delaune et al. 2008), to several enrichment factors such as the ratio between metal concentration in potentially polluted and unpolluted areas (e.g. Massas et al. 2009) or between the concentration in the topsoil and in deeper layers (e.g. Blaser et al. 2000; van Gaans et al. 2007). Unfortunately these approaches may give unsatisfactory results in areas showing a broad heterogeneity of the parent material, thus of natural sources of metals, such as alluvial plains. The large range of variation might impede the evaluation of outliers, and the input of sediments from upland erosion will bias the calculation of enrichment factors. The assessment of isotopic abundance of Pb, Zn and Cd allowed to trace the source of contamination in several case studies (e.g. Bi et al. 2009; Cloquet et al. 2006; De Vleeschouwer et al. 2009), but the approach may not be suitable to all metals and cannot be applied on a routine basis.

The evaluation of the characteristics of the potentially incoming sediments might however contribute to establish a regional baseline, and to assess if it is possible to evidence anthropogenic contamination in areas with high natural background. In this work, we evaluated the contents of Ni and Cr in Alpine soils developed on serpentinites, where the contamination from anthropogenic sources is very unlikely, and where, because of the low development stage of these soils, an important pedogenic mobilisation of elements should not have occurred yet. These conditions allowed us to relate the metal concentration to soil mineralogy using simple indexes and to discuss if the approach may be useful in establishing the natural background for Ni and Cr.

2 Materials and methods

Nineteen soil profiles were described and sampled on the left side of the Susa valley, North-western Italy (Alpine samples, Fig 1), at elevations ranging from 1100 to 1,360 m a.s.l., on the area belonging to the greenstone belt of the Alps. This metamorphic unit is mainly composed of ophiolites, but variable amounts of micaceous and calcareous schists are also present, giving rise to the so-called complex of “calcschists and greenstones” (Servizio Geologico d’Italia 1999). A large variability in the amounts of

serpentine minerals is therefore expected. All sites have similar forest cover (mainly pure or mixed beech stands), are on steep slopes (~30–60%), contain up to 70% of coarse fragments in some C horizons (field estimate) and are poorly or very poorly developed: according to the USDA Soil Taxonomy (Soil Survey Staff, 1999), 13 are Entisols (12 Typic Udorthents and 1 Typic Eptaquent), and 6 are Inceptisols (3 Typic Dystrudepts, 2 Humic Dystrudepts and 1 Typic Eutrudept), thus the only pedogenic processes which have occurred are related to initial weathering of the parent material and formation of cambic horizons, or accumulation of organic matter in the soil mineral horizons with the development of umbric epipedons.

Samples were taken from the 66 genetic soil horizons, air dried and sieved through 2 mm. The total Ni and Cr contents (Ni_T , Cr_T) were determined after HCl-HNO₃ and HF digestion (Bernas, 1968), by atomic absorption spectroscopy (AAS, Perkin Elmer 3030). The wavelength for Ni measurements was set at 232.0 nm, and for Cr at 357.9 nm. The linear calibration was obtained for both elements in the range 0.50 to 4.00 mg L⁻¹ by using 5 freshly prepared standard solutions. On a subset of 36 soil horizons the acid-extractable contents Ni of Cr (Ni_E , Cr_E) were also analysed, following the first step (acetic acid extraction) of the BCR procedure (Davidson, 1998). In this procedure the fraction extracted in the step is thought to represent the fraction which is available to organisms. On the same subset, the exchangeable Ni contents (Ni_{ex}) were determined after extraction with BaCl₂ at pH 8.1 (SISS 1985). On the extracts the metal concentrations were analysed by AAS (HGA700, Perkin Elmer 4100), using the same wavelengths as reported above, and a calibration range of 5-20 µg L⁻¹ for Ni and 1-10 µg L⁻¹ for Cr. The total Fe oxide contents (Fe_D) were estimated by treating the samples with Na-dithionite-citrate-bicarbonate (Mehra and Jackson 1962) and analysing the solutions by flame AAS. The amount of clay (<2 µm) was determined by the pipette method after dispersion of the sample with Na-hexametaphosphate. For mineralogical analyses, the clay fraction was then separated by sedimentation, Mg saturated with MgCl₂, washed until free of Cl⁻, and freeze-dried. The X-ray diffraction (XRD) analyses were carried out using a Philips PW1710 diffractometer (40kV and 20 mA, Co-K α radiation, graphite monochromator) on air dried (AD), ethylene glycol solvated (EG), and heated (550°C) oriented mounts. Scans were made from 3 to 35 °2 θ at a speed of 1 °2 θ min⁻¹. The presence of serpentine minerals was ascertained by the presence of the 0.73 and 0.36 nm peaks, corresponding to the 001 and 002 reflections of all serpentine species, which do not change upon solvation or heating. Chlorite was identified by the presence of a 1.4 nm peak after heating the sample to 550°C, illite by the 1.0 nm peak in the AD diffraction pattern, swelling clay minerals by the appearance of a peak or shoulder at 1.6–1.7 nm after EG solvation. The other non-pedogenic minerals

(mainly talc and amphiboles) were identified by peak position according to the data reported by Brown (1980). For the semiquantitative evaluation of mineral abundance, the background was subtracted from the AD XRD patterns and the peak intensities and positions were calculated using the second derivative option of the PowderX software (Dong, 1999). A simple index of abundance (IA) of serpentines was then obtained from the ratio between the intensity of the 0.73 nm peak and the sum of the intensities of the 0.73, 1.4 and 1.0 nm peaks in the AD sample.

To check the relations between IA and metal contents, 5 topsoil samples (0–20 cm) of Typic Udifluvents from a public garden in the town of Torino were analysed for Cr_T and Ni_T and the IA was determined, following the methods described above. The public garden develops on the recent alluvial plain of the Susa valley (urban samples, see Fig. 1) and dates from the fifties of the 20th century; since then it was exposed to anthropogenic contamination (Bonifacio et al. 1995).

All analyses were duplicated. The statistical data treatments were carried out using SPSS 17.0.

3 Results

The total Ni and Cr contents were highly variable in all soil horizons, as expected from the differences in parent material, and reached in some cases the extremely high contents which are typical of soils on ultramafic rocks (Table 1). The lowest mean Ni_T concentrations were found in the Bw horizons, while the average Ni_T concentrations were 890–1,148 mg kg⁻¹ in the other horizons. The Cr_T concentrations showed the same trend, but the range was wider: the minimum values may be as low as 20 mg kg⁻¹, and maxima in A, AC and C horizons were above 2,000 mg kg⁻¹. The ratio between Cr_T and Ni_T was relatively constant and a significant correlation between the two metals was found ($r=0.877$, $n=66$, $p<0.001$). Even within the relatively more developed Inceptisols (Fig. 2a), an increase in the Cr_T to Ni_T ratio in Bw horizons was found only in profile 19; in the other cases an almost constant ratio or a slightly increasing trend towards the bottom of the profile was visible. In Entisols, no general trend was discernible (see Fig. 2b) with some profiles showing higher values of the Cr_T to Ni_T ratio in the surface horizons, others (profiles 5 and 14) evidencing an increase of the ratio with depth, and profiles 6, 12 and 16 that showed a relative slight increase in the AC horizons.

The acid-extractable forms of Ni (Ni_E , see Table 1) ranged on the average between 12 and 20 mg kg⁻¹ and the highest variability was found in C horizons, which showed both the minimum (0.3 mg kg⁻¹) and the maximum concentration (78 mg kg⁻¹). The acid-extractable Cr was always very low and the

concentrations ranged from 0.1 to 0.8 mg kg⁻¹. The acid-extractable forms of Ni and Cr were not related to each other, but Ni_E was correlated to Ni_T (r=0.829, n=36, p<0.001). The acid-extractable Cr was instead poorly correlated to Cr_T (r=0.405, n=36, p<0.05). On the average, approximately 2.3% of total Ni was extractable with acetic acid, while the proportion was lower and more variable for Cr (mean=0.2%, standard deviation=0.4).

The lowest exchangeable Ni concentration was in Bw horizons (see Table 1) and Ni_{ex} was correlated with both total and available forms (r=0.749 and r=0.958, respectively, n=36, p<0.001). On the average less than 1% of Ni_T was exchangeable.

Low amounts of clay were found in all samples and the Bw horizons were only very slightly enriched (Table 2). The total Fe oxides contents (estimated by Fe_D) were highly variable even within the same type of horizon (see Table 2). Fe_D was not correlated with the acid-extractable forms of Ni and Cr, but a significant correlation was found with Ni_T (r=0.537, n=66, p<0.001) and Cr_T (r=0.750, n=66, p<0.001).

Variable amounts of serpentine minerals were found in the samples, as visible from the index of abundance (IA, see Table 2) and as expected from the sampling strategy. Besides serpentines, the clay fraction was composed of chlorite, illite, talc and amphiboles. In three profiles swelling clay minerals were also detected upon EG solvation (Fig. 3), either in pure form as in Profiles 3 and 5, or as component in interstratified minerals (Profile 7).

In the C horizons the index of abundance reached a maximum value of 0.93 (see Table 2), hence indicating that the clay fraction was made almost only of serpentine. Inceptisols generally showed lower IA than Entisols (Fig. 4), but even in these more developed soils, only in a few cases an appreciable decrease in serpentine abundance in the Bw horizons was visible (see Fig. 4a). In Entisols no general trend was found and, with the exception of profiles 8 and 10, the difference in IA from surface to bottom horizons was lower than 10% (see Fig. 4b).

The IA was well correlated to the total contents of both Ni and Cr and to the acid-extractable and exchangeable forms of Ni (Table 3). When the data set was divided according to the horizon type, the correlations were still valid. The correlations between IA and Cr were slightly lower, but generally still significant.

Using the total metal concentrations and the whole dataset, we found the following regression equations:

$$\text{Ni}_T \text{ (mg kg}^{-1}\text{)} = 84 + 1944 \times \text{IA} \quad r^2=0.861, \quad p<0.001$$

$$\text{Cr}_T \text{ (mg kg}^{-1}\text{)} = -12 + 1932 \times \text{IA} \quad r^2=0.737 \quad p<0.001$$

In the case of Ni_T , the intercept, thus the amount of Ni that is expected in soils in the absence of serpentine in the clay fraction, was also significant ($p < 0.05$), while it was not for Cr_T . As visible in Fig. 5a, when serpentine minerals predominated in the clay fraction (i.e. $IA > 0.50$), the Ni_T concentrations were always extremely high: from 800 mg kg^{-1} they increased to $1,600\text{--}1,800 \text{ mg kg}^{-1}$ when serpentines made up more than 80% of the clay fraction.

In the case of Cr_T , the percentage of variance explained by the regression was lower (74%), and the data were more scattered (Fig. 5b). The trend was however evident, and Cr_T concentrations above 2000 mg kg^{-1} were present only when serpentines formed about 80% of the clay fraction.

As shown in Fig. 6, the distribution of the standardised residuals closely followed a normal distribution for both elements indicating that no systematic bias was present in estimating the total Ni and Cr concentrations from the regressions. In all soil horizons, the mean predicted Ni_T values (Table 4) were very close to the measured ones, reported in Table 1, and the variability in the sample dataset was maintained, as visible from the standard deviation. There was a good agreement between predicted and measured mean values in all horizons also in the case of Cr_T (see Table 4), but the overestimate for minimum values was higher than in the case of Ni_T , and up to 6 times the measured concentration in the A horizons. The maximum Cr_T contents were approximately 30% underestimated, with the exception of Bw horizons, which showed the best agreement between observed and predicted values.

The topsoil samples from the public garden had Ni_T and Cr_T concentrations ranging from 125 to 196 and from 193 to 273 mg kg^{-1} , respectively, and showed low amounts of serpentine minerals (Table 5). The metal contents estimated from the linear regressions ranged from 372 to 405 for Ni_T and from 274 to 307 mg kg^{-1} in the case of Cr_T , with an overestimate in both cases. The residual values ranged from 199 to 268 mg kg^{-1} for Ni_T , while they were much lower for Cr_T ($24\text{--}107 \text{ mg kg}^{-1}$). The half of width of the 95% confidence interval was on the average 75 and 111 mg kg^{-1} for Ni and Cr, respectively (see Table 5). The Cr residual values fell therefore always within the calculated 95% confidence intervals, but in the case of Ni they exceeded the confidence intervals, thus indicating a lower accuracy of the model.

4 Discussion

As expected from the sampling strategy, the Ni_T and Cr_T concentrations in the uncontaminated Alpine soils were extremely variable and may reach very high values. Ni_T showed however a more homogeneous distribution, with a smaller range than Cr_T . This may be related to the differences in Cr- and Ni-rich

minerals; while serpentine are present in all studied soils, although in variable amounts, chromites and other Cr-bearing minerals are likely to be more scattered in the area. In the most serpentine-enriched soils the Ni_T and Cr_T concentrations were in agreement with those commonly found on soils developed from ultramafic rocks: Massoura et al. (2006) reported that total Ni concentration varied from 863 to 2,600 $mg\ kg^{-1}$ in poorly and medium developed soils of temperate and Mediterranean environments; Bulmer and Lavkulich (1994) found that total Cr concentration varied between 800 and 5,500 $mg\ kg^{-1}$ in Canada, and the data reported by Rabenhorst et al. (1982) for Californian serpentinitic soils were also similar (500–6,000 $mg\ kg^{-1}$). On the other hand, D'Amico et al. (2009) reported similar concentration for Cr (up to 2,800 $mg\ kg^{-1}$), but lower amounts of Ni (300–1,100 $mg\ kg^{-1}$) in podzolic serpentinitic soils of the Aosta valley in Italy, thus confirming the higher mobility of Ni when soil forming processes, such as podzolisation, have acted. Cr-magnetites and other Cr-bearing iron oxides are commonly found in serpentine soils (e.g. Kierczak et al. 2007; Caillaud et al. 2009), thus their presence may justify the high correlation coefficient we found between Cr_T and Fe_D . Ni is mainly concentrated in serpentine minerals (Caillaud et al. 2009), although its contents in magnetites and other oxides may be relevant too (Oze et al. 2004b). Thus, the relation between Ni_T and Fe_D may arise from the presence of Ni in Fe oxides or may instead be indirect, and linked to the higher abundance of Fe_D at the sites where also serpentine minerals were abundant.

The acid-extractable Ni and Cr contents were correlated to the total concentrations, and the low proportion of extractable forms with respect to total amounts is in agreement with the data found by Hseu (2006) in the least developed terms of a serpentinitic toposequence. The effect of parent material prevailed on the enhancement in metal availability induced by organic matter which is generally reported (Tiller 1989) and the maximum concentrations were found in C horizons. The low pH of acetic acid, the reactant of the BCR procedure we used, has probably induced a partial dissolution of serpentine minerals, which are easily weathered in acidic medium (Dixon, 1989), thus accounting for the high correlation coefficient we found between total and acid-extractable Ni forms. On the other side, the differences in the pH of the reactants justify the differences between acid-extractable and exchangeable concentrations. The Ni_{ex} concentrations were, however, ten times lower than those reported by Caillaud et al. (2009), and accounted, on the average, for less than 1% of total Ni. This is probably related to the scarce presence of secondary phases that provide sorption sites, such pedogenic layer silicates and Fe (hydr)oxides, which are the responsible for the increase in metal sorption with soil development (Uren 1992). No correlation

was in fact found between Ni_E or Ni_{ex} and the total Fe oxides, that are mostly of lithogenic origin as indicated by the low variability among soil horizons, and should therefore have a low specific surface area (Schwertmann and Taylor 1989). Smectites contribute to Ni sorption and form during the very first steps of serpentine weathering (Caillaud et al. 2006), but only seldom we found swelling minerals in these Entisols and Inceptisols. The presence of swelling minerals, with high cation exchange capacity, apparently did not induce any difference in the Ni_E and Ni_{ex} concentrations ($p=0.538$ and 0.873 , respectively, $n=8$, oneway Anova), thus indicating that also the extractable forms are linked to the composition of the parent material in these poorly developed soils.

No distinct differences in metal distribution or in metal ratio were found between Entisols and Inceptisols or among soil horizons, confirming that pedogenic processes have not proceeded enough to influence leaching and accumulation of Ni or Cr. Cambic Bw horizons showed, on the average, the lowest Ni_T concentrations, but they also generally belonged to the soils with the lowest abundance of serpentine minerals in all horizons. In addition they also had the lowest Cr_T concentrations, confirming that the differences are linked to the variability in the soil parent material and not to pedogenic processes. As a consequence of the absence of redistribution of metals in the profiles, the actual concentration in soil horizons from uncontaminated sites is linked only to the presence of Cr- and Ni- rich minerals.

Serpentines may constitute more than 90% of the clay fraction and the high percentage of variance explained by the IA alone might indicate that these minerals are the direct responsible of the Ni contents in soils. The Ni concentration of serpentine ranges from 0.2 to 0.4 % (Kierczak et al. 2007), while some oxides may contain up to 6% of Ni (Massoura et al. 2006); however, serpentines are by far the most common minerals in the study area, therefore they should deeply influence the total metal contents. The percentage of variance of Cr_T explained by the regression with the IA was lower, and confirmed that the Cr-bearing phases were different. Chlorites are reported as important Cr-bearing minerals (Caillaud et al. 2009), thus we calculated the IA for chlorites as the ratio between the intensities of the 1.4 nm peak and the sum of the 1.7, 1.4, 1.2, 1.0 and 0.73 nm peaks on the EG-solvated XRD patterns. The relation between Cr_T and the IA of chlorites was negative ($r=0.572$, $p<0.01$, $n= 66$), likely because in the study area these minerals are generally more abundant in the clay fraction of serpentine-poor soils. Apparently therefore the most important Cr-bearing minerals are oxides.

Although the regressions were satisfactory in terms of explained variance, predicted average concentration and distribution of residuals, when we used the index of abundance of serpentine minerals

to calculate the total metal contents of external samples, we obtained an overestimate of both Cr_T and Ni_T . In the case of Cr_T , the predicted concentrations fell within the 95% confidence limits and the actual concentration was on the average 75% of the estimated one. In the case of Ni_T instead, the estimate may be up to three times higher than the actual concentration. Both the uncontaminated samples and those taken in the alluvial plain belong to same river basin, therefore no a priori differences in the metal ratio are expected. The different performance of the predictions may be thus related to the different geochemical behaviour of Cr and Ni during soil development. Although a limited development is typical for the Typic Udifluvents we selected, some Ni leaching may have occurred, and may justify the discrepancies in the estimate errors for the two elements. No leaching of Cr was instead expected and therefore the actual concentration better reflected the prediction.

In both cases, the metal concentrations expected because of the presence of serpentine minerals were extremely high, and even a small amount of serpentines (i.e IA~0.10) would determine Ni and Cr total concentrations in soils above 200 mg kg^{-1} . Thus, when serpentines are present in the soil, even in small amounts, the natural metal contents will exceed the threshold limits fixed by legislations for non-industrial use in several countries, including those located around the Alps and ultramafic massifs. Most threshold limits refer to aqua-regia-extractable metal concentrations, which are typically lower than those obtained by total dissolution. However, trioctahedral minerals, such as serpentines, easily dissolve in HCl (Wilson, 1987), thus only small differences between the two methods are expected in soils from ultramafic areas. According to the metal screening values of European countries (Swartjes et al. 2007), 200 mg kg^{-1} of Cr or Ni would determine the shift of the assignment of a soil from the “negligible risk” class to the “warning risk”, and sometimes even to the “potentially unacceptable” risk class (e.g. in the case of Ni in the Czech Republic and in The Netherlands). In addition, the 95% confidence limits were close to 100 mg kg^{-1} for both metals, and it will be therefore almost impossible to identify anthropogenic inputs of Ni and Cr to soils where natural and industrial sources of contamination overlap, unless a substantial pollution has occurred.

5 Conclusions

Uncontaminated poorly-developed soils on serpentinites showed extremely high Ni and Cr concentrations related to the abundance of serpentine minerals in the clay fraction. Even a small amount of serpentines will lead to soil metal concentrations above the limits allowed by legislation, impeding therefore to share anthropogenic from natural contribution using threshold concentrations when these minerals are present,

unless the pollution event was extremely severe. The results of our study therefore cast doubt on the use of metal concentration for land use planning if not coupled with mineralogical investigations in areas with a high geochemical background.

Acknowledgements We thank Franco Ajmone-Marsan and Mattia Biasioli for providing the urban soil samples we used to check the estimate and Alessia Traina for help with chemical analyses.

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Table 1: Ni and Cr concentrations in soil horizons

	Horizon	n	Mean	St. dev.	Min	Max
Ni _T mg kg ⁻¹	A	31	907	585	173	1887
	AC	10	1148	609	119	1818
	Bw	7	478	404	131	1304
	C	18	890	641	80	1861
Cr _T mg kg ⁻¹	A	31	822	661	20	2218
	AC	10	1074	706	79	2151
	Bw	7	378	227	119	682
	C	18	745	648	20	2085
Ni _E mg kg ⁻¹	A	17	18.4	16.9	2.6	59.6
	AC	5	20.3	13.9	3.2	34.1
	Bw	3	11.5	10.5	4.6	23.6
	C	11	17.4	22.9	0.3	78.1
Cr _E mg kg ⁻¹	A	17	0.4	0.2	0.2	0.8
	AC	5	0.4	0.2	0.3	0.8
	Bw	3	0.3	0.1	0.3	0.4
	C	11	0.3	0.1	0.1	0.5
Ni _{ex} mg kg ⁻¹	A	17	5.6	5.4	0.9	18.9
	AC	5	6.0	4.4	1.2	11.5
	Bw	3	1.9	0.3	1.6	2.2
	C	11	4.8	6.8	1.0	24.1

Table 2: Clay and total Fe oxides (Fe_D) concentrations and index of abundance of serpentine minerals (IA) in soil horizons

	Horizon	n	Mean	St. dev.	Min	Max
Clay g kg ⁻¹	A	31	58	23	21	110
	AC	10	63	15	43	88
	Bw	7	83	27	36	117
	C	18	74	30	27	142
Fe _D g kg ⁻¹	A	31	17.1	6.1	9.0	31.1
	AC	10	20.4	6.2	12.4	28.7
	Bw	7	16.7	3.4	12.4	21.1
	C	18	15.4	5.8	5.5	27.6
IA	A	31	0.425	0.289	0.066	0.844
	AC	10	0.581	0.239	0.185	0.875
	Bw	7	0.168	0.118	0.065	0.400
	C	18	0.407	0.300	0.043	0.929

Table 3: Correlations between mineral abundance (IA) and metals in soils, computed for the whole dataset and separately for soil horizons

	Ni _T	Ni _E	Ni _{ex}	Cr _T	Cr _E
Soils	0.928**	0.882**	0.816**	0.858**	0.207
A	0.962**	0.901**	0.876**	0.909**	0.625**
AC	0.931**	0.828	0.818	0.870**	-0.557
Bw	0.857*	nd ^a	nd	0.103	nd
C	0.883**	0.889**	0.767**	0.780**	-0.174

^a nd: not computed because of the low number of cases (3 Bw horizons)

** p<0.001; * p<0.01

Table 4: Predicted Ni and Cr concentrations from the regressions

Horizon	n	Predicted Ni (mg kg ⁻¹)				Predicted Cr (mg kg ⁻¹)			
		Mean	St. dev.	Min	Max	Mean	St. dev.	Min	Max
A	31	910	562	213	1726	809	559	116	1619
AC	10	1213	466	444	1785	1110	463	345	1678
Bw	7	410	231	211	862	312	229	114	761
C	18	875	583	167	1891	774	579	71	1783

Table 5: Observed, predicted, unstandardised residuals, and half width of 95% confidence interval values of Ni and Cr (mg kg⁻¹) and index of abundance of serpentine minerals in the topsoils from the public garden

Sample	Ni _T ^a	Ni _{Test}	Ni _{res}	Ni _{CI/2}	Cr _T	Cr _{test}	Cr _{res}	Cr _{CI/2}	IA
I	146	372	226	76	193	274	81	113	0.148
II	196	395	199	75	273	297	24	111	0.160
III	157	405	248	74	224	307	83	110	0.165
IV	143	401	259	74	196	303	107	110	0.163
V	125	393	268	75	212	295	83	111	0.159

^a Ni_T, Cr_T: total observed concentration; Ni_{Test}, Cr_{Test}: total predicted concentrations; Ni_{res} and Cr_{res}: difference between observed and predicted Ni and Cr; Ni_{CI/2} and Cr_{CI/2}: half width of the 95% confidence interval for Ni and Cr predictions

Fig. 1 The study area

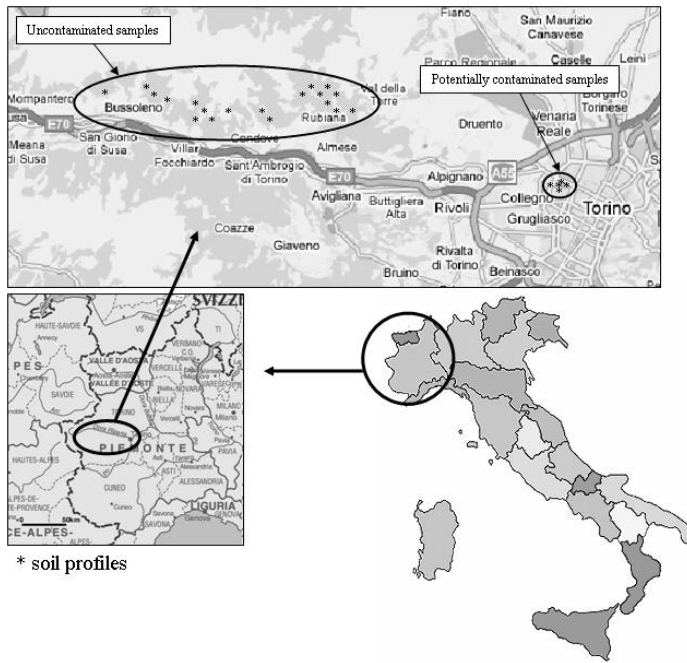


Fig. 2 Ratio between total Cr and Ni in Inceptisols (a) and Entisols (b)

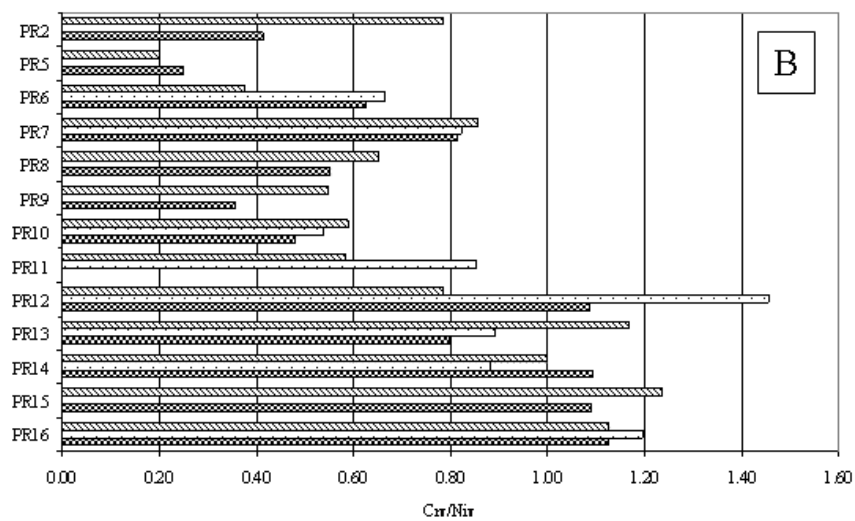
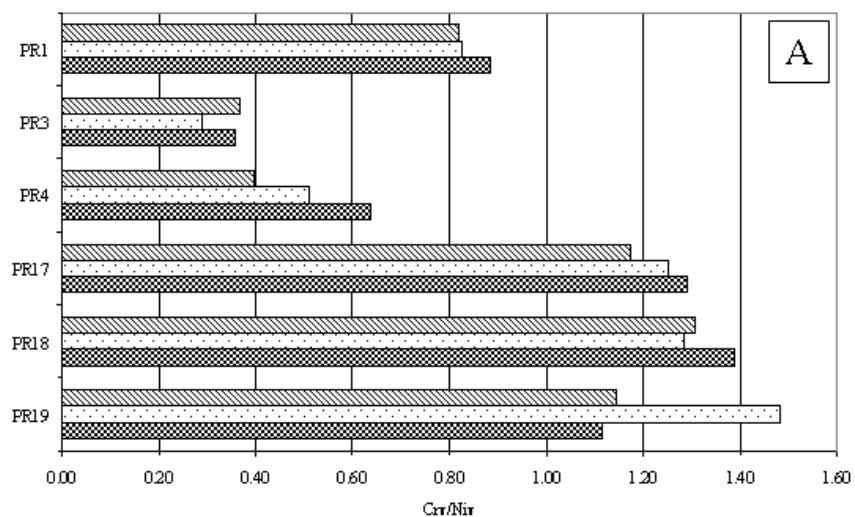


Fig. 3 XRD patterns after EG solvation of the clay fraction from selected soil horizons

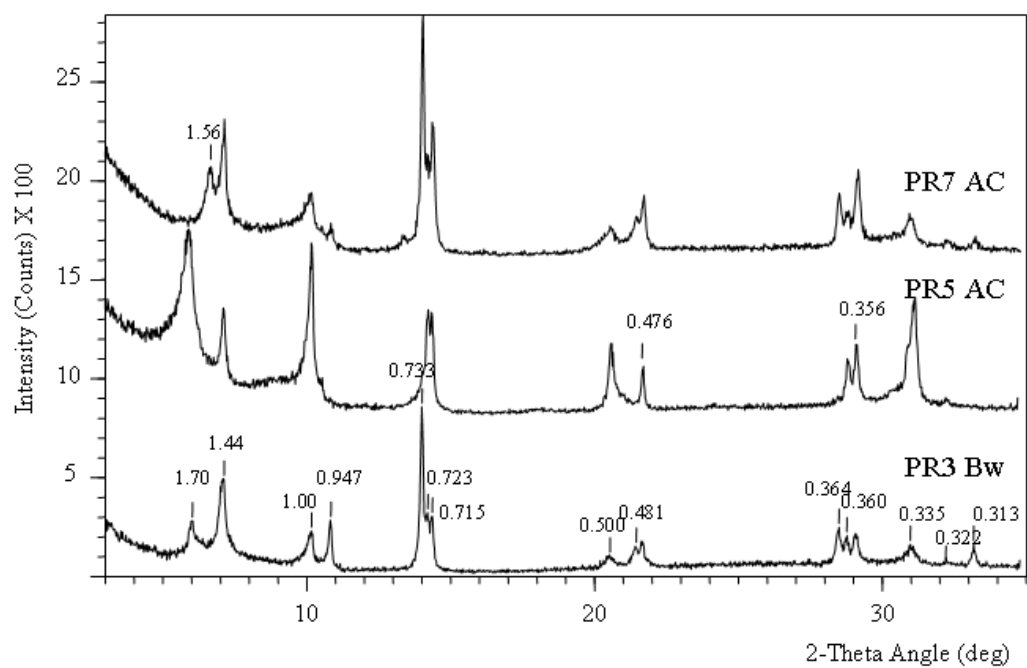


Fig. 4 Index of abundance (IA) of serpentine minerals in Inceptisols (a) and Entisols (b)

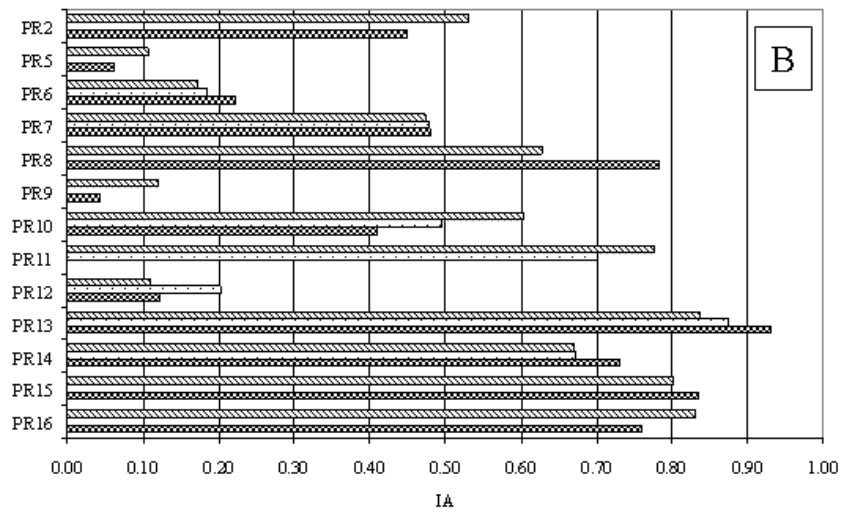
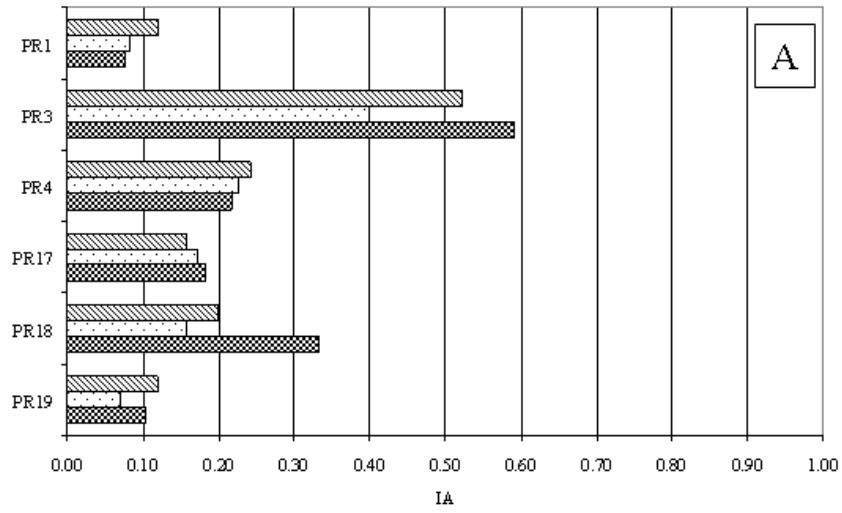


Fig. 5 Relation between abundance of serpentine minerals (IA) and total Ni (a) and Cr (b) in soils

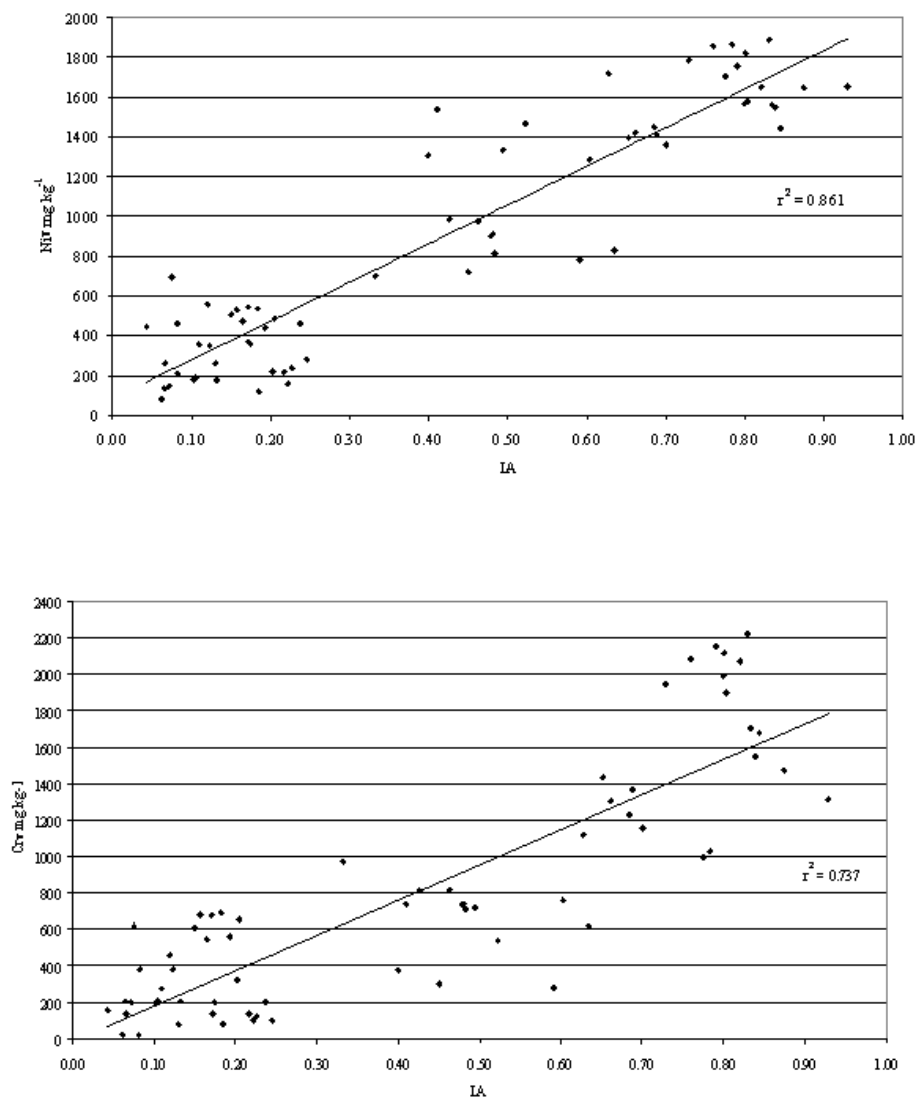


Fig. 6 Distribution of standardised residuals of the regression for total Ni (a) and Cr (b)

