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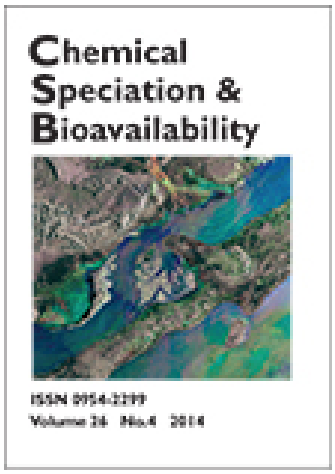

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Metals distribution in the organic and inorganic fractions of soil: a case study on soils from Sicily

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ABSTRACT

The content of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, has been determined in the organic and inorganic fraction of eight soil samples from Sicily. A modified type-Tessier sequential extraction procedure has been used to recognize metals in five different fractions categorised as follows: (a) exchangeable metals, (b) metals bound to carbonates, (c) metals bound to iron and manganese oxides, (d) metals bound to organic matter, and (e) metals in residual fraction. The mineralogical composition of soils samples was characterized by X-ray diffraction. Humic substances were extracted by means of an alkaline extraction procedure. It has been found that both the mineralogical composition and the different content of humic fraction of organic matter in the soils investigated are responsible for the observed trace metal distribution. The obtained data show that a significant amount of trace metals is bound to the organic fraction where different binding sites are present simultaneously. In particular, Pb and Cu seem to be the elements more tightly linked to the organic fraction of soils, whilst cadmium is mostly concentrated into the iron and manganese oxides fraction. The presence of clay minerals in soil is significant for metal distribution, playing a fundamental role in binding metal ions. Besides, it has been observed that the calcophile metal mobility is strongly dependent on the presence of sulfide phases. Applying the Risk Assessment Code to the analyzed soils, it appears that they contain, generally, less than 30% of metals in the exchangeable and carbonate fractions. Calcic brown soil from Piano Zucchi exhibits a medium up to very high risk for Pb, Cd, Co, Zn and Mn. It also been recognized the elevated presence of Cd in the exchangeable and carbonate fractions of andic brown soil on volcanites from Pachino.

Keywords: soils, heavy metal distribution, metal speciation, sequential extraction

INTRODUCTION

Soil is the result of chemical, physical and biological weathering reactions, acting upon parent rocks and conditioned by factors of climate, vegetation and time of reaction, which all together determine its chemical features, mineralogical composition and metal content. Soil is a geochemical highly variable product made up of both inorganic and organic material and is supporting the continental plant life. It is also one of the most important factor affecting human health and wellbeing (Abrahams, 2002). As a consequence, there is a great concern about contamination of the soil ecosystem by potentially toxic metal ions because of their threat to human life and environments, particularly with regard to plant uptake, deterioration of soil microbial ecology and contamination of groundwaters or surface waters (Cunningham *et al*., 1975; Riekerk and Zasoski, 1979; Kabata-Pendias and Pendias, 1992; Vaughan *et al*., 1993).

The presence of heavy metals in soils arises from a multitude sources. It is firstly dependent on natural phenomena, such as weathering and mechanical degradation of rocks. Although the geogenic contents of toxic heavy metals in soils are generally low they may be greatly enhanced by human activ-

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ities. The increased agricultural applications, in addition to uncontrolled discharge of urban solid wastes and sewage sludge on soils, are the main causes of heavy metal accumulation in soils and sediments.

The geochemical mobility of toxic metals in soils depend on how and which soil phase they are bound to and their chemical form, which, in turn, is related to the physicochemical and biological characteristics of the environmental system. The understanding of the occurrence way of elements in soils is therefore essential for the assessment of soil contamination and to elucidate the role that each fraction plays in controlling the adsorption/release processes and the metal bioavailability in the environment. In general, the mobility of heavy metals in soils is severely limited by strong sorption reactions between metal ions and negatively charged surfaces particles of soils (Stumm, 1987). However, several long-term experiments have evidenced an enhanced mobility of metal ions in organic matter rich soils (Berggren *et al*., 1990; Li and Shuman, 1996; Streck and Richter, 1997; Kalbitz and Wennrich, 1998). The presence of different binding sites in the soil organic matter (O-, N-, S- and HS-donor groups) leads to the formation of soluble metal organic complexes which facilitate the metal transport in soils and groundwater (McCarthy and Zachara, 1989; Temminghoff *et al*., 1997). Humic and fulvic acids, being characterized by the simultaneous presence of different binding sites in their structure (McCarthy, 2001; Gaffney *et al*., 1996; Stevenson, 1994) are the most important components of the organic fraction in determining both transport and fixation of metal ions in soils and sediments (Vaughan *et al*., 1993; Wood, 1996; Tipping, 1998, 2002). In spite of their considerable cation exchange capacity, the humic substances are a minor part of soil and sediment bulk. Most of soils or sediments are constituted by electrically charged inorganic components, such as carbonates, silicates (chiefly clays) and secondary metastable iron manganese sesquihydroxides, which also contribute, to different extent, in controlling the metal absorption-release surface process (Kraepiel *et al*., 1998; Sposito, 1984). These mineral particles have very large specific area per unit volume which significantly influence the partitioning of trace metals between soil solutions and the surface of minerals. As an example, the interactions between metal ions and iron and manganese biogenic oxides are very important in determining the distribution and geochemical fate of trace elements, as shown by different authors (Catts and Langmuir, 1986; Dong *et al*., 2000; Bellanca *et al*., 1996; Tessier *et al*., 1996; Nelson and Lion, 2003 and refs therein). As the mobility of heavy metals in ground waters results both from dissolution of the organic substance and desorption from the surface of the inorganic components, the relative abundances of organic matter and soil minerals play a key role in soil solution chemistry with respect to remobilization phenomena and to decontamination treatment of polluted soils. On the basis of the above considerations, it is clear that in studying metal distribution in soils and sediments, the role of both organic and inorganic fractions must be considered.

The aim of this paper, which is part of a greater project studying the presence of heavy metals in the environment (Dongarrà *et al*., 2003a, 2003b; Varrica *et al*., 2003) and their chemical speciation in the presence of naturally occurring ligands (De Stefano *et al*., 2002, 2004; Gianguzza *et al*., 2004), is to establish the possible forms or phases in which heavy metals are associated in several soils of Sicily and to discuss the relationships between soil composition and metal sequestration capacity. Here we report results on the distribution of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, in the organic and inorganic fractions of eight soil samples by using a modified sequential extraction (Tessier *et al*., 1979) which allowed us to recognize metals in five different fractions categorised as follows: (a) exchangeable metals, (b) metals bound to carbonates, (c) metals bound to iron and manganese oxides, (d) metals bound to organic matter, and (e) metals in residual fraction. An alkaline extraction procedure has also been carried out to isolate the soluble humic fraction and to assess the different binding capacity of the humic and fulvic compounds. The amount of humic substance recovered by the organic fraction was related to the total organic carbon content in each soil sample. Atomic absorption spectroscopy and X-ray analysis have been used to determine metal content in the different fractions and to characterize the mineralogical composition of soils, respectively.

METHODOLOGY

Sampling sites

Eight soil samples were collected in Sicily in areas characterized by different lithology (Fierotti *et al*., 1988) to represent a wide range of compositions in terms of organic matter and mineral content. All but one of the sampling sites were chosen to be as far as possible from urbanized or cultivated areas, in order to avoid anthropogenic sources of pollution. Only one soil (sample number 7) is related to heavy metal pollution from an old mining activity in the area. Samples were collected from the superficial horizon (20 cm), then placed in plastic bags and transported

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to the laboratory at 4°C for analysis. All samples were dried in a stove overnight, sieved through a 2 mm sieve and milled in an agate pot, before analysis. Code numbers were assigned to the samples as follows:

1. *Piano Zucchi*. Calcic brown soil on limestone and flyschoid sequences. (Mountain soil from Madonie Mounts, 1200 m. a.s.l.);
2. *Ficuzza*. Leached brown soil on limestone rock (Mountain soil from the forested area near to Palermo);
3. *Buonfornello*. Alluvial soil, sedimentary area;
4. *S. Cataldo*. Regosol on rocks of the ''Gessoso-Solfifera'' evaporite series. (Hill soil from a forested area);
5. *Etna Volcano*. Lithosol on volcanic rocks (Mount Etna);
6. *Peloritani Mounts*. Alluvial soil (Peloritani Mounts); metamorphic area;
7. *Old Mine*. Soil close to an old mining area (Peloritani Mounts); metamorphic area;
8. *Pachino*. Andic brown soil. Soil originated from the weathering of the the Iblean volcanites with mesozoic calcareous intercalations (Iblea Zone).

Sampling sites are indicated on the map of Sicily

Figure 1 Location of the sampling sites.

reported in Figure 1.

Materials and reagents

All the reagents used were of analytical grade. Commercial samples of humic substances, used for comparative purposes, were from Fluka lot no. 41968/1 894; peat and aquatic standard humic acids from IHSS. Class A glassware was always employed.

Equipments

X-Ray analysis: The main mineralogical phases in the soil samples were determined by powder X-ray diffraction using a Philips PW 1729, model RX, diffractometer. After the organic matter was removed from samples by means of H_2O_2 0.5 M (Fluka ultrapur), the X-ray analyses were carried out on the samples previously dried and reduced to a <2 mm size. Mineral percentages were obtained by semi-quantitative analysis of the intensity of each specific peak. The samples were also X-rayed after saturation with ethylene glycol to examine the clayey fractions.

Total organic carbon and pH measurements: Organic fraction of soils was determined as total organic carbon (TOC) measured by loss on ignition in electrical muffle furnace at 450°C, according to Dean's method (1974). Since this procedure could over-estimate the organic matter content owing to the simultaneous elimination of volatile carbonates (Bengttson and Enell, 1986), we carried out the measurements after carbonates removal by adding HCl 6 N to the original sample. The results, reported in Table 1, show a large variability, from 4 up to 32%, with the highest value found at site sample 8. In the same table the pH values, obtained by measurements carried out on soil suspension [50 g (<2 mm sieved) in 50 mL distilled water], are reported. These values range from 6.2 to 8.0 showing a near neutral or slightly alkaline nature of the soil samples under investigation.

Table 1 Total Organic Carbon (TOC) and pH measurements in soil samples

Soil sample[a]	pH	TOC %
1	7.2	15
2	7.6	7
3	7.8	20
4	7.9	4
5	6.7	8
6	7.6	10
7	6.2	15
8	8.0	32

[a]Number soil samples refers to Figure 1.

Metal analysis: Metal ion concentrations in each sequentially extracted fraction were determined by AAS-GF technique using a Perkin-Elmer model Analyst 3000 atomic absorption spectrophotometer equipped with graphite furnace and auto-sampler. In order to minimize the matrix effects, the calibration standard solutions were prepared by adding known quantities of the metal, in turn under investigation, to the same matrix derived from the sequential extraction and by comparing the results obtained with reference blank solutions.

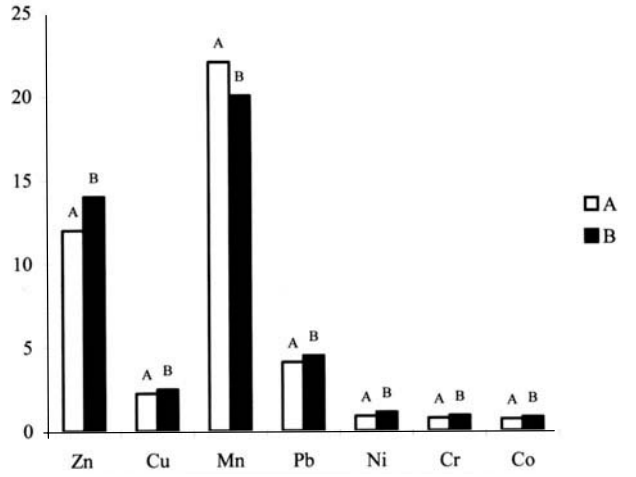

Figure 2 Comparison between the metal content in the organic fraction extracted from a soil sample (sample 2) according to the Tessier's classical procedure (A) and by mineralization with HNO_3/H_2O_2 oxidizing solution (B).

Sequential metal extraction procedure

A modified type-Tessier (1979) partitioning procedure was used to separate the operationally determined specific fractions of soils containing metals differently bound. In order to optimise the procedure for the purposes of this work, particular attention was paid in determining the reaction times of each extraction step. To find the best experimental conditions and extraction times to be used, different attempts were carried out on reference samples to which known amount of metals were added. The extraction procedure employed, by means of which at least 80% of metals recovery was obtained, is reported hereafter:

Fraction 1 (*exchangeable metals*): 1 g (dry weight) of <2 mm sieved soil sample was treated with 16 mL of 1 M sodium acetate solution for 1 hour under continuous stirring. A residue was obtained after centrifugation.

Fraction 2 (*metals bound to carbonates*): the residue obtained from step 1 was stirred with CH_3COONa/CH_3COOH solution at pH $\sim$ 5 for 4 hours. A new residue was obtained after centrifugation.

Fraction 3 (*metals bound to Fe and Mn oxides*): the residue from step 2 was treated with 0.04 M NH_3OHCl solution in 25% CH_3COOH (v/v) under stirring at 96°C, until the free iron-manganese oxides were completely dissolved. The reaction time was 6 hours.

Fraction 4 (*metals bound to organic matter*): the organic fraction of the residue from step 3 was mineralised in a high performance microwave digestion unit (Milestone, mod. mls 1200 mega) by means of 3 mL HNO_3 + 0.5 ml H_2O_2 oxidizing solution. A new residue was obtained after centrifugation and solution removal.

Fraction 5 (*metals bound to silicates*): the last residue was digested with HF and $HClO_4$ mixture and dissolved in a microwave digestion unit.

To reduce the extraction time, the step 4 of Tessier's original procedure was substituted by the mineralization with a HNO_3/H_2O_2 oxidizing solu-

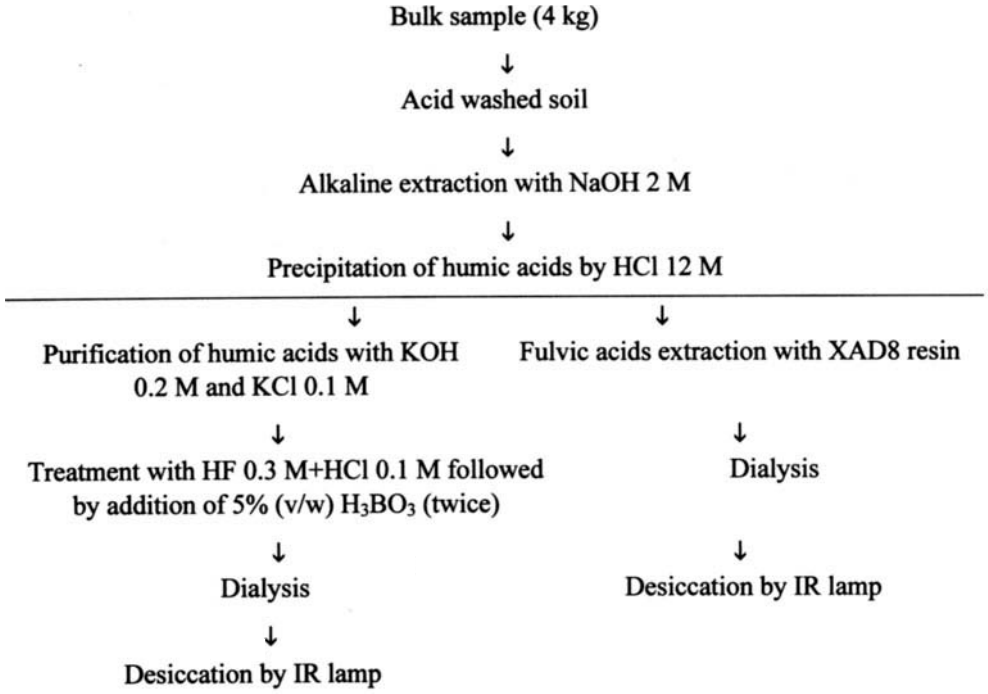

Figure 3 Procedure for the extraction of humic and fulvic fraction.

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tion. As shown in Figure 2, a satisfactory agreement was found between the results obtained using both the original and the modified Tessier procedure.

Extraction procedure of humic and fulvic fractions

To extract and separate humic and fulvic components of organic matter the classical procedure indicated by Stevenson (1994), also recommended by the International Humic Substances Society (IHSS) was carried out. To reduce the reaction times, some steps of the procedure were slightly modified by using more concentrated reagents (see the scheme outlined in Figure 3).

RESULTS AND DISCUSSION

Metals distribution in the organic and inorganic fractions

The results of metal analysis in the sequentially extracted fractions from soil samples are reported in Table 2, as average of three measurements. The following method detection limits (μg/L) have been considered for the different metals: Zn (1.0), Fe (10.0), Cu (5.0), Mn (5.0), Pb (20.0), Ni (25.0), Cr

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Table 2 Metal ion concentrations (mg/kg dry weight) in the different fractions from sequential extraction carried out on soil samples

Soil sample[a]	Fraction	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	1	1.6	2.2	1.5	0.3	3.7	92	0.1	2.7	6.2
	2	–	3.5	1.3	0.4	37.5	253	0.5	2	25.2
	3	0.7	2.2	1.0	2.2	584	64	0.7	2.2	17.6
	4	2.8	3.7	6.4	4.3	525	50	1.2	5.9	24.4
	5	–	0.1	2.8	0.6	297	4.5	0.6	2.3	7.2
2	1	–	–	–	0.1	5.5	–	0.2	0.9	2.5
	2	–	0.3	–	0.1	7.7	20.5	0.2	1	8.2
	3	0.3	5.9	0.7	0.3	850	160	0.9	1.9	36.8
	4	–	0.7	0.8	3.5	860	22	0.9	4.1	12
	5	–	1.3	8.2	1.4	654	4.5	0.8	1.4	8.7
3	1	–	0.5	0.2	1.1	1.2	4.2	0.1	0.8	2.1
	2	0.2	2.1	2.7	1.7	20	8.3	1.3	1.2	5.9
	3	0.7	2.0	4.0	1	836	16.7	2.2	1.6	22.5
	4	–	2.5	28.9	15.6	1374	23.3	3.1	3	27.8
	5	0.1	0.7	13.8	6.1	655	8.3	1.1	1.6	12.1
4	1	–	–	–	0.1	2.7	1.1	0.5	0.8	4.7
	2	–	0.1	0.2	0.1	5.5	68.7	0.6	1.0	6.2
	3	0.3	1.7	–	0.2	624	150.8	0.6	1.2	13.6
	4	–	–	1.6	1.7	888	20.8	1	2.6	7.6
	5	–	1.3	11.4	1.3	715	9.0	1.7	1.8	14.5
5	1	–	–	–	0.1	–	–	–	1.1	1.2
	2	–	–	–	0.4	7.7	9.2	0.1	1.2	10.2
	3	0.8	5	–	0.4	1950	160	0.5	1.6	25
	4	–	0.1	1.5	4.0	1900	14.4	0.6	3.4	8.8
	5	–	0.3	1.4	1.1	383	13.7	0.2	1.8	4.75
6	1	0.1	0.5	0.4	0.1	2.5	4.2	0.6	1.1	–
	2	–	1.5	0.5	0.3	12.5	2.0	1.2	1.2	6.5
	3	–	1.6	1.5	0.2	600	13.2	1.4	1.4	18.4
	4	1.7	3.8	3.9	2.3	800	16.8	3.6	3.0	50
	5	–	2.3	2.5	0.7	250	10.5	1.4	1.8	9.2
7	1	–	0.8	0.7	0.1	6	6.2	0.3	0.1	18.5
	2	0.2	0.6	0.5	0.4	1250	2.0	0.8	1.7	187.5
	3	4.4	2.1	1.1	0.1	400	10.0	1.0	4.5	392
	4	1.8	4.1	10.4	5.1	800	13.2	5.5	12	388
	5	0.4	1.0	2.6	1.1	250	8.2	1.2	3.3	53.7
8	1	0.2	2.1	1.5	0.1	19	122	0.3	1.3	1.2
	2	0.2	0.1	0.4	0.1	16	29	0.9	1.4	2.4
	3	0.3	2.8	1.8	–	1750	447	3.5	1.4	13.8
	4	–	5.0	6.7	5.5	3285	202	6.4	2.7	58.5
	5	0.1	3.5	4.3	3.8	2187	196	3.3	0.9	21.1

[a]Sample number refers to Figure 1; (–) under detection limit.

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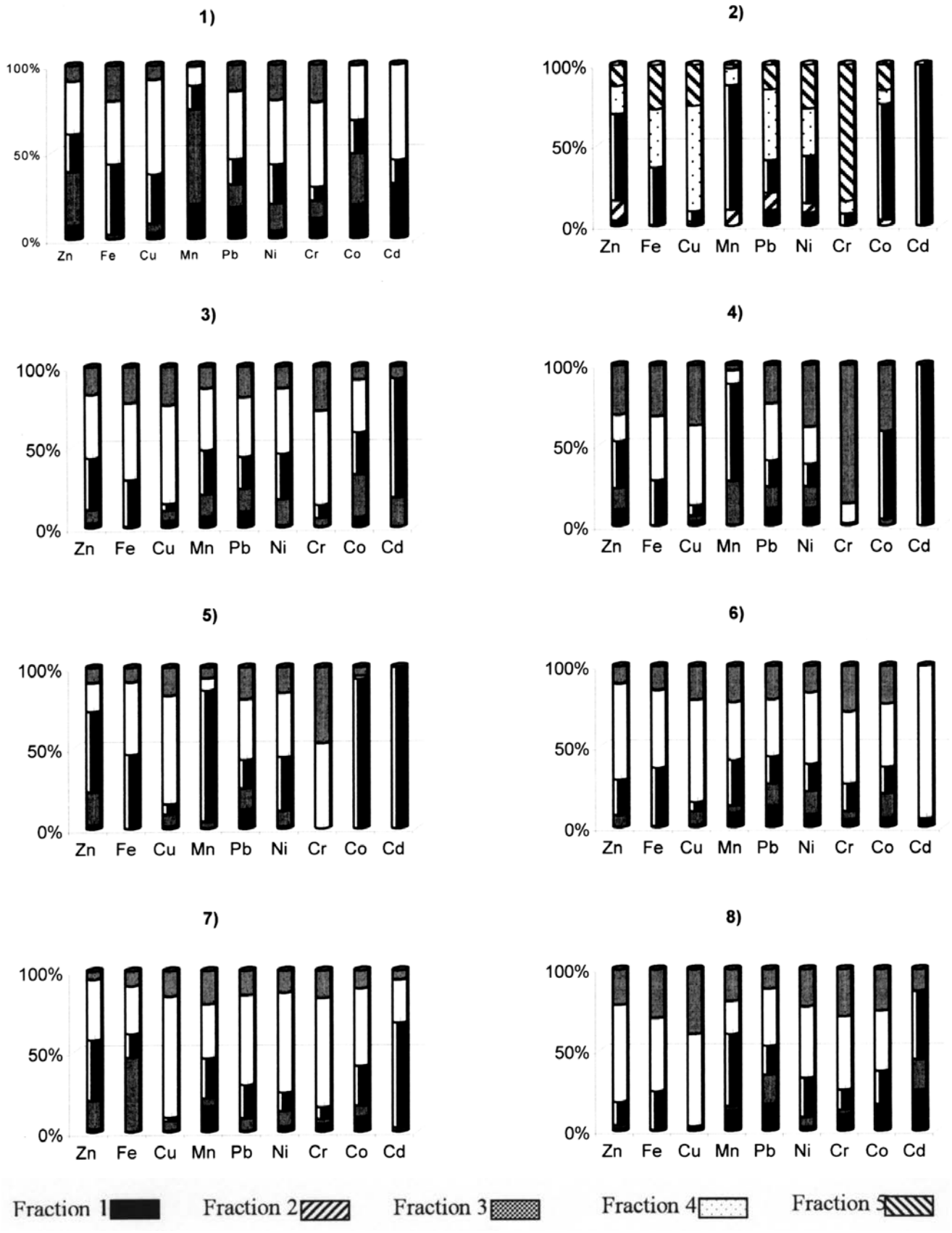

Figure 4 Percentage distribution of metals in the different fraction obtained from the sequential extraction procedure.

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(5.0), Co (10.0), Cd (1.0). In Figure 4 we also report the metal percentage distribution in each sequentially extracted fraction.

It may be observed that the amount of metal bound to the residual fraction, that is the less bioavailable form, is always lesser than the total amount present in the sum of the other fractions. Among the analyzed metals, iron, manganese and zinc, show the highest concentrations in all the samples.

Iron and manganese are mainly associated with the non residual fraction. Excluding the fraction 3 (Fe–Mn oxides), the highest percentages of iron are found in the fourth fraction of the extraction procedure, *i.e.*, metals bound to organic matter, thus indicating the strong influence of complex species formation in the mobility of metals. Iron is abundant in the fraction 2 of sample no. 7, collected close to an old abandoned mine on the Peloritani mountains, North-Eastern Sicily, where ore deposits of various types are present. Such high concentrations suggest that in these samples there is a significant portion of iron present as non residual fractions (carbonate and iron-manganese oxides) and residual fraction. This is consistent with the mineralogical composition of the local metamorphites made up of quartzitic phyllites with iron carbonates (siderite, $FeCO_3$; ankerite, $Ca(Mg,Fe)(CO_3)_2$) and of the volcanic bulk rich in iron silicates (Censi and Ferla, 1989). Iron is also particularly abundant in fractions 3, 4 and 5 of sample no. 8 belonging to the Iblea zone where volcanites with mesozoic calcareous intercalations are largely present. Mn appears more abundant in the soluble organic phase in soils from volcanic (5, 8) and metamorphic (6, 7) areas. It is also significantly present in fraction 2 of those samples (1, 4) rich in carbonate minerals where it may replace calcium diadochically. Mn is particularly abundant in sample 1, especially bound to the carbonate fraction. This may be attributed to the presence in the area of the Numidian Flysch (Oligocene–Miocene), consisting of alternance of quartzarenites and argillites with intercalated beds ascribed to a clay-ironstone in Mn-rich carbonate facies (Calderone *et al*., 1980; Dongarrà and Ferla, 1982).

In addition to iron and manganese, zinc shows higher concentrations than the other metals investigated, especially in the soil sample from the mineralized area (sample 7). This element is rather uniformly distributed among the carbonate, Fe–Mn oxides and organic phases, whilst lower contents are associated with the exchangeable fraction. It has been documented that Fe–Mn oxides may adsorb Zn on their surface (Catts and Langmuir, 1986) with high stability constants.

Copper is associated mainly with the organic fraction and the residual fraction. Lower contents of Cu are associated with exchangeable and carbonate fractions. This finding is consistent with the pronounced tendency of Cu(II) to form highly stable organic complexes, as already described by several authors (McLaren and Crawford, 1973; Adamo *et al*., 1996; Barona *et al*., 1999; Banerjee, 2003), and also reported in many compilations concerning the metal complexes stability (Martell and Smith, 1997; Pettit and Powell, 1993; Sillén and Martell, 1964, 1971).

The fractionation profile of lead shows that the main fractions containing lead are the organic matter, Fe–Mn oxides and the final residue, with the major portion bound to the first one. The geochemistry of lead in the earth-forming rocks is characterized by its strong affinity for sulfur and oxygen, thus forming sulfides, sulfates, phosphates and silicates. In the last minerals lead diadochically replaces potassium. During weathering it is extracted from its minerals and transported as soluble compound. In the present study lead exhibits a pronounced tendency to accumulate in the organic/sulfide fraction suggesting the complex species formation with the organic matter and/or its presence as sulfide phases. The lack of a significant correlation between the total organic content (TOC) and Pb bound to the organic matter indicates that in these samples part of lead may be held in primary sulfide minerals. This is particularly evident in the samples 6 and 7 from Peloritani mountains where soils are overlying metamorphic rocks. Pb is also associated to the fraction bound to Fe–Mn oxides. Our data support previous results (Ramos *et al*., 1994; Maiz *et al*., 1997) in indicating that adsorption may be an important control on Pb levels in soils, particularly at $pH > 7$ (Tipping *et al*., 1986). A minor contribution to the total content of lead is given by the exchangeable fraction.

The highest content of Ni was found in the samples 6–8 which belong to soils developed on metamorphic or volcanic rocks. In all the samples Ni resides prevalently in the organic and Fe–Mn oxides fractions. However, the contribution of Ni to the residual fraction is also important. These findings point to a mobilization and redistribution of Ni from parent rocks to soils. According to Bruemer *et al*. (1988) the relative large proportion of this element bound to the oxides fraction has to be attributed to its capacity of inducing an high field stabilization energy.

Cr is concentrated in the last two extraction steps. The other fractions are of absolutely minor importance, except in samples 6 and 8 where the Fe–Mn oxides fraction account for 13–17% of the total Cr in the soils. While the large presence of Cr in the

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residual fraction agrees with the observations of Banerjee (2003), it is rather uncommon to relate Cr with the organic fraction.

Cobalt is predominantly distributed in the Fe–Mn oxides, organic and residual fractions. Due to its calcophile nature it may be supposed that part of Co is associated to sulfides.

High concentrations of Cd in Sicilian soils were already found in clayey minerals and Fe–Mn oxides fractions (Bellanca *et al*., 1996; Palumbo *et al*., 2001). In the soils examined in the present study Fe–Mn oxides play a major role in binding Cd, sometimes reaching approximately 100% of the total soil Cd. Although numerous authors have described the low affinity of Cd for the organic phase (Ramos *et al*., 1994; Xiandong and Thornton, 2001; Banerjee, 2003), the samples 1 and 6–7 exhibit a relevant percentage of Cd bound to the organic phase.

Metal content and mineralogical composition

Results of metal analysis in each fractionation step have been evaluated also considering the mineralogical composition of the samples. The inorganic components of the analyzed soil samples consist largely of common rock-forming minerals, as calcite, quartz, plagioclase and clay minerals (Table 3).

In only one sample (no. 4), collected in the area of S. Cataldo (CL), where the ''Gessoso Solfifera formation'' outcrops, abundant amounts of gypsum were found. Clay minerals are present in all the samples but sample 5 from Etna Volcano. The dominant clay mineral types are kaolinite in soils 2, 3 and 4, montmorillonite in soils 1, 4, 6, 7 and 8. Chlorite and muscovite were found in samples from Peloritani mountains (6–7). It is well known that an important property of the clay minerals is their cation adsorption and exchange capacity (Bear, 1964). This capacity derives from the bonds breaking around the edges of silica-alumina units as well as the replacement of hydrogen of exposed hydroxyl groups in the kaolinite minerals and in the lattice substitutions in montmorillonite. In chlorite mineral both types of substitutions are involved. Generally, the cation exchange capacity of clay minerals follows the order: montmorillonite > chlorite > kaolinite.

Table 3 Semi-quantitative mineralogical composition of the soil samples

Mineralogical composition (%)	Sample[a] 1	2	3	4	5	6	7	8
Albite					50			60
Anorthite					30			
Diopside					20			
Quartz	40	50	40	20		28	22	13
Calcite	30	30	45	30				
Gypsum				40				
Kaolinite		20	15	3				
Montmorillonite	30			7		13	16	27
Chlorite						18	22	
Muscovite						41	40	

[a]Sample number refers to Figure 1.

Five of the eight samples we have investigated contain appreciable amounts of montmorillonite. It has been found that the content of some metals (Cd, Co, Cr, Fe, Mn and Pb), recovered after the first step of the sequential extraction procedure, generally enhances with the increasing of montmorillonite percentage in the inorganic fraction, confirming the high adsorption capacity of this clay mineral. The anomalously low values exhibited by Pb and Cd in sample no.7 (*old mine*) reflect the larger concentration of metal sulfides in this sample and consequently the significant decrease of the percentage of metal in the exchangeable fraction.

Different mineral species in soils have a controlling influence on the release of heavy metals, either present as structural ions or as exchangeable or adsorbed ions and, therefore, they have an important bearing on food production and human health. It is generally recognized that sequential extraction procedures, which differentiate the relative binding strength of metals in different mineral fractions, enable the estimation of risk connected with the presence of heavy metals and metalloids in soils. They can also indicate trends over time and area. Jain (2004) suggest a criterion to assess the risk (RAC, Risk Assessment Code) based on the amount of metal that can be released by a sediment. According to Jain's RAC, any sediment that can release from exchangeable and carbonate fractions less than 1% of the total metal content shows no potential ecological risk. According to the risk assessment code, different levels of risk are categorised on the basis of the amount of metals released: low risk 1–10%, medium risk 11–30% and high risk 31–50% or more. If we apply this code also to soils, it appears that the samples here investigated contain, generally, less than 30% of the metals in the exchangeable and carbonate fractions (Table 4). Sample no. 1 exhibits a medium up to very high risk for Cd, Co, Mn, Pb and Zn. It also worth noting that the elevated presence of Cd in the exchangeable and carbonate fractions in sample no. 8 (Pachino).

Metals in the humic fraction

As pointed out before, the binding of metallic cations by soil organic matter mostly depends on the

Table 4 Percentage of metals as sum in exchangeable and carbonate fractions referred to total metal content in the five extracted fractions of soil samples

Sample[a]	Metal content as sum of percentages in exchangeable and carbonate fractions								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	31	49	22	9	3	74	20	31	39
2	–	3	–	3	1	10	14	20	16
3	18	33	6	11	1	21	18	24	11
4	–	4	2	6	0.4	28	24	24	24
5	–	–	–	9	0.2	5	11	25	23
6	5	21	10	10	1	13	22	27	8
7	2	16	8	7	46	21	13	8	20
8	44	16	13	3	0.5	15	8	35	4

[a]Sample number refers to Figure 1; (–) under detection limit.

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presence of polyfunctional binding sites. Humic and fulvic acids acids are very important components but it must be noted that they are not the only ones: other components such as polysaccharides, polyamines, polyamino acids, phytic acid, *etc*., contribute to bind metal ions ion soils. In general, we found the fulvic fraction less than the humic one and, therefore, metal analysis was carried out only in the humic fraction extracted from the organic component of soil, according to the scheme reported in Figure 3. Results are reported in Table 5.

As can be seen, with the exception of Fe, the concentration of metals in the soluble humic fraction of samples 1, 2 and 7 represents a not negligible portion of the total metal content in the organic fraction (see for comparison Table 2). This is consistent with the high HA percentages observed in these samples. Such a trend confirms the primary role in metals sequestration played by the organic fraction of soils and, in particular, by humic substance where different binding sites are present.

CONCLUSIONS

As the toxicity of heavy metals in soils and sediments is dependent on their chemical form more than their total concentration, it becomes fundamental to know the metal distribution between different mineral phases. The sequential extraction procedure adopted in this work allowed us to recognize that Zn, Fe, Cu, Mn, Pb, Ni, Cr, Co and Cd are associated to a significant extent with reactive forms such as the organic fraction and carbonates, or adsorbed on clays and amorphous oxy-hydroxides of Fe and Mn. In general, all the analyzed elements exhibit a not negligible association with the organic substance, whose cation exchange capacity is partly due to the presence of humic acids. Since pH values of soil samples range around the neutrality with some slightly alkaline value (Table 1), we can affirm that the main binding sites of organic matter in soils under investigation, involved in metal sequestration process, are the carboxylic groups which are present in both humic and fulvic fractions. In order to confirm this hypothesis, preliminary results have been obtained by determining the concentration of carboxylic groups by means of titrations with $(CH_3COO)_2Ca$, according to the method reported by Masini *et al*. (1998). These analysis will provide more information on binding sites available for the metal complexation and will be useful for the investigation, in progress in our laboratories, on the stability of metal-complexes formed.

The well known high mobility in soils of nickel ion is confirmed by its consistent presence in the organic fraction. In addition, a close association of Zn, Pb, Ni, Cd, and Co with Fe–Mn oxides has been observed.

Table 5 Metal content in humic fraction extracted from the organic matter (TOC) in soil samples

Sample[a]	HA % in TOC	Metal content (mg*10^2/kg of soil dry weight)								
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	1.9	0.02	1.5	3.8	4.18	199.5	13.1	0.7	3.6	20.21
2	1.2	0.02	0.5	0.7	3.1	63	5.5	0.2	0.2	1.7
3	0.05	–	0.02	0.02	0.03	12.5	0.09	0.01	–	0.2
4	0.63	–	–	0.04	0.04	0.72	0.5	0.02	0.02	0.2
5	0.6	–	0.3	0.3	3.7	44.6	0.4	0.1	0.1	0.8
6	0.04	-	0.06	0.4	0.1	14.4	0.9	0.1	0.06	0.5
7	6.2	0.2	4.0	9.8	4.9	46.5	6.6	3.8	4.5	63.9
8	1.0	–	0.6	1.1	2.0	1112	11.4	0.5	0.2	4.4

[a]Sample number refers to Figure 1; (–) under detection limit.

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The carbonate phase contribute in a relevant way for Mn, Pb and Zn in carbonate soils suggesting that in such types of substrates the presence of calcite or other carbonate minerals is an important factor, often under-estimated, to be addressed when interpreting trace metal enrichment.

In the metals sequestration process a relevant role is also played by expandable clay minerals, as shown by the relationship between metal content and mineralogical analysis. As the desorption of heavy metals from clay minerals decreases at high pH value, it may represent a valid control on the solubility of heavy metals. This is especially important in soils with relatively high pH values, where a significant dissolution of humic acids and their metal complexes occurs.

The metal ions distribution in organic and inorganic fractions indicates that, in spite of the total concentration of an element in the bulk soil, are the inorganic-solid-fluid phase interactions (ion exchange and adsorption) and the binding ability of the organic fraction responsible for the mobility and transport of metals in soils. This means that changes in the physico-chemical and biological characteristics of soils may result in a transfer of elements from the solid phase to the mobile phase and thus permitting contamination of ground waters and an enhanced uptake from plants and other living organisms.

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