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SOIL GEOCHEMISTRY AND PEDOLOGICAL PROCESSES. THE CASE STUDY OF THE QUATERNARY SOILS OF THE MONTAGNOLA SENESE (CENTRAL ITALY)

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ABSTRACT
The role of soil as an environmental filter is widely acknowledged, although not fully understood in all the processes involved. Unfortunately in the monitoring of some environmental parameters indicative of soil quality, such as heavy metals, we can observe a general tendency to simplify the issue. In fact, data refer only to a part of soil, i.e. the uppermost part, or the plow layer, while characteristics and processes which occur in the lower parts of the profile are neglected. On the other hand many soils, like Paleosols, which are quite widespread in Italy, have a very thick and complex profile, in which a significant elemental concentration can take place as a result of natural, pedological processes. This stresses the importance of in-depth investigation when the object of laboratory analysis is to provide advice for specific land uses.
Aim of this work was to study the role played by soil forming processes in addressing element behaviour in some soils of the Montagnola Senese territory.
Results of this work show an accumulation of many elements with respect to parent material. However this trend was not uniform in all cases, pointing out that their re-distribution in soil horizons can be related to different pedogenetic processes. The accumulation of some elements in soils can be to some extent related to organic matter content, pH and cation exchange capacity, but mainly in the upper horizons, while clay richness seems to play a more important role in determining the element concentration in all soil horizons: correlation coefficients with high level of significance have been found between clay and Ti, K and Cr, but also Fe, Zn and Pb are correlated with clay content, with the exception of those horizons, which are affected by element redistribution caused by oxidative-reductive processes.
Several elements show a time dependent concentration process. Ti, K, Na and Mn seem to increase through time from the Holocene, to the Upper and Middle Pleistocene; Cr, Pb and Zn, similarly to Fe, from Holocene up to the Lower Pleistocene.
The accumulation process proceeds along with clay neo-genesis and illuviation, but it can be affected by clay impoverishment, due to ferrolysis, together with the element mobilisation produced by reducing conditions. If clay impoverishment is characteristic of eluvial horizons and bleached streaks of fragipan and glossic horizons, mobilisation of Fe, Zn and Pb is manifested in the reduced parts of almost all the horizons with bad drainage.

RIASSUNTO
L'importanza del suolo come 'filtro ambientale' è generalmente riconosciuta, sebbene non ancora pienamente compresa in tutti i processi che ne sono coinvolti. Nel monitoraggio di alcuni parametri ambientali indicativi la qualità del suolo, come ad esempio i metalli pesanti, si tende in genere a semplificare le cose, riferendosi solo ad una parte del suolo, quella più superficiale, o strato lavorato, mentre le caratteristiche degli orizzonti sottostanti ed i processi che avvengono nella parte profonda del profilo non sono considerati. D'altra parte molti suoli, in particolare i paleosuoli, piuttosto diffusi in Italia, sono caratterizzati da un profilo molto profondo e complesso, nel quale si può verificare un significativo incremento di elementi per cause naturali, legate a processi pedologici.
Scopo di questo lavoro è quello di studiare il ruolo svolto dai processi pedogenetici nell'indirizzare l'accumulo di elementi nei suoli della Montagnola Senese.
I risultati del lavoro evidenziano il verificarsi di un accumulo di elementi rispetto al materiale parentale; tuttavia questa tendenza non si è realizzata allo stesso modo per tutti i suoli. Ciò suggerisce che la ridistribuzione degli elementi negli orizzonti pedologici può essere messa in relazione con differenti processi pedogenetici. L'accumulo di alcuni elementi nei suoli è stato correlato al contenuto in sostanza organica, al pH e alla capacità di scambio cationico, soprattutto nei primi orizzonti, mentre un ruolo maggiore è svolto dall'argilla nel determinare il contenuto in elementi di tutti gli altri orizzonti. Coefficienti di correlazione altamente significativi sono stati riscontrati tra argilla e Ti, K e Cr ma anche con Fe, Zn e Pb. Tuttavia questa evidenza non si manifesta negli orizzonti caratterizzati da una ridistribuzione degli elementi provocata da processi di ossidoriduzione.
Molti elementi evidenziano un processo di accumulo dipendente dal tempo. Ti, K, Na e Mn mostrano di aumentare col tempo passando dall'Olocene al Pleistocene superiore e medio; Cr, Pb e Zn, analogamente al ferro, dall'Olocene fino al Pleistocene inferiore.
Il processo di accumulo procede di regola assieme alla neogenesi ed accumulo di argilla, ma può essere influenzato da altri due processi: l'impoverimento di argilla, attivo negli orizzonti eluviali, glossici e nei fragipan, e la mobilizzazione degli elementi, che avviene in tutti gli orizzonti che presentano condizioni riducenti.

Key words: trace and heavy metals, soil geochemistry, Paleosols, Siena, Italy
Parole chiave: metalli pesanti ed in traccia, geochimica dei suoli, paleosuoli, Siena, Italia.

1. INTRODUCTION

Knowledge of the concentration of trace elements in soil, especially heavy metals, is of utmost environmental relevance when the purpose is to determine the pollutant rate related to anthropogenic influences. In the last decade several western countries have carried out many research programs to establish valid background levels to be used as reference points to discriminate contamination. Unfortunately in our country a systematic and organic national program to assess trace element distribution and background values in soil is far from being completed. As a direct consequence we can witness the great difficulties encountered by national and regional legislation to establish valid and useful reference points to assess contamination. However, little is known about the thresholds which can cause damage to the soil-plant ecosystem and the limits can vary widely according to the different countries' approach to this problem (Adriano *et al.*, 1995; Tab. 1). Besides, recent studies have demonstrated the irreversible effects upon the soil microbial ecosystem of soil metal concentrations having values which are well below European and Italians limits (Brookes, 2001). Element content in soils may vary according to agricultural practices, but, to a great extent natural causes also play a role. The influence of parent material, for instance, is well-known (Fergusson, 1990; Angelone & Bini, 1992); nevertheless the contribution of long-lasting natural processes, like those occurring in paleosols, has not been well-established yet.

Moreover, legislation related to soil quality and pollution generally tends to simplify the issue, in particular it refers to only a part of the soil, that is the uppermost part, or the plow layer, while characteristics and processes of the lower parts of the profile are often neglected. This simplification does not take into account the possibility that the upper part of the soil can be thinned, or even removed by some agricultural practices or because of soil erosion. Another simplification concerns soil horizons often considered to be homogeneous, whereas element accumulation in soils, and particularly in paleosols, can occur only in parts of some horizons. This can be of great relevance in interpreting analytical results for practical purposes, not only those related to the environment, but also to the agricultural uses of soils (Costantini, 1999), and should steer the soil sampling.

In Mediterranean countries, and particularly in Italy, Paleosols are quite widespread and a significant elemental concentration can occur in some parts as a result of paleopedological processes. These processes are usually accompanied by a more or less pronounced soil reddening or the formation of nodules, but exceptions are frequent.

In this work, the elemental distribution in some soils of the Montagnola Senese territory has been studied and put in relation to main soil properties (pH, clay, OM, CEC), major elements (Fe, Al), estimated soil age, soil morphology (genetic horizons, redoximorphic features) with the aim of studying the role played by soil forming processes in addressing element behaviour.

2. MATERIALS AND METHODS

2.1 Soil analysis

The soils of the Montagnola Senese territory have been previously studied by Costantini et al. (1996) to explain the genesis of fragipan and other close-packed horizons. More than 50 profiles of the area have been described and analysed. A dozen of them, developed on acid metamorphic rocks and on mainly siliceous colluvial and alluvial deposits, were also studied for their element composition.

Soil description followed the Soil Survey Staff methodology (1993), routine analysis was in compliance with the Italian official methods (SISS, 1985). Plinthite nodules were submitted to the test of Wood and Perkins (1976), with immersion of samples for two hours in water, to check the persistence of aggregation. The counting of nodules and pseudomorphic nodules in the sands was made on 26 horizons pertaining to seven selected soils, utilising the optical microscope at different magnifications and considering 300 grains from each sand class; percentage values of nodules were then referred to percentage of fine earth, without taking into account possible differences in specific gravity.

Geochemical analysis was performed on 67 soil horizons belonging to 12 representative profiles. Soil samples were dried beforehand at 40°C, ground and sieved through a 2 mm Teflon coated sieve. Homogenised sub-samples were ground with an agate ball mill to obtain a fraction < 0.1 mm. Approximately 500 mg of homogenised sub-sample were weighed in a Teflon bomb. Metal extraction was carried out adding a mixture 5 ml of Aqua Regia (5 ml) and ultra pure HF (2 ml). Saturated H_3BO_3 was successively added to buffer the excess of HF. Major and trace element analysis was carried out by Perkin Elmer 5100 AAS at flame (K, Na, Mn); and with an AAS equipped with a Zeeman background corrector for Cd, Cu, Cr, Pb and Zn. ICP was used to analyse Ca, Al, Mg, Fe and Ti. All the analytical procedures were tested beforehand with a data quality control programme using international soils CRMs, samples duplicate and reagent blanks.

		Total soil metal concentration, mg kg^{-1} soil				
European Union	Year	**Cd**	**Cu**	**Cr**	**Pb**	**Zn**
Community	1986	1-3	50-140	100-150	50-300	150-300
France	1988	2	100	150	100	300
Germany	1992	1.5	60	100	100	200
United Kingdom	1989	3	135	400	300	300
Italy	1992	1.5	100	(a)	100	300

(a) = Bartlett test for soil oxidation capacity <1

Table1 - Maximum concentrations of metals allowed in agricultural soils treated with sewage sludge (after Adriano *et al.*, 1995).

Concentrazioni massime di metalli permesse nei suoli agricoli trattati con fanghi di depurazione (da Adriano et al., 1995).

3. RESULTS AND DISCUSSION

3.1. General outlines of the area

The study area is a small ridge located in Central Tuscany, covering just under 20 km^2. It is made up of several hills, with dominant heights ranging from 400 to 500 meters and a maximum of 671 meters a.s.l. The area underwent intense geomorphological evolution during the Pliocene and Quaternary, with alternating periods of erosion and stability. The rising of the ridge led to the erosion of the slopes, but several surfaces remained stable (e.g. karst depressions) or were stable over a long period (e.g. colluvial areas). Four main lithological units could be distinguished: i) acid metamorphic rocks, consisting of chloritic and sericitic fine-grained schist, jasper, quartzose micro and macro conglomerate and violet schist breccias (Mesozoic); ii) calcareous rocks, composed of flint limestone, marble, dolomite and cavernous limestone Mesozoic in age, but partially reworked by the Miocene sea; iii) mainly calcareous or iv) mainly siliceous colluvial and alluvial deposits, the mineralogy of which derives from the mixing of the above mentioned rocks. Climatic data for the area were obtained from Simignano (SI) and Siena. At Simignano (43°18' Lat. N; 419 m a.s.l., 8 km west of Siena) the average annual rainfall is 1019 mm, with maximum in October (119.8 mm) and minimum in July (36.4 mm). In Siena (43°19' Lat. N; 348 m a.s.l.) the average annual temperature is 13.2°C, the warmest month is July (22.1°), the coldest is January (5.8°). The soil moisture regime, evaluated by the Newhall Computation (Newhall, 1972) is "udic" with a water holding capacity of 200, 100 and 50 mm, whereas the soil temperature regime, according to Soil Taxonomy (Soil Survey Staff, 1999) is "mesic" (8<T<15° C). Land use of the area is mainly woodland, with dominance of chestnut trees (Castanea sativa) on acid metamorphic rocks and acid soils, and evergreen holm oak (Quercus ilex) on shallow soils on limestone. Agricultural lands are limited by the stoniness of the soils on limestone and the steepness of morphology; however, almost a third of the area is cultivated with small grain crops and maize, grasslands, vineyards, olive groves and orchards. Possible sources of soil contamination are limited to the few farms which practice spreading pig slurries on soils before cereal cultivation. These soils, however have not been included in this study.

3.2 Soil classification and estimated age

Regarding soil age, the only available dating is from the bottom of a studied profile, ascertained to be at least Cromerian (Lower Middle Pleistocene, Panizza, 1985) by means of paleonthological finds (Fondi, 1972). However, on the basis of a geomorphological reconstruction, the micromorphological evidence and chemical characteristics, it was possible to assess the approximate age of the selected soils as dating back to Holocene, Upper and Middle Pleistocene, and to Lower Pleistocene ages (Costantini *et al.*, 1996). Micromorphological results, in particular, concur with those found by Cremaschi & Sevink (1987) in soils belonging to the same Pleistocene ages in Italy.

According to the Soil Taxonomy (Soil Survey Staff, 1999) the soils were classified as Udorthents, Dystrudepts, Hapludalf, Fragiudalf, Fraglossudalf, Paleudalf and Plinthaqualf, or as Leptosols, Cambisols, Luvisols, Alisols and Plinthosols according to the World Reference Base for Soil Resources classification (FAO *et al*, 1998). Clay neo-genesis and accumulation within B horizon is a common feature of many of them, as well as iron release from parent material leading to soil reddening. Iron and manganese mobilisation and concentration, due to oxidation and reduction processes and expressed as bleached streaks, reddish and black mottles or as nodule elaboration, is another frequent process. Other processes, such as fragipan and glossic horizon formation, clay impoverishment inside bleached streaks (i.e. ferrolysis, Brinkman, 1970) and soil acidification, are connotative of specific environmental conditions (Costantini *et al.*, 1996).

3.3 Overall geochemical characteristics and trends

Descriptive statistics of major and trace element concentration are reported in Table 2, while the rock composition can be seen in Table 3.

On average, the heavy metal concentration of these soils is similar to or lower than those considered typical for Italian not-polluted soils (Angelone & Bini,1992). Amongst the studied elements, aluminium and iron are the most abundant, as expected considering the nature of the parent material (Duchaufour, 1977); however, maximum values of Cd, Cu, Cr, Pb and Zn are more interesting, being close to or higher than the regulation threshold (Tab.1). These limits can be exceeded in superficial horizons (Cu, Cr) as well as within the B horizons (Cd, Cu, Cr, Pb, Zn) and, only in the case of Cu and Cr, also in the deepest horizons. The recorded data do not allow us to assume soil pollution (Kabata-Pendias & Pendias, 1992); however they do emphasise the practical interest of knowing the possible causes of high element content of some of these soils.

Although we can observe a probable accumulation of many elements in soil, with respect to the parent material, this trend has not taken place in the same way for each element. This suggests that element re-distribution within the soil horizons can be related to different pedogenetic processes. Actually, some elements tend to slightly increase or remain constant with depth (Zn, Al, Mg, Cu, Na), some others localise within surface (Ca) and B horizons (Mn) or concentrate in B horizons (K, Cd, Ti, Cr, Pb and Fe).

A first step towards the understanding of the causes of accumulation was obtained by correlating the element concentration in soil horizons to clay and organic matter, pH and cation exchange capacity.

Organic matter was found significantly correlated ($P<0.01$) with Cd ($r=0.99$) and, considering only the superficial A and E horizons, with Ca ($r=0.52$); pH was found to be well correlated with Cd ($r=0.98$) and, only in the upper horizons, with Cu ($r=0.62$); CEC was correlated with Cd ($r=0.87$) and, also in this case only for the A and E horizons, with Al ($r=0.72$), Mg ($r=0.56$), K ($r=0.72$), Mn ($r=0.54$) and Zn ($r=0.85$). These results seem to indicate that, as already observed by others authors (Kabata-Pendias & Pendias,1992, McKeague & Wolynetz, 1980), standard chemical parameters, and in particular organic matter, can significantly influence the accumulation of some elements in soils, mainly in the upper horizons.

	Al	Ca	Mg	K	Na	Fe	Mn	Ti	Cd	Cu	Cr	Pb	Zn	O.M.	C.E.C.	Clay	pH
All soil horizons																	
Mean	20737	455	1954	13889	2807	29677	537	1526	0,13	50,3	79,1	26,4	64,0	0,63	10,2	27,6	6,2
Minimum	5000	20,0	22,0	4600	720	5600	34,0	178	0,01	13,0	19,0	1,00	12,0	0,01	5,0	5,0	4,2
Maximun	66800	2580	5020	42200	15600	93000	2630	3790	1,70	114	168	120	160	4,20	20,6	60,0	8,3
Standard errpr	12154	497	1011	5624	2425	17443	558	745	0,28	25,3	36,1	21,3	31,9	0,12	0,4	1,6	0,1
Number of data	67	67	66	67	67	67	67	67	53	67	67	67	66	53	55	67	66
Only A and E horizons																	
Mean	19247	872	1937	11184	2405	24243	605	1225	0,08	46,5	72,3	20,7	50,1	1,59	10,4	18,7	6,1
Minimum	5400	36,0	664	4600	1210	10200	163	293	0,03	13,0	26,0	1,00	12,0	0,70	5,0	5,0	4,5
Maximum	39700	2580	3460	16100	4600	43900	2050	2290	0,15	111	166	46,0	116	4,20	15,0	37,0	7,5
Standard error	10124	727	848	3740	823	10200	461	731	0,04	29,5	42,1	12,4	27,9	0,26	1,5	2,7	0,3
Number of data	15	15	15	15	15	15	15	15	12	15	15	15	15	15	6	15	14
Only B horizons																	
Mean	21045	337	1914	15004	2937	32809	536	1712	0,16	48,8	83,7	30,3	67,9	0,22	10,2	31,9	6,3
Minimum	5000	20,0	236	7100	870	8000	34,0	178	0,01	15,0	19,0	4,0	15,0	0,01	5,4	10,0	4,6
Maximum	66800	1390	4240	42200	15600	93000	2630	3790	1,70	113	168	120	160	0,80	20,6	60,0	8,3
Standard error	1886	80,4	140	859	387	2778	88	100	0,05	3,1	4,9	3,37	4,5	0,03	0,5	1,7	0,2
Number of data	47	47	47	47	47	47	47	47	38	47	47	47	47	36	46	47	47
Only C horizons																	
Mean	22320	314	2496	11524	2788	16530	346	686	0,04	75,4	55,8	6,40	70,3	0,80	10,5	14,0	4,9
Minimum	12200	220	22,0	6630	720	5600	55,0	330	0,02	28,0	33,0	1,00	16,0	0,10	5,7	10,0	4,2
Maximum	38700	446	5020	18700	9170	22450	847	1670	0,07	114	114	13	133	1,50	13,1	22,0	5,1
Standard error	5338	39,2	1022	2222	1605	2907	147	248	0,01	16,9	14,9	2,40	25,0	0,70	2,4	2,2	0,2
Number of data	5	5	4	5	5	5	5	5	3	5	5	5	4	2	3	5	5
Typical values for Italian not-polluted soils (afeter Angelone and Bini, 1992)						37000	900		0,53	51,0	100	21,0	89,0				

Table 2 - Descriptive statistics of major and trace element concentration (ppm) compared to main chemical values

Statistiche descrittive della concentrazione degli elementi maggiori e in tracce (ppm), confrontati con i principali caratteri chimici

On the other hand, the clay content seems to be more relevant. Correlation coefficients with a high level of significance have been found between clay of each horizon and Ti (r=0.65), K (r=0.58), and Cr (r=0.55), while the correlation was less evident with Zn (0.38), Fe (0.31; P<0.05) and Pb (0.29; P<0.05). On the other hand, Fe (r=0.91), Zn (r=0.58) and Pb (r=0.57) were found highly correlated with clay in all horizons, excluding those with plinthite and the reduced parts. Thus these last three elements show a concentration trend similar to the others, i.e. they follow the time and pedoclimate dependent clay increase, but it is also influenced by the oxidative-reductive processes.

Aluminium and iron are the dominant elements in the studied soils, so it could well be that other elements were associated with them. In actual fact, the former was found well correlated only with Mg (r=0.68), and the latter with Cr (r=0.58). If we do not take into account plinthite and reduced horizons, however, aluminium is fairly correlated with Mg (r=0.69) and Cd (0.57), as well as iron with Ti (r=0.47), K (r=0.42), Pb (r=0.59) and Zn (r=0.41). Even in these cases, the prominent role played by the element mobilisation, due to the change in their chemical state, is highlighted.

Finally, aluminium was found correlated with Ca (r=0.52), but only in the superficial horizons.

3.4 Element concentration and soil age

In a previous work, it was demonstrated that the ageing of the studied soils is characterised by a progressive increase in the clay content, a slight reduction of the CEC of clay and a marked increase in total and free iron content, which is particularly impressive in the oldest soils (Costantini *et al.*, 1996). In this work we have grouped the studied soils according to their estimated age – Holocene, Upper and Middle Pleistocene, Lower Pleistocene - and statistically tested them to underline possible significantly differing element concentrations. Although the relationships between element supplying and age have to be considered only as indicative, because of the several other factors affecting the element concentration - viz. lithological and chronological discontinuities between horizons of the same soil, or differences between parts of the same horizon - some possible indications about the elements which are more time dependent can be pointed out (Table 4). Among the studied soil components, Al, Cd, Cu and Mg do not show any significant trend related to soil age. On the other hand, Cr, Pb and Zn show an accumulation process similar to that of iron, i.e. a progressive increase with age, which is particularly evident for Cr (Fig. 1); Ti and K are significantly lower in Holocene soils, rather than in older soil horizons, whereas Na and Mn have higher mean values in soils and horizons attributed to

	Al	Ca	Mg	Fe	Ti	K	Na	Mn	Cd	Cu	Cr	Pb	Zn
Quartzose micro conglomerate	9000	176	320	6900	430	5830	1030	50	0,06	4	192	155	61
Sericitic fine-grained schist	61200	296	4300	39200	3540	24000	3815	2190	0,06	87	107	325	138
Violet schist	58000	320	600	26000	1980	28100	4190	51	0,05	12	136	210	73
Chloritic schist	3000	360	220	7000	180	4600	2250	6	0,21	8	6	32	24
Jasper	11700	140	1320	9400		5500	740	258	0,04	48	10		28
Mean	28580	258	1352	17700	1533	13606	2405	511	0,08	32	90	181	65

Table 3 - Element concentration in some samples of the main parent material lithotypes of the studied soils (ppm).

Concentrazione degli elementi in alcuni campioni dei litotipi principali del materiale parentale dei suoli studiati (ppm).

	Ca	Fe	Ti	K	Na	Mn	Cr	Pb	Zn	O.M.	C.E.C.	Clay	pH
						Holocene soil horizons							
Mean	745	18039	757	8886	1896	664	46.1	12.3	41.9	1.23	8.06	12.6	5.26
Number of data	18	18	18	18	18	18	18	18	17	16	11	18	17
						Upper and Middle Pleistocene soil horizons							
Mean	351	26402	1870	17115	4398	802	73.4	21.6	67.6	0.31	11.2	28.9	5.78
Number of data	20	20	20	20	20	20	20	20	20	11	18	20	20
						Lower Pleistocene soil horizons							
Mean	347	39159	1767	14771	2276	276	103	38.4	74.4	0.39	10.4	35.9	6.95
Number of data	29	29	29	29	29	29	29	29	29	26	26	29	29

Table 4 - Element concentration in soil horizons of different estimated age (ppm) compared to main chemical values; elements, pH and clay are significantly different for soil age with the Kruskal-Wallis test with p<0.001, C.E.C. and O.M. with p<0.05.

Concentrazione degli elementi negli orizzonti pedologici di differenti età stimate (ppm) confrontati con i principali caratteri chimici; gli elementi, il pH e l'argilla sono differenti significativamente per età del suolo con il test di Kruskal-Wallis con p<0.001, C.E.C. e O.M. con p<0.05.

the Upper and Middle Pleistocene.

Finally there is a clear decrease in Ca with soil ageing, possibly due to the leaching process and the scanty supply from the parent material.

3.5 Element accumulation pathways and soil morphology

Three profiles have been selected to exemplify how the accumulation process becomes evident in soils. They illustrate different profile morphology and element accumulation pathways, as a consequence of the pedogenetic processes which have occurred.

Profile 9 - Fragic Paleudalf (Soil Taxonomy 1999); Chromi-Profondic Luvisol (Bathifragic) (WRB 1998). Holocene in age in its upper part (A, E and Bt horizons), Pleistocene in age in the deepest horizons, it is characterised by evident weathering, leading to the release of elements, in particular iron, which gives the soil its reddish-brown colour, as well as clay neo-formation and illuviation into depth. Moreover, a close-packed horizon has been formed (fragipan) which limits water and root penetration and causes the formation of bleached tongues (Figures 2 and 3; A, E, Bt, 2Btx1, 4BC, R, etc.: designations for soil horizons[1]).

In this profile, iron distribution is similar to that of clay; inside the bleached streaks, where root penetration is active, ferrolysis determines clay and iron depletion, but does not affect Ti and K (photo 1).

Profile 47 - Aquic Fraglossudalf (Soil Taxonomy 1999); Glossalbi-Stagnic Luvisol (Profondic, Chromic, Fragic) (WRB 1998). Lower Pleistocene in age, it is older and redder than the previous soil; pedological processes are similar to those of profile 9, but more pronounced (photo 2). In particular, depletion in the reduced zones affected not only clay and iron, but also potassium and titanium (Figures 4 and 5).

In the same geomorphological unit, but in a lower position, soils like profile 48 - Plinthaquic Paleudalf (Soil Taxonomy 1999); Eutri-Endostagnic Plinthosol (WRB 1998) - are widespread (photo 3). They have neither fragipan nor clay impoverishment inside the bleached streaks. The groundwater has been fluctuating inside this iron-rich soil for so long that iron movement and aggregation in form of concretions and nodules of plinthite has been produced (photo 4). The presence of water has provoked iron reduction and removal from the streaks, but clay has not been removed, rather it tends to concentrate inside the bleached zones. As a result, the oxidised zones of the profile became coarser in particle size and a residual concentration of clay and titanium in the bleached mottles took place (Figures 6 and 7).

The process of iron concentration, from dispersed in the groundmass to aggregated in nodules, can be better appreciated by optical stereo-microscope. The

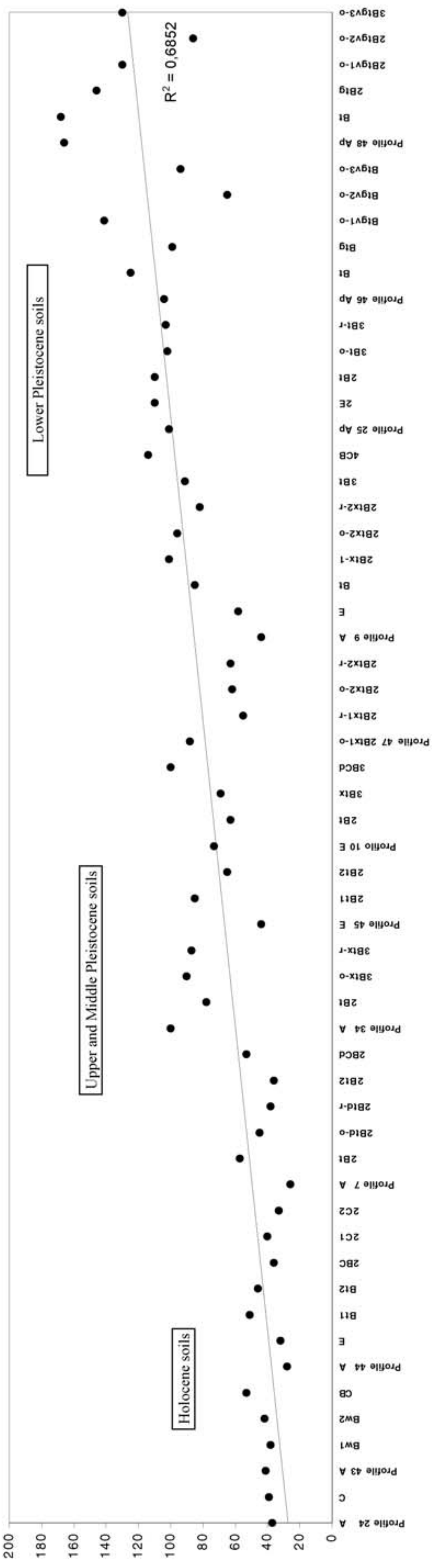

Fig. 1 - Cr content of studied profiles according to their estimated age (ppm)

Contenuto in Cr dei profili studiati in relazione alla loro età stimata (ppm)

[1] A = surface horizon with organic matter accumulation, Ap = ploughed horizon, E = eluvial horizon, Bt = horizon with clay accumulation, Btx = fragipan, Btg = bad drained horizon with clay accumulation, Btgv = as before with plinthite, BC = weathered and partially structured bedrock, R = hard bedrock. Number preceding letters indicates lithological and/or chronological discontinuity; those following letters indicate sub horizon; red or -o: reduced, bleached streaks or tongues; ox or -o: oxidized masses.

frequency of nodules and pseudomorphic nodules in four sand fractions of two horizons from seven of the examined soils are reported in Figure 8. Nodules in the sand fractions were present in all the studied profiles, but reached striking percentages in the profile 48 (up to more than 30% of the fine earth), especially in the finer sand fractions. In most cases, the colour of the nodules fell to Hue 2.5 YR (Munsell soil colour charts), but could reach 10 R in the most rubified soils (profiles 25 and 47) and 10 YR in the yellowish ones (profiles 46 and 48). As a general rule, the finer the sand fractions, the redder the nodules. This could be related to the presence of a

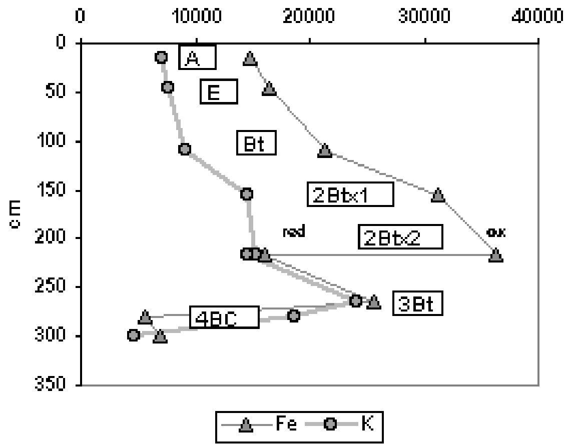

Fig. 2 - Fe and K distribution within profile 9

Distribuzione del Fe e del K all'interno del profilo 9

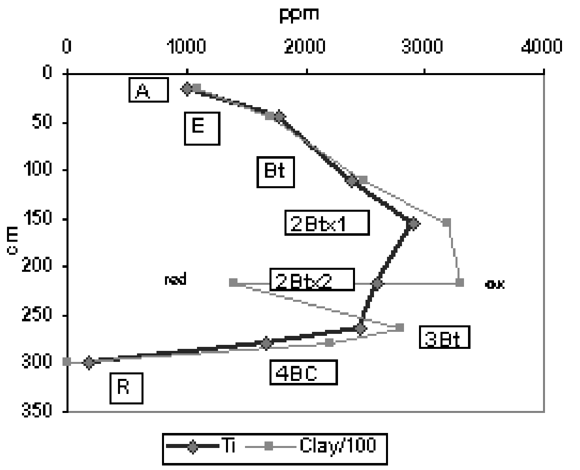

Fig. 3 - Ti and clay distribution within profile 9

Distribuzione del Ti e dell'argilla all'interno del profilo 9

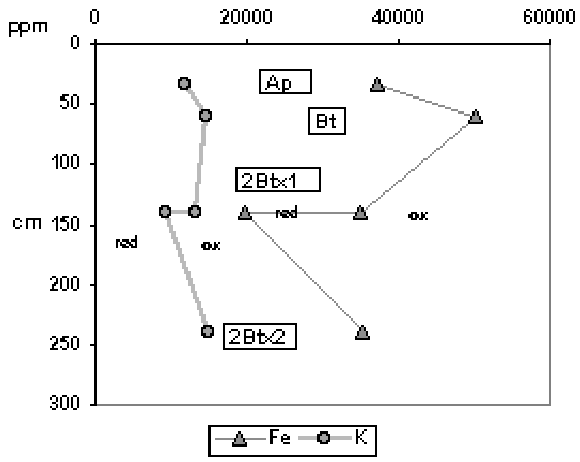

Fig. 4 - Fe and K distribution within profile 47

Distribuzione del Fe e del K all'interno del profilo 47

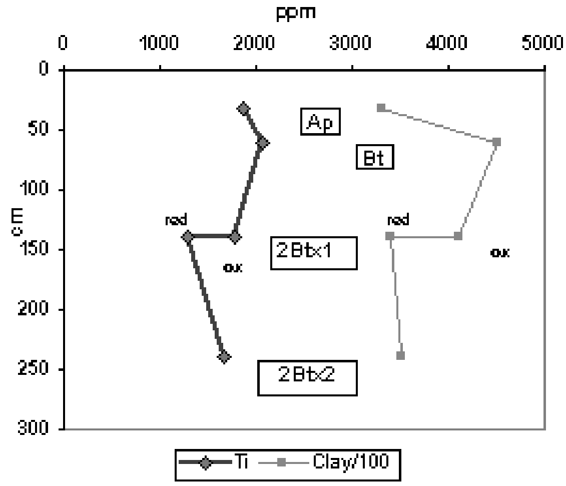

Fig. 5 - Ti and clay distribution within profile 47

Distribuzione del Ti e dell'argilla all'interno del profilo 47.

Photo 1 - Particular of the bleached streaks inside the fragipan of profile 9, where ferrolysis takes place.

Particolare delle striature biancastre all'interno del fragipan del profilo 9, dove vi è ferrolisi.

progressive long-lasting process, which induces transformation of iron from hematite into goethite, as already observed by other authors in some Oxisols of Central Brazil and in Laterite (Jeanroy *et al.*, 1991; Curi & Franzmeyer, 1984, 1987; Da Motta & Kämpf, 1992; Macedo & Bryant, 1987; Nahon, 1991).

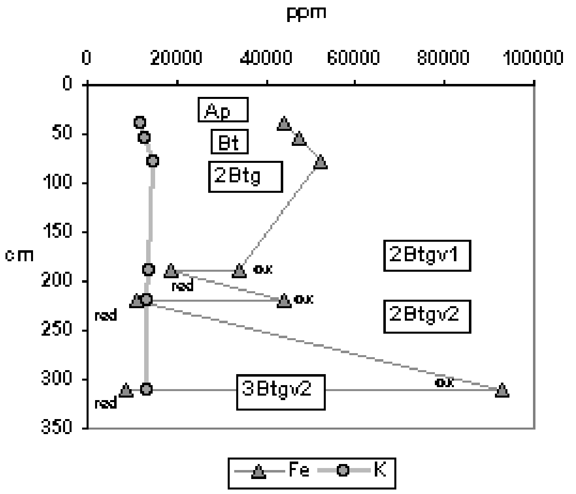

Fig. 6 - Fe and K distribution within profile 48

Distribuzione del Fe e del K all'interno del profilo 48

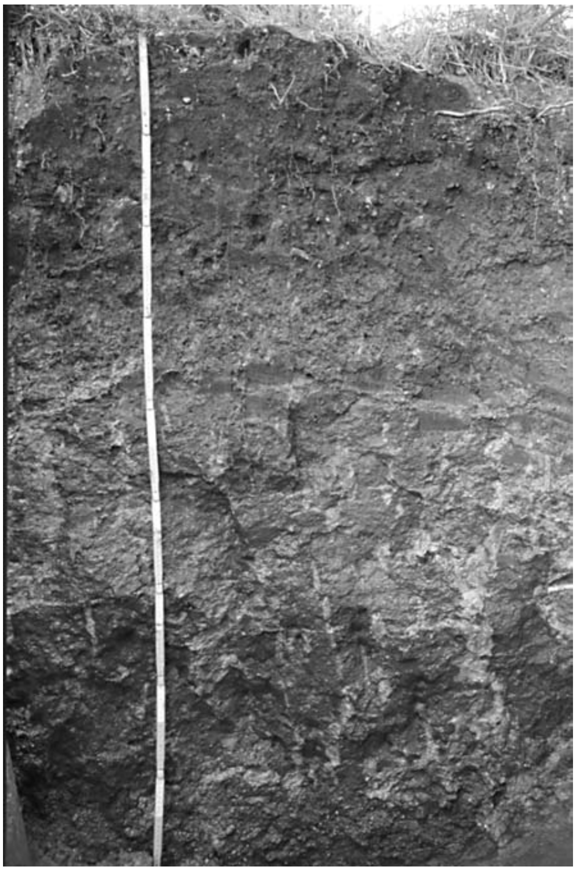

Photo 2 - The soil profile 47 is older and redder than the former profile 9; depletion in the reduced zones affected not only clay and iron, but also potassium and titanium.

Il suolo del profilo 47 è più antico e più rosso del precedente profilo 9, l'impoverimento nelle zone ridotte interessa non solamente l'argilla e il ferro, ma anche il potassio e il titanio.

4. CONCLUSIONS

Element distribution along soil profiles well reflects the long-lasting influence of weathering and of soil forming processes that have been operating on the area. The accumulation of some elements in soils can to a certain extent be put in relation to organic matter content, pH and cation exchange capacity, but mainly in the upper horizons. On the other hand, clay richness seems to play a more important role in determining the element

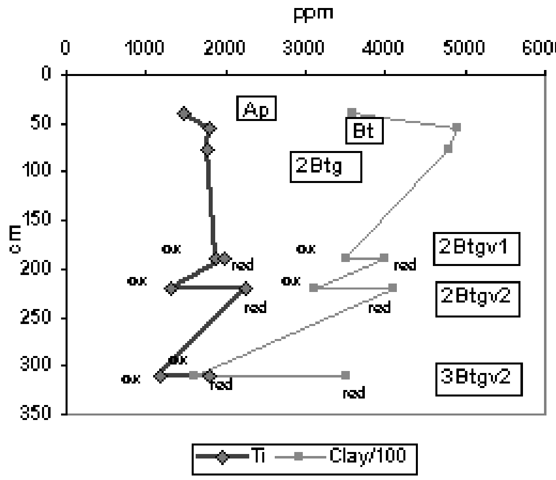

Fig. 7 - Ti and clay distribution within profile 48

Distribuzione del Ti e dell'argilla all'interno del profilo 48

Photo 3 - Profile 48. The groundwater has been fluctuating inside this iron-rich soil so long as to produce an huge iron aggregation in the form of concretions and nodules of plinthite.

Profilo 48. La falda freatica ha fluttuato così a lungo in questo suolo ricco di ferro da produrre un enorme accumulo di ferro sotto forma di concrezioni e noduli di plintite.

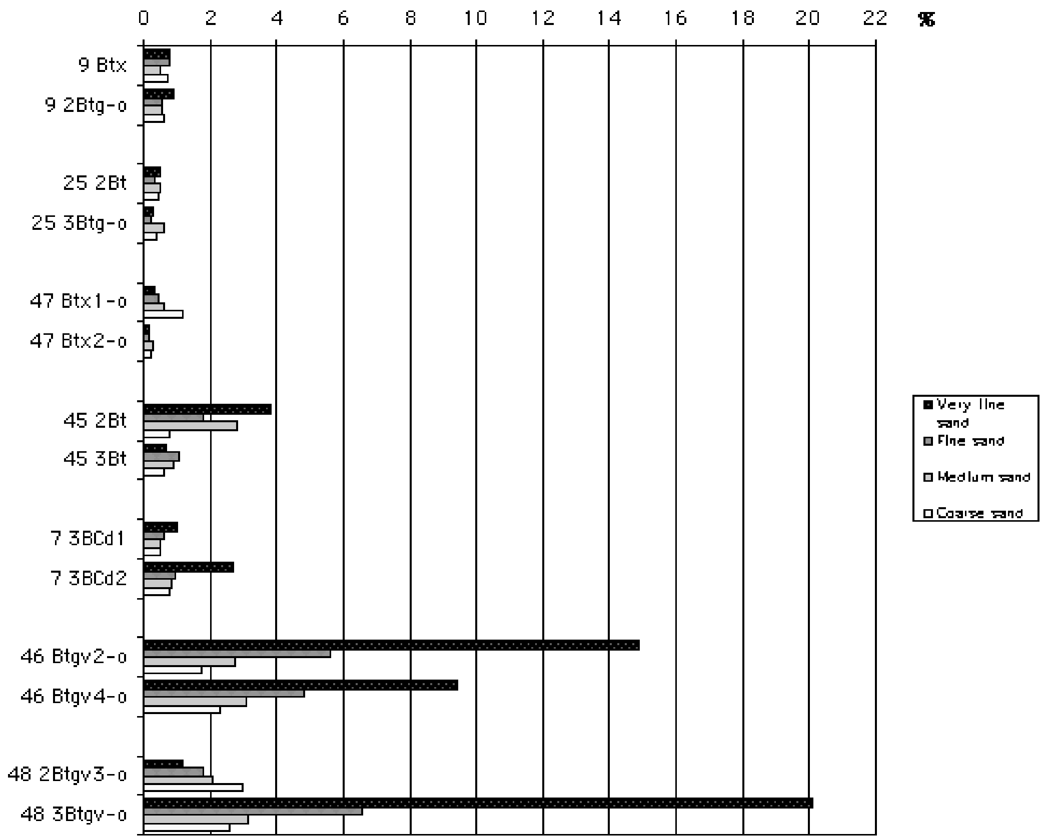

Fig. 8 - Nodules and pseudomorphic nodules in the sand fractions of selected soils (%)

Noduli e noduli pseudomorfi nelle frazioni sabbiose di suoli selezionati (%)

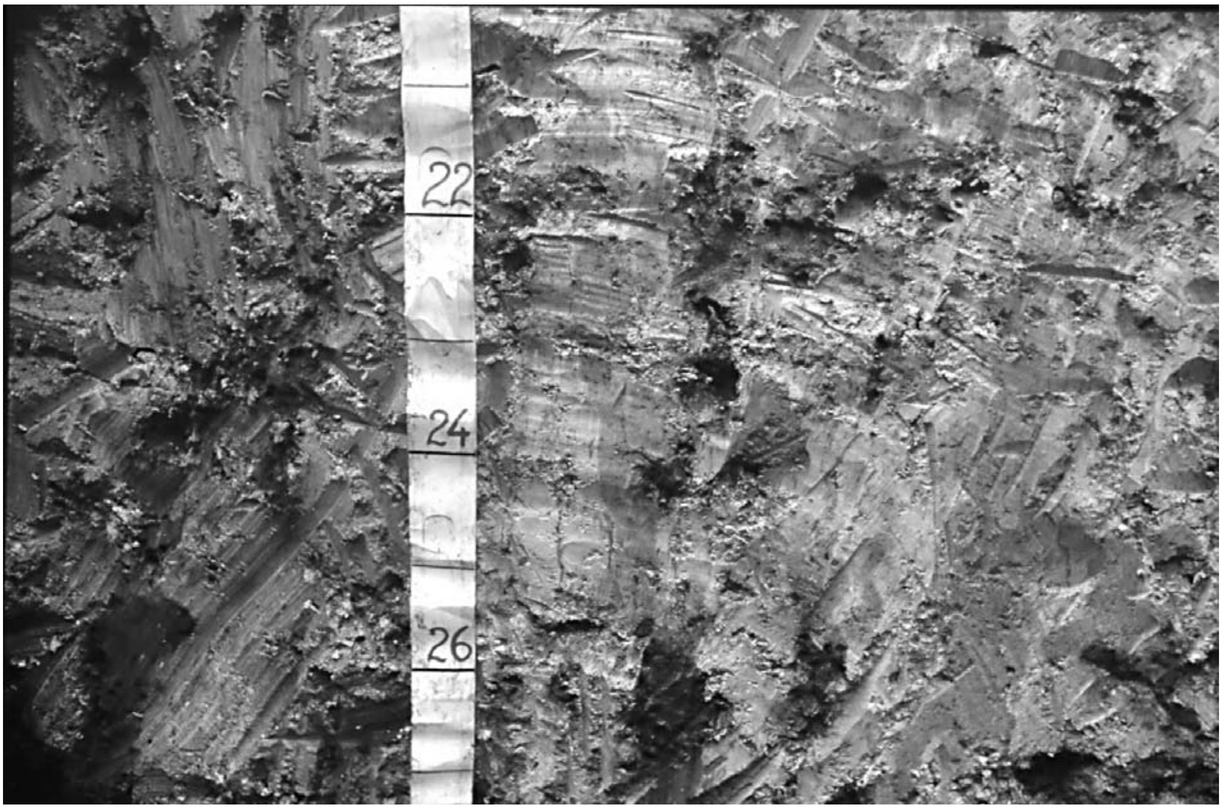

Photo 4 - Particular of the horizon with plinthite nodules. The anaerobic conditions have provoked iron reduction and removal from the streaks, but clay has not been removed, rather it tends to concentrate inside the bleached zones, and along with it titanium. The yellowish mass is very rich of nodules and concretions.

Particolare dell'orizzonte con noduli di plintite. Le condizioni anaerobiche hanno provocato la riduzione del ferro e la sua rimozione dalle striature, ma l'argilla non è stata rimossa, piuttosto tende a concentrarsi all'interno delle zone biancastre, e con lei il titanio. La massa giallastra è molto ricca di noduli e concrezioni e, al suo interno, gli ossidi di ferro sembrano essersi trasformati da ematite a goethite.

concentration in all soil horizons. Correlation coefficients with high level of significance have been found between clay and Ti, K and Cr. Also Fe, Zn and Pb are related to clay content, especially if the horizons which are affected by element redistribution caused by oxidative-reductive processes are excluded.

Several elements show a time dependent concentration process. Ti, K, Na and Mn seem to increase with time from the Holocene, to the Upper and Middle Pleistocene; Cr, Pb and Zn, similarly to Fe, from Holocene up to the Lower Pleistocene.

The accumulation process proceeds along with clay neo-genesis and illuviation, but it can be affected by clay impoverishment, due to ferrolysis, besides element mobilisation, produced by reducing conditions. If clay impoverishment is characteristic of eluvial horizons and bleached streaks of fragipan and glossic horizons, mobilisation of Fe, Zn and Pb is manifested in the reduced parts of almost all the horizons with bad drainage.

All in all, the soils of the Montagnola Senese highlight that in the study of soil geochemistry there is a need for careful investigation of what is often a complex reality. Soils, and particularly Paleosols, where a significant element accumulation can take place as a result of natural pedological processes, have to be considered not only in terms of their superficial aspects (the plow layer), but also in the characteristics of the entire profile. For this reason, a thorough soil field survey is essential in evaluating the capacity of the site to accept pollutants, in order to guarantee the maintenance of soil filter and sink capacity, and should be provided for by regulations.

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