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# Influence of Soil Organic Matter on Copper Extraction from Contaminated Soil

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*Column experiments of copper extraction from four contaminated soils characterized by a content of Soil Organic Matter (SOM) ranging from 1% to 25% are presented and discussed. The extraction was performed by flushing the soil with an aqueous solution of a sodium salt of ethylene diamminotetraacetic acid (EDTA). Preliminary tests were performed on a soil containing 25% of organic matter, to investigate the influence of pH, concentration and volumes of EDTA on its chelant action and on the dissolution of SOM. Having selected the optimal conditions for the extraction process, a further series of tests was conducted on the four soils to evaluate the influence of organic content on copper extraction yields. EDTA solutions at 0.01 M, 0.05 M, 0.1 and 0.2 M were injected at 0.33 ml/s; copper and organic matter extraction yield were determined. At a pH of 5, 15 pore volume (PV) of a solution containing 0.05M EDTA, extracted about 99% of copper contained by the soil with the higher organic matter content. Under the same conditions, and for soil with >6% SOM, extraction yields over 80% were achieved, while at lower organic content, copper extraction was dramatically reduced. This was attributed to the formation of highly stable copper-humate complexes and to their increasingly dissolution that occurred in the soils with higher organic matter level.*

*Experimental tests performed at different contamination levels (1200 mg/kg, 2400 mg/kg) showed that EDTA extraction effectiveness also depended upon initial soil Cu concentration.*

**Keywords** Soil flushing, copper extraction, EDTA, soil organic matter, copper-humate complexes

## 1. Introduction

Soils are porous natural bodies, composed of both organic and mineral matter, water and air; the proportions of these components may vary between horizons in a soil or between similar horizons in different soils (Manahan, 1994; Mulligan *et al.*, 2001).

The term Soil Organic Matter (SOM) is generally used to represent the organic constituents in the soil, including undecayed plant, animal tissues, their partial decomposition products and the soil biomass.

SOM consists of humic and nonhumic substances. Nonhumic substances are all those materials that can be placed in one of the categories of discrete compounds (sugars, amino acids, fats). Humic substances are all the other, unidentifiable components; they constitute

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70–80% w/w of the organic matter and have a strong ability to interact with metal ions, oxides, hydroxides, minerals and other organic substances to form water-stable associations (Schnitzer, 1989; Hayes and Swift, 1990; Weng *et al.*, 2001).

Soil may be contaminated by heavy metals due to the use of sludge or urban compost, mineral fertilizers, pesticides, and from emission by waste incinerators, car exhausts, residues from metalliferous mining, and the metal smelting industry. Sites located near high traffic roadways, such as urban locations and intersections of major highways, are numerous and exhibit high levels of trace metals in the upper soil horizon (Howard and Sova, 1993).

The fate and bio-availability of heavy metals in contaminated soil is largely controlled by sorption reactions to soil mineral surfaces and humic substances. Colloidal particles of soil organic matter, clay, silicates and metal hydroxides, which have a large surface area and are often electrically charged, are considered important adsorptive surfaces to bind heavy metals.

Copper contamination can originate from the use of fertilizers, building materials, rayon manufacture, pesticide sprays, agricultural and municipal wastes, and industrial emission (Cameron, 1992).

At low levels, copper has a toxic effect on the soil biochemical life and its low mobility promotes its permanence in the soil upper horizon, abounding in humus (Sequi, 1989). Hence, in addition to physical entrapment of metal hydroxide or carbonate solids, the soil can accommodate metals through more direct interaction, including surface complexation and surface precipitation mechanism (Peters, 1999; Martinez, 2000; Kedziorek and Bourg, 2000).

Heavy metals are highly persistent in soil, with residence times of thousands of years (McGrath and Cegarra, 1992), and the clean-up of soil contaminated with heavy metals is a difficult tasks for environmental engineering.

A number of techniques have been developed to remove heavy metals from contaminated soil. Soil washing and in situ soil flushing are techniques that transfer the contaminants to a liquid phase by desorption and solubilization. In situ flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process and allows soil to be treated without being excavated and transported, as required for the soil washing technique (Sims *et al.*, 1986).

The effectiveness of flushing is closely related to the ability of the extracting solution to dissolve the metal contaminants in soils, during the time of percolation of the solution.

Since a strong limitation in the application of soil extraction processes is the possibility to affect soil composition, only chemicals capable of dissolving large quantities of metals while preserving soil proprieties would be suitable for cleaning purposes (Reed *et al.*, 1996; Sun *et al.*, 2001). EDTA was chosen, because it forms a strong bond with copper as reflected by its high equilibrium formation constants (Bottari and Liberti, 1985; Tunay *et al.*, 1994; Di Palma *et al.*, 2003) and it is less destructive to soil proprieties compared to other acidic compounds (Yu and Klarup, 1994).

The main purpose of the present study was to investigate the extent and mechanism of soil organic matter extraction during the flushing treatment of a soil contaminated by copper, in the conditions that ensured the higher copper extraction. The study was performed by flushing EDTA solution on samples of soils characterized by different organic contents, in the range between 1% and 25%. To assess the extent of soil organic matter extracted during the flushing treatment, the organic content of the leachate recovered in the extraction process was determined.

While a wide variety of papers deal with the extraction of heavy metals from soils, few studies evaluate the influence of SOM, and the potential dissolution or change of soil matrix caused by the remediation processes, in particular washing process (Barona *et al.*, 2001; Fanguiero *et al.*, 2002; Shen, 1999).

Other studies have already assessed that extraction depends on many factors such as the availability of metals in soil, pH and soil matrix (Heil *et al.*, 1999; Papassiopi *et al.*, 1999, Kim *et al.*, 2003).

In this study, preliminary tests were performed to investigate the influence of pH, concentration and volumes of EDTA on its chelating action and on the dissolution of SOM. Having selected the optimal conditions for the extraction process, a further series of tests was conducted on the four soils to evaluate the influence of SOM on copper extraction yields.

Two different levels of contamination (1200 mg of Cu per kg of soil and 2400 mg of Cu per kg of soil) were tested; the objective of the tests was to achieve a residue Cu concentration in soil suitable for industrial or civil reuse, according to Italian Regulation (Italian Environmental Regulation, 1999b).

## 2. Materials and Methods

### 2.1. Soil Characterization and Contamination

The experimental tests were performed on four different soils named A, B, C and D. They were characterized by an SOM ranging between 1% (soil A) to 25% (soil D) as shown in Table 1.

To evaluate the ASTM soil size fraction classification, meshes of 10 (2mm), 40 (0.425 mm), 200 (0.075 mm) were used, respectively, for coarse, medium, fine sand, and total silt and clay. After an acid digestion performed according to EPA3050B method (USEPA, 1996), the total concentration of heavy metals in each soil was determined with a Philips PU9200 flame atomic adsorption spectrophotometer.

Soil pH and cation exchange capacity (CEC) were determined according to standard methods (Italian Environmental Regulation, 1999a). Total porosity was calculated according to Wasay *et al.* (2001). Hydraulic conductivity was determined according to Falling Head Method described by the ASTM standard test D 2434 (Liu and Evett, 2002). The test was

**Table 1**

Selected characteristics of the investigated soils

| Soil characteristics | Soil A | Soil B | Soil C | Soil D |
|---|---|---|---|---|
| Sand coarse (%) | 5.43 | 3.46 | 4.54 | 0 |
| Sand medium (%) | 92.87 | 82.17 | 66.61 | 42.4 |
| Sand fine (%) | 1.52 | 11.0 | 23.2 | 44.35 |
| Silt and clay (%) | 0.18 | 3.37 | 5.65 | 13.25 |
| Organic fraction (%) | 1 | 6 | 12.5 | 25 |
| pH | 8.68 | 8.10 | 7.93 | 7.58 |
| Pore volume (ml/100 g) | 40 | 65 | 110 | 160 |
| Porosity (%) | 41 | 51 | 62 | 68 |
| Hydraulic conductivity (cm/s) | $4.5 \cdot 10^{-1}$ | $1.1 \cdot 10^{-1}$ | $8.0 \cdot 10^{-2}$ | $6.2 \cdot 10^{-2}$ |
| Hydraulic conductivity (EDTA) (cm/s) | $6.1 \cdot 10^{-2}$ | $4.0 \cdot 10^{-2}$ | $2.9 \cdot 10^{-2}$ | $1.8 \cdot 10^{-2}$ |
| Cation exchange capacity (cmol/kg) | 11.28 | 15.81 | 21.70 | 33.04 |

performed using both tap water (total hardness 13,5°F) and a 0.05 M aqueous solution of EDTA.

The pore volume of the soil (PV) was calculated using:

$$\mathrm{PV} = \frac{\mathrm{f}}{100} \cdot \mathrm{V_c} \tag{1}$$

where $V_c$ was the column volume.

For all the four soils, the mineral composition determined by X-ray analysis using a Siemens type diffractometer showed a prevalent content of illite, quartz, calcite, and the presence of lower amounts of muscovite, kaolinite, dolomite and feldspars.

Contamination was carried out on two 1-kg samples of each soil. An aqueous solution of di-hydrated copper chloride ($CuCl_2$, Carlo Erba Reagents, Milano, Italy) was added to obtain a final soil copper concentration of two (in the samples named A1200, B1200, C1200, D1200, called 1200 series) or four times (in the samples named A2400, B2400, C2400, D2400, called 2400 series) the limits fixed by Italian Environmental Regulation (600 mg/kg for an industrial site, Italian Environmental Regulation, 1999b).

Subsequent to preliminary acid digestion, a Philips PU 9200 atomic absorption spectrophotometer was used to determine the metal content of six 1 g samples of each contaminated soil. The average Cu concentration for the 1200 series was 1272 mg Cu/kg with a standard deviation of ± 62 mg; the average Cu concentration for the 2400 series was 2480 mg/kg with a standard deviation of ±102 mg.

The contaminated soil samples were then dried at room temperature and stored in plastic containers for 90 days before extraction.

### 2.2. Experimental Apparatus and Materials

The experimental apparatus consisted of a series of Plexiglas columns with an internal diameter of 50 mm and a height of 100 mm. Samples (100 g) were prepared from the 1 kg contaminated soil samples, and then placed in the column above a layer of glass wool, so as to ensure uniform distribution of the liquid.

The flushing solution was introduced from the top of the column by means of a peristaltic pump at a flow rate of 0.33 ml/s. In each test, before percolating the extractant solution, the columns were flushed with a volume of water corresponding to the sample pores volume. All tests were performed in triplicate.

Four flushing solutions were prepared by dissolving $Na_2$-EDTA·$2H_2O$ (Carlo Erba Reagents, Milano, Italy) in tap water; EDTA concentrations were, respectively, 0.01 M, 0.05 M, 0.1 M and 0.2 M, to correspond to the typical range generally adopted for the extraction of metals from contaminated soils.

The flushing solutions were injected in a plateau mode (constant concentration in the feed solution) at a $\mathrm{pH} = 5$ (the proper pH of EDTA solutions) or $\mathrm{pH} = 8$. Alkaline conditions of the flushing solution were realized by addition of NaOH (Carlo Erba Reagents, Milano, Italy).

In all tests, leachate samples were filtered (Whatman 0.45 $\mu$m) before copper determination (by flame atomic absorption spectrophotometry). Total organic carbon (TOC) was determined using a Total Carbon Analyser (TOC 5000A, Shimadzu). pH was measured with a GLP22 pH meter (Crison).

### *2.3. Experimental Procedure*

A preliminary series of experiments was performed on sample D1200 (soil D with 1200 mg/kg of Cu) to find the optimal conditions for copper extraction. The influence of pH on the metal mobility was investigated by percolating 1 L of a 0.05 M EDTA solution at $pH = 5$ and $pH = 8$; copper extraction yield and DOM were then determined in the leachate samples.

To verify the extent of humic acid extraction in a wide pH range, a series of additional tests was also carried out on 10 g samples of soil D (1200 mg/kg), by washing for 24 hours at 175 rpm with aqueous solutions of $H_2SO_4$ or NaOH at a Liquid/Solid (L/S) ratio of 10.

In all the tests, the possibility of EDTA recovery after the treatment by percolating 1 L of pure water was then investigated.

A second series of tests was then performed on samples A1200, B1200 and C1200 by percolating the 0.05 M EDTA solution at $pH = 5$, to investigate the influence of the organic content of soil on copper extraction mechanism.

Finally, additional tests at the optimal conditions determined in the pilot studies were performed on the samples of the 2400 series, to evaluate the influence of the extent of contamination on copper extraction yield.

## 3. Results and Discussion

### *3.1. Parameters Affecting Copper Extraction*

Figure 1 shows the results of the flushing tests performed on soil D. The increase of EDTA concentration, from 0.01 M to 0.05 M, resulted in a strong increase in metal extraction yield (from about 53% to 83.6%), while in the tests performed at higher chelant concentration (0.1 and 0.2 M) only a slight further increase (of about 6%) was observed. The molar ratio [EDTA]/[Cu], using the 0.05 M EDTA solution was about 25, and this already represented a large excess in complexing agent. Furthermore, the use of higher chelant concentration

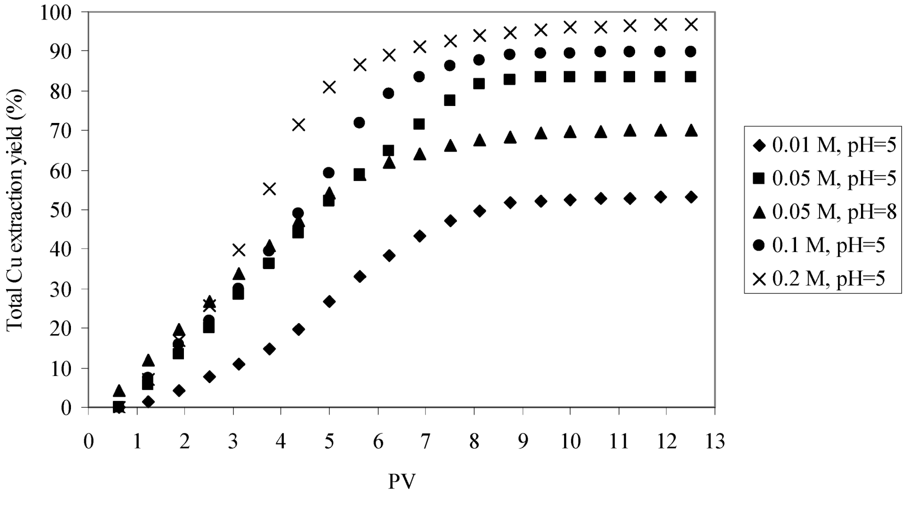


**Figure 1.** Influence of pH's flushing solution on soil D by use of EDTA 0.05 M on copper extraction yields.

generally resulted in a higher EDTA residue in the soil. For all these reasons, an EDTA concentration of 0.05 M was choosen for further investigation.

Figure 1 also shows the results obtained in the tests performed on soil D using the 0.05 M EDTA solution at pH 5 and 8. Extraction yields of 60.0% and 83.6% were achieved by percolation of EDTA (1000 ml) at pH 8 and 5, respectively.

The flushing tests performed at pH 5 resulted in a better heavy metal removal for any injected volume of flushing solution; nevertheless, a high extraction yield was also obtained at pH 8. This can be attributed to the buffer properties of the investigated soil; the pH measured in the extracted solutions recovered at the bottom of the columns were in fact 6.2 in the tests performed at pH = 5 and 7.2 in the tests performed at pH = 8. In addition, other studies have also indicated that the formation of metal-EDTA complexes was nearly pH-independent when a large EDTA:Cu ratio was used (Ghestem and Bermond, 1998; Barona *et al.*, 2001).

Acidity, in fact, is the main factor regulating mobility of heavy metals in soil (Howard and Sova, 1993). Alkaline conditions promote the precipitation of their hydroxides and carbonates onto soil mineral phase, while a decrease in pH will cause an increase in the mobility of metals due to their desorption from the soil surface ($M^{2+}_{soil}$) onto the aqueous phase ($M^{2+}$) according to the equilibrium (Alloway, 1990):

$$M^{2+}_{\text{soil}} + 2H^{+} \Leftrightarrow 2H^{+}_{\text{soil}} + M^{2+} \qquad (2)$$

At the same time, pH influences EDTA speciation and the corresponding constant values in the complexation reactions are higher in alkaline conditions (Sun *et al.*, 2001).

At pH 5, that is the pH of a solution of EDTA disodium salt in water, the EDTA predominant form is the $H_2EDTA^{2-}$. Assuming that chelant action could be described by the equilibrium reaction:

$$M^{2+}_{\text{soil}} + H_2EDTA^{2-} \Leftrightarrow 2H^{+}_{\text{soil}} + \text{M-EDTA}^{2-} \qquad (3)$$

The increase in $H^{+}$ content contributes to the displacement of equilibrium (equation 2) to the right and, as a consequence, the formation of metal-EDTA complex $\text{M-EDTA}^{2-}$. The soil buffer power has a greater influence on pH than the pH of the initial flushing solution.

### *3.2. Soil Organic Matter Dissolution*

Another aspect is the amount of SOM dissolved by water and EDTA. Figure 2 shows the results obtained in tests performed on soil D prior and after the contamination by percolating 0.05 M EDTA solution at pH = 5 or distilled water at the same pH value. The dissolved organic matter during the percolation treatment was estimated by measuring the TOC concentration in the extracted solution. Results show that a higher SOM dissolution was observed in the presence of EDTA from the contaminated samples.

Humus organic substances associate strongly with Cu in soil (Bolt and Van Riemsdijk, 1987), because they may form water insoluble metal complexes (Abumaizar and Khan, 1996). Most metal cation form “outer sphere” complexes with humus functional groups (amino, carboxyl and hydroxyl); then they remain fully hydrated and there is not a direct coordination with the ligand. Conversely, copper forms “inner sphere” complexes; functional groups on the humate replace some of the hydration water molecules and, as a result, these complexes are very stable (Wu *et al.*, 2001).

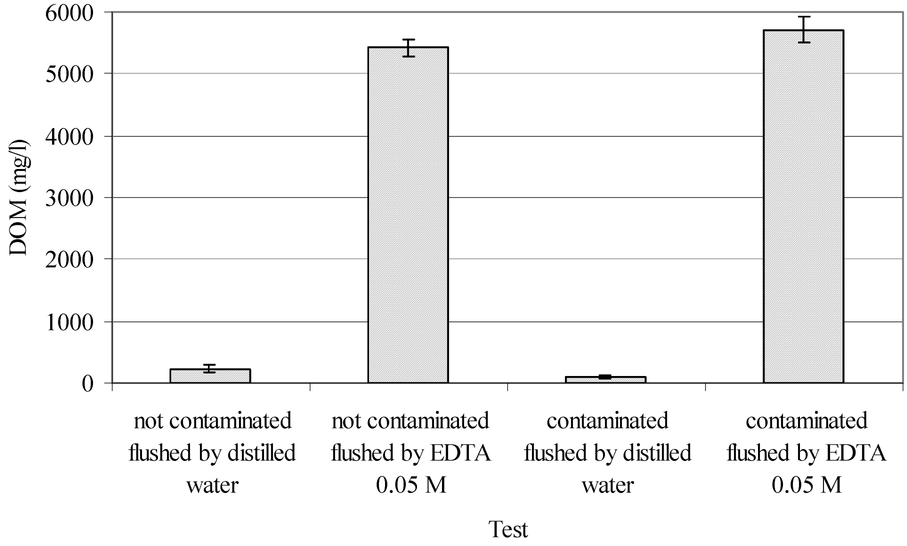


**Figure 2.** Organic matter dissolved (DOM) in the leachate after the percolation of distilled water or 0.05 M EDTA solution on samples of soil D prior and after contamination (pH = 5).

Figure 2 shows that in flushing tests performed on uncontaminated samples, flushing with the EDTA solution resulted in a TOC concentration of the extracted solution about 23 times greater with respect flushing with distilled water; this indicates that during flushing treatment a substantial dissolution of soil organic matter occurred. The increased dissolution in the presence of EDTA is due to its high affinity for organic substances.

Comparing the two tests performed with distilled water, the lower extraction of organic matter from the contaminated samples can be explained by the formation of low water solubility copper-humate complexes (Wu *et al.*, 2001).

In addition, a further increase of TOC in the leachate was observed when the soil sample subjected to the extraction tests was previously contaminated. This can be attributed to the enhanced dissolution of humate-copper complexes caused by EDTA (Wu *et al.*, 2001).

On the basis of such considerations and as a result of the trend shown in Figure 1, performing the extraction at pH = 5, using a 0.05 M EDTA solution, provided an optimal copper extraction but also resulted in a dramatic change in soil characteristics (considering the contribution of EDTA to the TOC, about 0.016 g of SOM per g of soil was dissolved).

The washing tests (Table 2) confirm that the dissolution of SOM was significantly affected by pH. Dissolution increased with pH, because higher negative charges on both

**Table 2**
Dissolution of soil organic matter in washing tests at L/S = 10 performed on soil D

| pH | DOM (mg/l) |
|---|---|
| 5.28 | 309.3 |
| 7.38 | 404.5 |
| 9.14 | 660 |

**Table 3**

Total organic carbon of the leachate collected after each subsequent water injection following the percolation of EDTA 0.05 M at pH = 5 (test 1) or $H_2O$ at pH = 5 (test 2) on soil D

| Water injected (PV) | TOC test 1 (mg) | TOC test 2 (mg) |
|---|---|---|
| 0.625 | 507.1 | 28.1 |
| 1.25 | 345.0 | 23.7 |
| 1.875 | 128.2 | 20.2 |
| 2.50 | 90.6 | 16.6 |
| 3.125 | 61.1 | 13.4 |
| 3.75 | 40.3 | 11.4 |
| 4.375 | 27.5 | 8.2 |
| 5.00 | 17.3 | 5.0 |
| 5.625 | 9.2 | 3.7 |
| 6.25 | 6.2 | 3.1 |

the organic matter and the soil inorganic solid surfaces result in repulsion effects causing desorption (You *et al*., 1999).

### *3.3. EDTA Recovery from Soil*

It is known that the low EDTA biodegradability in groundwater (Nowack, 1996) and soils (Wang and Banerji, 1997) requires its removal from treated systems. The presence of residue EDTA after the treatment may represent a limit in EDTA utilization as extracting agent.

Figure 1 also shows that the percolation of 6.25 PV (about 1 L) of tap water subsequent to the percolation of the EDTA solution was necessary to remove the residue copper-EDTA complexes entrapped in soil. The total organic carbon (TOC) content (due to both EDTA and dissolved SOM) of the leachate collected during the final percolation of pure water after the flushing treatment of soil D is reported in Table 3. The results reported in Table 3 show that about the 84.9% (as TOC) of the total amount of organics were washed out after the percolation of 2.5 PV of pure water (when a constant level in copper extraction was simultaneously obtained, as shown in Figure 1).

The results reported in Figure 1 and Table 3 show that the organics washed out during the percolation of the EDTA solution were mostly copper-EDTA compounds. When copper extraction ended, and this occurred after the percolation of about 2.5 PV of the final washing solution (tap water), the nature of organics leached changed; the contribution of SOM was not more negligible, and also free EDTA was eluted from soil pores.

### *3.4. Flushing Tests*

Having selected the optimal pH conditions for copper extraction, the influence of EDTA concentration on the extraction yield was investigated, to optimize the operative conditions for the extraction.

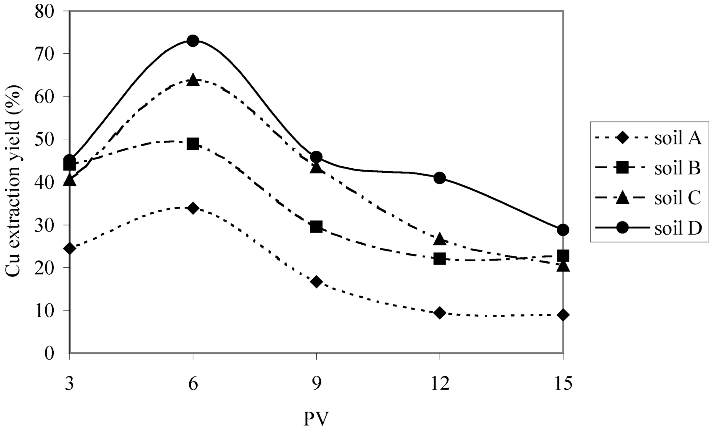


**Figure 3.** Copper extraction yield achieved after subsequent injection volumes of 3 PV of a 0.05 M EDTA solution on soil A, B, C and D (Cu = 1200 mg/kg; pH 5).

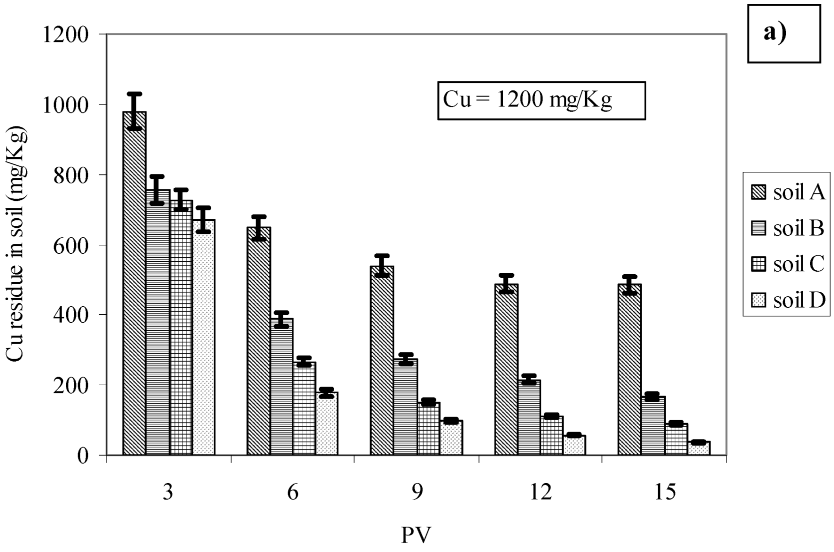
Metal's extraction yields calculated after each subsequent percolation of 3 PV of the 0.05 M EDTA solution are reported in Figure 3 for all soils at a contamination level of 1200 mg/kg. The extraction yields have been calculated with respect to the actual copper concentration in the soil at the beginning of each 3 PV percolation step.

Since porosity is quite different among the investigated soils, a comparison of results in flushing experiments can be made only when considering equal PV injections for the extraction treatment. The dilution effect, due to the water injected at first to saturate the soil pores and the time required for EDTA diffusion through the porous medium, led to an enhancement in metal extraction that reach a maximum at 6 PV for all soils. The subsequent decrease of metal available in soils led to a drop in extraction efficiency. EDTA rapidly exhausted the available copper and the prolonged percolation became useless. In order to increase extraction yields it was necessary to increase EDTA concentration.

Figure 4 shows that metal removal is related to both the porosity and the content of organic matter in soils. Metal extraction yield, at a fixed organic content, increased at increasing soil porosity. In addition, an increase in the soil organic matter level, leading to an increase in the dissolution of soluble organic carbon, increases the extraction of heavy metals (Project FAIR–CT 96-1983, 2001). This is less evident when considering the results obtained for soil B, C and D, where similar Cu extraction yield were calculated at different SOM content. In soils B, C and D, the content of organic matter did not play a crucial role in determining copper extraction. The higher CEC and clay contents in soil A, together with the very high SOM content, ensured copper mobilization.

Figure 4 shows that for each soil, a total solution volume of 9 PV resulted in a copper residual concentration suitable for an industrial reuse. In addition a residue concentration of then pollutant suitable for a civil reuse of soil C was obtained after injecting a volume at least equal to 12 PV. On the contrary, for soil A, even after the injection of a volume of 15 PV, the possibility of civil reuse was not achieved.

Further experiments were performed on the 2400 series to investigate the effectiveness of EDTA on the same soils at a higher level of Cu contamination. Soil samples were flushed with a total volume of 15 PV of extracting solution followed by the percolation of an equal



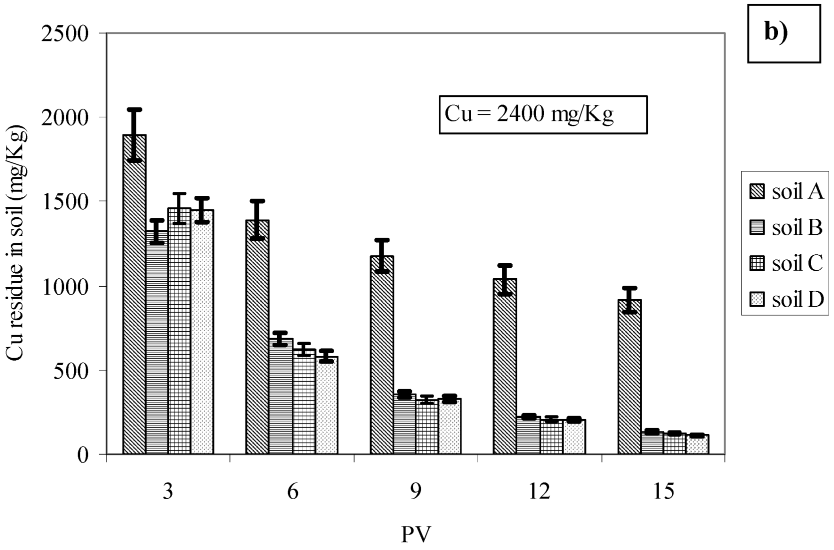


**Figure 4.** Copper residue in soils (dotted line defines copper maximum allowed concentration in soil for a civil use, the other line is the limit for an industrial use).

volume of water. Data reported in Figure 4b show that a civil reuse was possible only on soil D, which contained the highest amount of organic matter, using volumes of 15 PV.

Under the same operative conditions, values within the allowed limits (Italian Environmental Regulation, 1999b) were obtained for soil B and C, while no satisfactory results were achieved on soil A.

Final results, at the two investigated levels of metal contamination, are shown in Figure 5. Copper extraction yields were quite similar, showing that, at a given concentration, EDTA action (evaluated in terms of copper concentration in the eluate solution) was more effective at higher level of contamination.

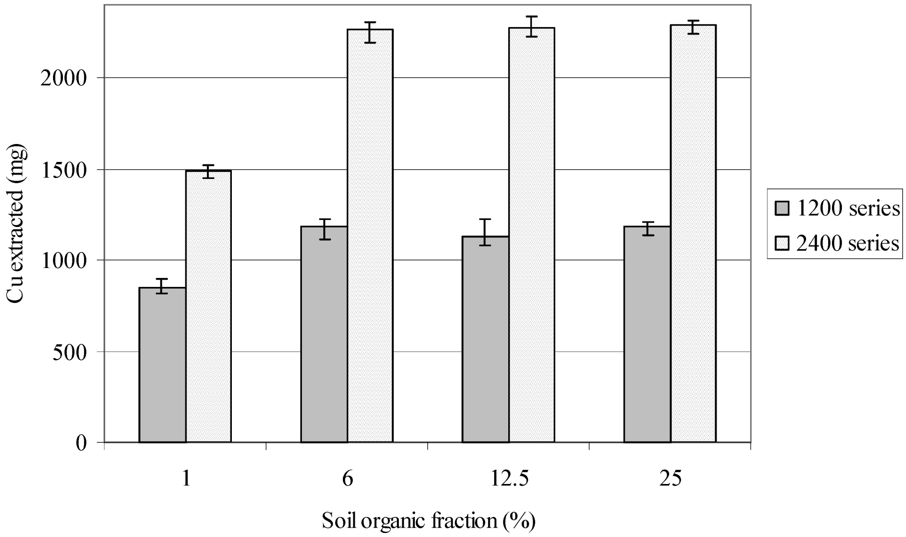


**Figure 5.** Total extraction yield (after the injection of 15 PV of a 0.05 M EDTA solution followed by 15 PV of $H_2O$) at two levels of contamination investigated.

## 4. Conclusions

Column experiments of copper extraction with EDTA from four contaminated soils characterized by a different organic content, in the range of 1%–25%, were performed. The Cu extraction yield and soil organic matter dissolution were determined.

A first series of tests performed on the soil characterized by the highest organic content (25%) showed that the dissolution of organic matter was significantly affected by pH, and increased greatly in alkaline condition. In addition, the use of an organic agent such as EDTA to extract copper from the soil may modify soil matrix, due to its natural affinity to SOM.

The optimal operating conditions for copper extraction were achieved by flushing a 0.05 M EDTA solution at $pH = 5$. In such conditions, after the percolation of 15 PVs of solution, more than 95% of Cu was extracted together with the dissolution of about 0.016 g of SOM per g of soil.

In addition, an almost total removal of residue EDTA entrapped into the soils was achieved by flushing with a volume of tap water equal to the total one used in flushing treatment.

The results of experiments performed on all the four soils show that soil organic matter enhanced Cu extraction, due to SOM solubilization, which improves the mobility of the metal. Conversely, this effect was negligible when SOM was higher than 6% and copper mobilization was ensured by soil structure itself (high clay content, high CEC, high SOM).

In addition, the results of tests performed at higher contamination levels show that, at a given concentration (0.05 M), EDTA action (evaluated in term of copper concentration in the eluate solution) was more effective at higher levels of contamination.

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