ANL/ES/CP-- 85526

A251

CONF-950646--25

Sequential Extraction Evaluation of Heavy-Metal-Contaminated Soil: How Clean is Clean?

RECEIVED
JUN 19 1995
OSTI

Wen Li
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Robert W. Peters, Michael D. Brewster, and Gregory A. Miller
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 35

MASTER

INTRODUCTION

As a result of industrial and military operations, large amounts of land have become contaminated with heavy metals. A growing public awareness of metal toxicity in soils and water has forced increased treatment and improved remediation techniques. To develop an adequate knowledge base to definitively judge the usefulness of the remediation technology requires some basic research in how the contaminants are bound in the soil.

Heavy metal contaminants may be distributed among many components of the soil and may be associated with them in different ways. The nature of this association has often been referred to as "speciation." It is the chemical species or form that determines the mobility and bioavailability of the soil metals to their surrounding environment. To determine the speciation of metals in soils may eventually provide a comprehensive technical basis to select remediation techniques for contaminated sites, such as soil washing or flushing, addition of chelating agents, or application of electrochemical techniques. In addition, it may be possible to predict heavy metal removal efficiencies and establish realistic, site-specific cleanup levels for the target heavy metals.

In this study, the classic five-step sequential extractions were performed on heavy-metal-contaminated soil from Aberdeen Proving Ground to determine the speciation of the metal forms. This technique speciates the heavy metal distribution into an easily extractable (exchangeable) form, carbonates, reducible oxides, organically-bound forms, and residual forms. In order to compare the results of these fractionations with the amount of heavy metals extracted by chelating agents, multi-stage extractions with EDTA were also performed. The results were used to determine the feasibility of using soil washing and soil flushing techniques for remediating the Aberdeen metals-contaminated soils.

EXPERIMENTAL APPROACH

Site Characteristics and Use

The subject site is J-Field, located in the Edgewood Area of Aberdeen Proving Ground in Harford County, Maryland. Soils were contaminated as a result of past disposal activities, which included the open burning and open detonation (OB/OD) of chemical agents and munitions. The Toxic Burning Pits (TBP) area at J-Field consists of five disposal pits used for OB/OD. Two of these pits, known as the primary burning pits, are the subject of a Focused Feasibility Study (FFS) being performed at Argonne National Laboratory (ANL). The purpose of the FFS is to develop and evaluate alternative remedial actions to address contamination in the TBP area. The soils in the primary burning pits are contaminated mainly with volatile organic compounds, including 1,2-dichloroethene (up to 8,400 mg/kg), trichloroethane (up to 21,000 mg/kg), 1,1,2-trichloroethane (up to 1,600 mg/kg), and 1,1,2,2-tetrachloroethane. To the east of these pits, where material was pushed out into the adjacent marsh, soils are predominantly contaminated with heavy metals, including arsenic (up to 41 mg/kg), copper (up to 4,320 mg/kg), lead (up to 94,200 mg/kg), antimony (up to 501 mg/kg), and zinc (up to 6,690 mg/kg). Soil samples (background, representative, and worst case) were collected over a depth interval of four feet and brought directly from the field pits in sealed plastic bottles in the cooler. Before being shipped to ANL, all samples were screened and found to be free of agent materials.

Sequential Extraction Procedures

The five-step sequential extractions were performed according to the procedure developed by Tessier et al.[1]. One gram of soil was used, and extractions were carried out directly in 50-mL Oak Ridge style FEP centrifuge tubes. The extracts were separated from the solids by centrifuging for 30 min at 4,000 rpm. The solid residues were rinsed once with 5 mL of deionized water. The rinsate is to be combined with the extractants. Metals contents of the five fractions and total extractable metal contents in the soil were determined by atomic absorption spectrometry. Standard solutions for the metals were prepared for each extraction step in a background solution of the extracting reagents. The extraction reagents and conditions used are listed in Table 1.

Multi-Stage Batch Extractions with EDTA

Nine-gram dry samples were extracted with 0.05M EDTA with the addition ratio of 9 mL EDTA per gram of dry sample. The samples' pH was adjusted to 4 for the first five runs and 9 for the last (6th) run by using either 1.0 M sodium hydroxide or 1N nitric acid. The plastic shaker containers containing the soil and extractant agents were shaken for 3 h and then filtered through a No. 42 Whatman filter. The solid residues were rinsed once with 100 mL of deionized water and dried for next-stage extraction. Samples of the filtrate from each run and its water washing were taken for analysis for Cu, Pb, and Zn. In addition, after the 5th and 6th runs, a sample of the soil was saved for sequential extractions. After the final run of each sample, the soil was saved for TCLP analysis.

RESULTS AND DISCUSSION

Soil Physical/Chemical Characterization

The TBP soils (worst case, representative, background) have the following characteristics: all are generally brownish in color, have a low cation exchange capacity (1.2 - 4.0 meq/100 g), are slightly alkaline (pH range of 7.5 to 8.4), have a moderate volatile solids content (2.5 - 8.8%), and are of a sandy loam texture. The particle size distribution determined from hydrometer tests indicated that the soil consisted of approximately 60% sand, 30% silt, and 10% clay. The results for the TCLP tests performed on the untreated soils are summarized in Table 2. Lead was the primary contaminant of concern because it was the only metal that leached appreciably from the representative and worst-case samples and caused the respective samples to fail the TCLP tests.

Sequential Extractions

Sequential extractions were performed on the untreated worst-case, representative, and background samples. The results obtained for metal partitioning and the sum of the metal extracted in the five fractions are given in Table 3; they are expressed as mg/kg of metal extracted in each step. Of all the contaminated heavy metals examined in the TBP soils, Pb was highest (85 - 25,600 mg/kg), followed by Zn (71 - 3,812 mg/kg) and Cu (83 - 1,420 mg/kg). The concentrations of Cr (41.22 - 183.55 mg/kg), Cd (undetected - 6.21 mg/kg), and As (undetected - 18.0 mg/kg) were much lower than those of Pb, Cu, and Zn. The soil matrix elements including Si, Al, Mn, Fe, and Ca were also analyzed. The representative and worst-case samples were very similar in heavy metal content.

The values obtained with the classical method used for the determination of total extractable metal have also been compared with the values corresponding to the sum of the five fractions. These results are also presented in Table 3. The two values' ratio generally ranged between 80 to 110% for almost 95% metals, which is within the analytical uncertainties.

Considering the worst-case soil, the amount of extracted trace metals in each fraction, as a percent of total metal content, was calculated and plotted (see Figure 1).

It can be seen from Figure 1 that the first important fraction for the metals Cu, Pb, and Zn is carbonates-bound. The amounts, determined as a sum of the exchangeable and carbonates fractions for metal, follow the order of Cd (67.1%)> Pb (57.8%)> Zn (54.9%) > Cu (44.9%). The first two fractions represent the bioavailabilities for the metal and are easily extracted by either using chelants or other heavy metal mobilization methods, such as electrokinetic treatment. The second important fraction for the metals is reducible oxides. Removal of metals present as reducible oxides depends greatly on the extracting agent used but is not efficient for the electrokinetic treatment technique. The first three fractions (i.e., exchangeable + carbonates + reducible oxides) are believed to be the species that are amenable to the soil washing technique. These fractions are also considered as the maximum extent of decontamination achievable by using the soil washing technique. The total amounts of metal in the first three fractions were in the order of Zn (89.2%) ≈ Cu (87.9%) > Pb (81.7%) ≈ Cd (79.2%). The last two fractions (organically-bound and residual) were believed to be difficult to extract by soil washing, soil flushing, or other soil remediation techniques. The amounts of metals associated with the last two fractions were Fe (57.7%) >> Pb (18.3%) > Cu (12.1%) ≈ Zn (10.1%). Therefore, in the case of the TBP soils, the metals Pb, Zn, Cu, and Cd have more than 80% of their distribution in forms that are amenable to soil washing techniques. However, iron is somewhat less responsive to soil washing by chelant extraction or other methods of heavy metal mobilization and removal.

Cadmium having the highest mobility in TBP soils agrees with the findings of Gibson et al.[2] and Ramos et al.[3] The results that Pb and Zn was mainly associated with carbonates and reducible oxides were reported by Kuo et al.[4] and Sheppard et al.[5]. The presence of heavy metals in the carbonate fraction may be caused by calcium carbonates, which act as a strong absorbent for heavy metals and could complex as double salts like $CaCO_3 \cdot ZnCO_3$ and $CaCO_3 \cdot PbCO_3$. Noll et al.[6] used scanning electron microscopy to confirm the presence of Pb as a carbonate fraction, being found as lead carbonate, lead sulfate, and various complex lead oxides.

Multi-Stage Batch Soil Extractions with EDTA

In order to compare the results of the metal speciations via sequential extractions, six-stage batch extractions with EDTA were carried out on the worst-case soil. In addition, TCLP (Toxicity Characteristic Leaching Procedure) tests were performed on the untreated soil and on the soils after 1st-, 3rd-, and 5th-stage extractions, respectively. The results, describing concentrations of heavy metals remaining in the soil, removal efficiency of heavy metals, and TCLP vs. number of stage extractions for Pb, Cu, and Zn, respectively, are presented in Table 4 and Figures 2 to 4.

The results show that the heavy metals, Cu and Zn, present as exchangeable and carbonates fractions were completely extracted in the first stage (Figures 3 and 4), whereas these fractions for Pb were not removed until after the second stage of extractions (Figure 2). Removal of Pb, Cu, and Zn present as exchangeable carbonates and reducible oxides species occurred between the fourth- and the fifth-stage extractions. Also between these two extractions stages, the TCLP Pb passed the EPA limit for lead of 5.0 mg/L (Figure 5). The corresponding Pb removal at this point was 86.1%, and the concentration of Pb remaining in the soil was about 5,000 mg/kg, well above the EPA Total Extractable Metal Limit for Pb of 500 mg/kg.

Metals distributions in the soils between untreated soil and soil after 5th-stage extractions by EDTA are compared in Figure 5. The results indicate that after five-stage extractions, most of the heavy metals (more than 80%) remain in the organic and residual forms, which were difficult to remove.

CONCLUSIONS

The results from metal speciation via sequential extractions and multi-stage batch extractions with EDTA have shown that the heavy metals present as organic and residual forms were very stable and not easily leached via TCLP; this strong retention of heavy metals in soils was considered an asset, because it served as a final barrier to contamination of groundwater. Therefore, removal of the contaminants held with organic and within the silica matrix is considered economically unnecessary. On the basis of this concept, a maximum removal efficiency was defined as the sum of exchangeable, carbonates, and reducible oxide forms, which were 87.9% for Cu, 81.7% for P, and 89.2% for Zn for TBP worst-case soil. Soil washing and soil flushing techniques have been proved to be a feasible method to achieve these maximum removal efficiencies; however, they required either a large amount of extractant or long extraction time. In an effort to enhance the effectiveness of soil washing and soil flushing by chelating agents, incorporating such pretreatment methods as REDOX manipulation and electrokinetic enhancement would be considered as practical strategies to remediate the TBP contaminated soils.

Combining REDOX manipulation, electrokinetics, and ultrasonic enhancement with chelating extractions to remove heavy metals in the soils has been investigated at ANL; the results will be reported in future publications.

Although sequential extraction procedures have provided useful information to the remediation technology field, further research and development work is still needed to standardize and validate sequential extractions methodologies.

ACKNOWLEDGMENTS

This work is funded by the U.S. Department of Defense, U.S. Army, Directorate of Safety, Health, and Environment, through the Environmental Assessment Division (EAD) at ANL. The authors wish to acknowledge the support provided by Ms. Terri L. Patton and Louis E. Martino of the EAD at ANL. In addition, the authors express their appreciation to John D. Taylor and Laura R. Skubal in the Energy Systems Division's Soils Lab at ANL for their contributions to the outstanding analytical support.

REFERENCES

1. A. Tessier, G.C. Campbell, and M. Bisson, "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals," *Analytical Chemistry* 51(7):844 (1979).

2. M.J. Gibson and J.G. Farmer, “Multi-Step Sequential Chemical Extraction of Heavy Metals from Urban Soils,” *Environ. Pollut. Ser. B* 11:117 (1986).

3. L. Ramos, L.M. Hernandez, and M.J. Gonzalez, "Sequential Fractionation of Copper, Lead, Cadmium and Zinc in Soils from or near Donana National Park," *J. Environ. Qual.* 23(1):50 (1994).

4. S. Kuo, P.E. Jeilman, and A.S. Baker, "Distribution and Forms of Copper, Zinc, Cadmium, Iron, and Manganese in Soils near a Copper Smelter," *Soil Sci.* 135(2):101 (1983).

5. M.I. Sheppard and D.H. Thibault, "Desorption and Extraction of Selected Heavy Metals from Soils," *Soil Sci. Soc. Am. J.* 56:415 (1992).

6. M.R. Noll, "Use of Sequential Selective Extraction Methods for Metals Speciation and Remediation Technology Evaluation," in *Proceedings of the 1994 Special Symposium, Industrial & Engineering Chemistry Division*, American Chemical Society, Atlanta, Ga., p. 1071 (1994).

Table 1. Sequential extraction reagents and conditions.

Species	Reagents and Conditions
Exchangeable	1M magnesium chloride for 60 min
Carbonate	1M acetate buffer (pH=5) for 5 h
Reducible oxides	0.04M hydroxylamine hydrochloride in 25% acetic acid @ 85°C for 6 h
Organic	30% hydrogen peroxide and 0.02M nitric acid @ 85°C for 2 h followed by extraction with 3.2M ammonium acetate in 20% nitric acid
Residual	Concentrated nitric acid @ 95°C for 8h

Table 2. TCLP results (mg/L).

Heavy Metal	Worst-Case Sample	Representative Sample	Background Sample	Regulatory Level
As	0.023	0.025	0.038	5.0
Cd	0.09	0.09	0.02	1.0
Cr	<0.01	<0.01	<0.01	5.0
Cu	5.71	6.86	0.22	--
Fe	0.01	0.18	0.13	--
Hg	NA	NA	NA	0.2
Mn	1.31	3.96	0.52	--
Ni	<0.1	<0.1	<0.1	--
Pb	340.91	113.23	0.48	5.0
Zn	56.07	46.18	0.31	--

Table 3. Sequential extractions results for untreated TBP soils (mg/kg).

Sample Code	Sequential Extraction Classification	Cu	Pb	Zn	Cd	Cr	As	Mn	Fe	Al
Worst Case	Exchangeable	5.20	1083.49	166.60	2.21	9.09	0.01	15.11	31.26	31.07
	Carbonate	167.70	11092.08	1906.23	1.95	22.08	0.07	47.02	195.91	550.42
	Reduc. Oxides	690.50	5048.56	1327.15	0.75	61.45	0.19	53.61	9443.14	1723.50
	Organic	114.80	2291.35	196.23	0.54	31.47	0.10	11.00	5233.35	560.88
	Residual	242.52	1562.00	215.93	0.75	59.45	0.40	58.62	7946.64	12203.75
	Total Fractions	1220.72	21077.48	3812.14	6.21	1.00	0.76	185.36	22850.30	15069.62
	Total Extractable Metal	1474.30	25968.40	3752.10	7.38	238.67	17.80	203.48	39858.00	None
Representative	Exchangeable	8.19	378.30	126.75	1.69	4.68	0.01	70.33	21.84	1.30
	Carbonate	468.91	8085.87	1275.04	1.17	14.30	0.05	40.95	335.53	266.37
	Reduc. Oxides	357.75	2158.25	758.75	0.75	34.50	0.08	27.25	2858.00	2858.00
	Organic	382.14	745.38	295.20	0.54	35.64	0.07	10.08	187.20	187.20
	Residual	339.16	6375.30	919.18	4.89	72.23	16.67	97.17	34653.52	4621.87
	Total Fractions	1556.15	17743.10	3374.92	9.04	161.35	16.87	245.78	38056.09	7934.74
	Total Extractable Metal	1533.20	15294.10	3677.00	6.60	311.73	21.83	286.32	48312.30	None
Background	Exchangeable	2.74	20.21	7.93	0.78	9.65	0.01	8.48	27.12	58.11
	Carbonate	21.38	22.17	5.85	0.39	7.95	0.01	9.26	24.90	51.74
	Reduc. Oxides	30.84	20.06	4.25	0.75	19.31	0.01	27.33	1113.34	405.00
	Organic	26.90	20.04	11.34	0.54	16.43	0.03	21.30	3716.27	1940.76
	Residual	0.75	2.51	41.24	0.75	22.82	7.42	50.15	3015.55	10958.50
	Total Fractions	82.62	84.98	70.61	3.22	76.16	7.48	116.52	7897.18	13414.11
	Total Extractable Metal	88.44	56.94	64.67	2.18	38.68	9.51	92.66	10913.30	None

Table 4 Multi-stage batch extrations with EDTA for Pb, Cu, and Zn on TBP worst-case soil

	Pb	Cu	Zn
Untreated Soil			
Total Extractable Metals (mg/kg)			
Exchangeable + Carbonates (%)	57.80	44.93	54.92
Exchangeable + Carbonates + Reduc. Oxides (%)	81.71	87.91	89.18
Organic + Residual (%)	18.28	12.09	10.82
TCLP (0) (mg/L)	340.91	5.71	56.07
After 1st Washing			
Metal Conc. Remaining in Soil (mg/kg)	13000.01	668.89	1365.15
Removal (%)	49.94	54.63	63.39
TCLP (1) (mg/L)	30.39	2.95	6.38
After 2nd Washing			
Metal Conc. Remaining in Soil (mg/kg)	10137.39	390.45	737.50
Removal (%)	60.96	73.52	79.33
TCLP (2) (mg/L)	NA	NA	NA
After 3rd Washing			
Metal Conc. Remaining in Soil (mg/kg)	8063.16	264.37	489.04
Removal (%)	68.95	82.07	86.46
TCLP (3) (mg/L)	29.31	0.32	1.31
After 4th Washing			
Metal Conc. Remaining in Soil (mg/kg)	7327.53	209.11	386.77
Removal (%)	71.78	85.82	89.41
TCLP (4) (mg/L)	NA	NA	NA
After 5th Washing			
Metal Conc. Remaining in Soil (mg/kg)	3383.45	112.68	208.36
Removal (%)	86.97	92.36	93.95
TCLP (5) (mg/L)	1.56	0.14	0.49

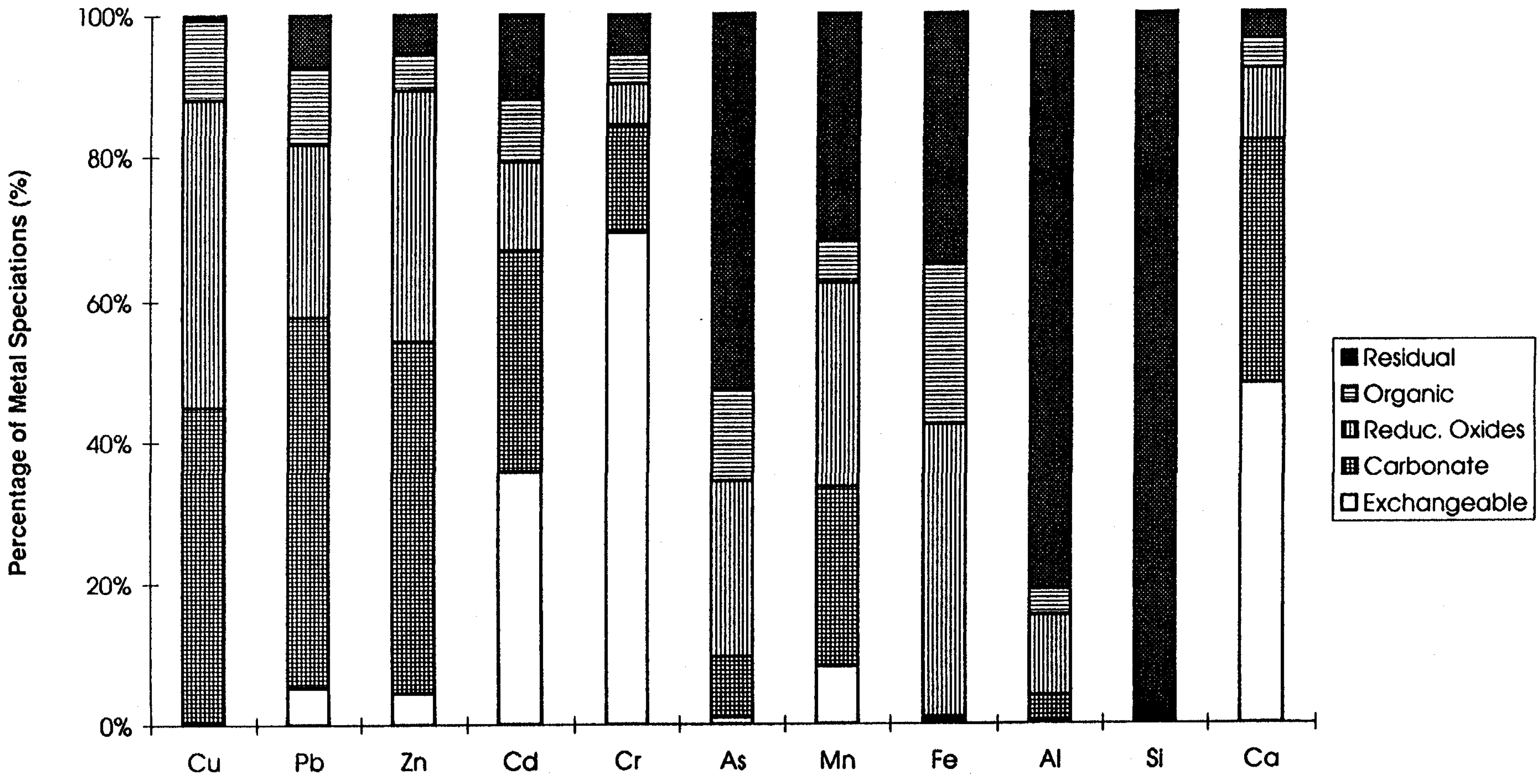

Figure 1. Distribution of metals as determined by sequential extraction for worst-case soil sample.

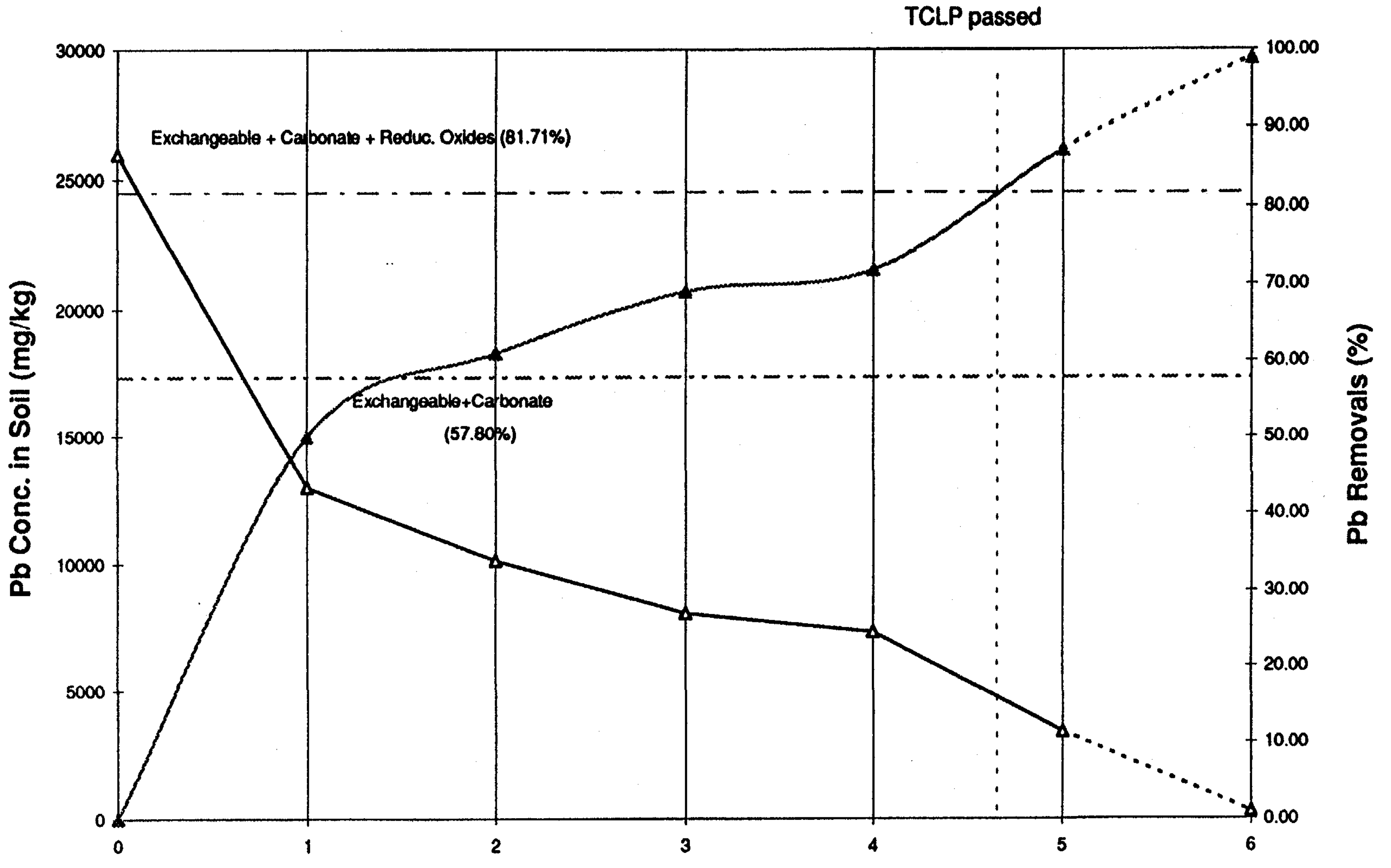

Figure 2. Sequential soil washing by EDTA extraction for Pb.

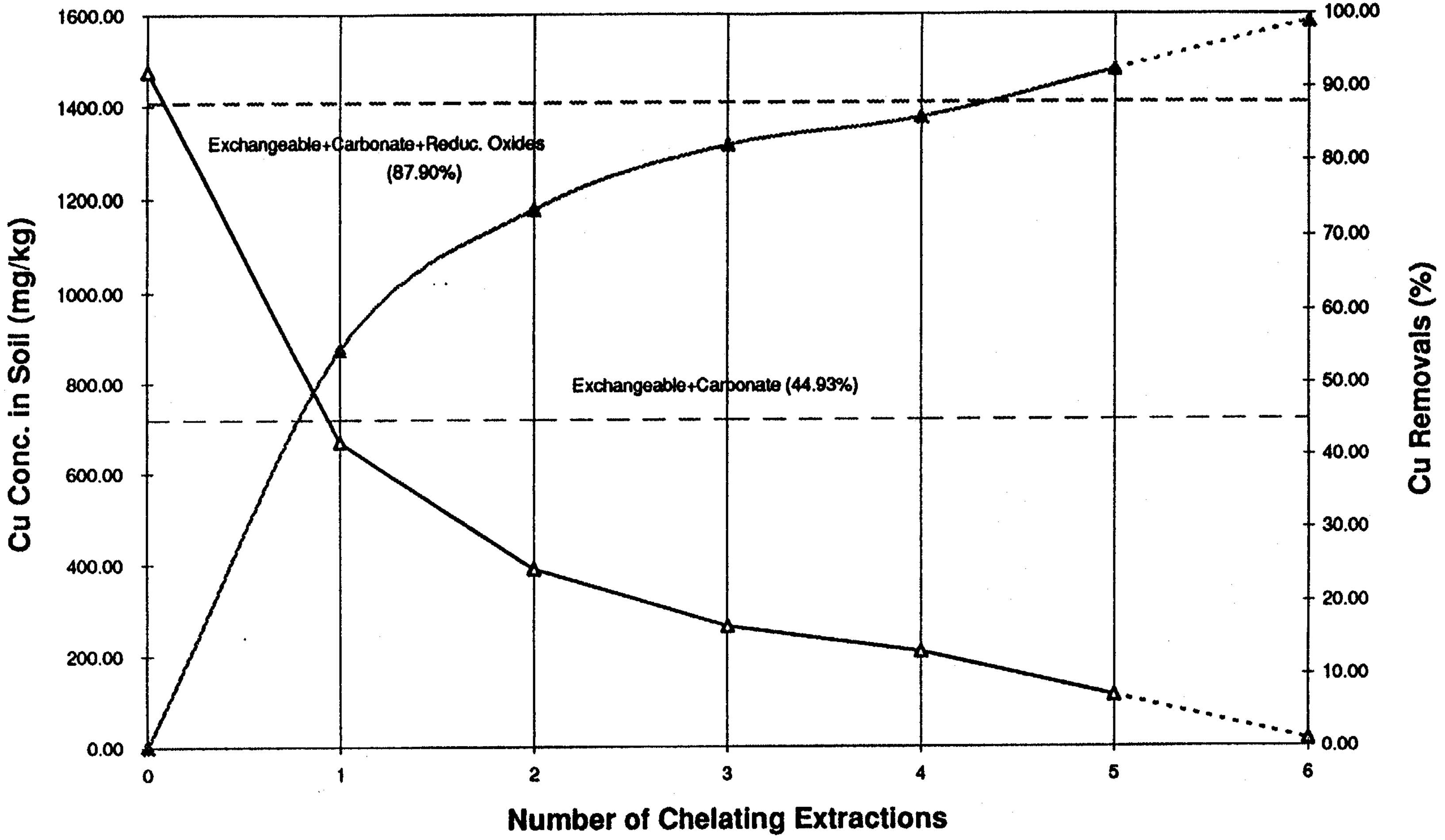

Figure 3. Sequential soil washing by EDTA extraction for Cu.

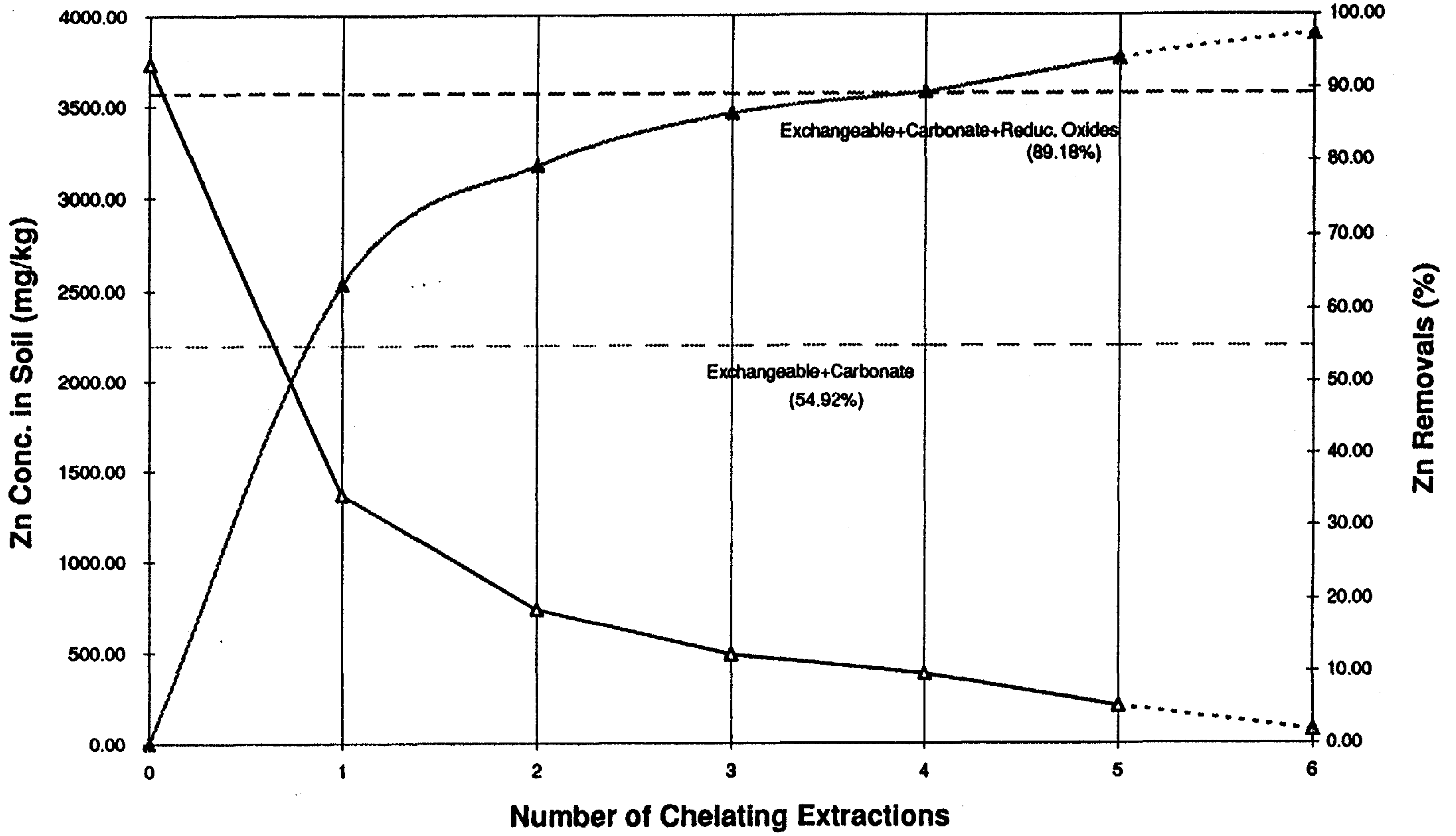

Figure 4. Sequential soil washing by EDTA extraction for Zn.

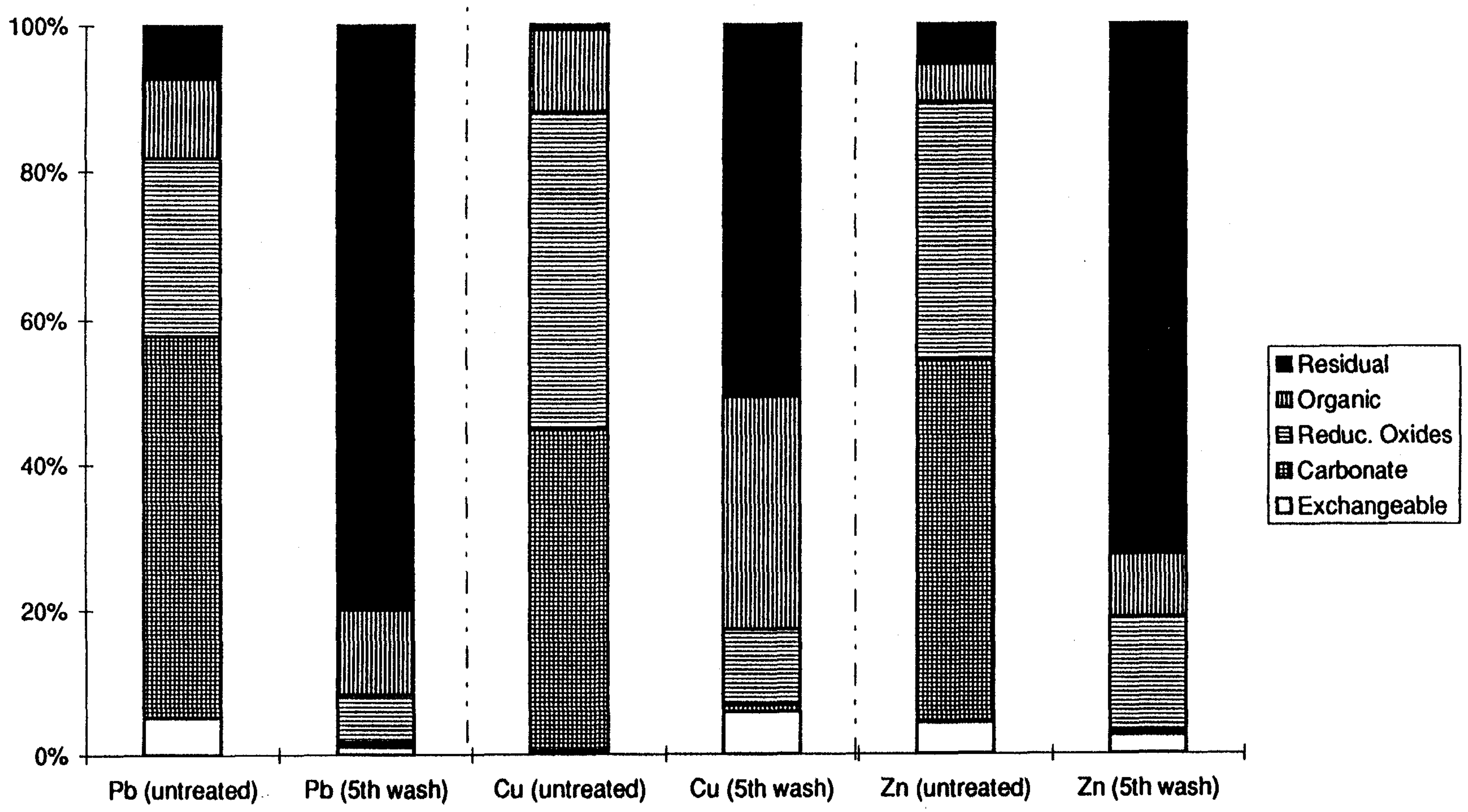

Figure 5. Comparison of metal speciations between untreated soil and soil after 5th extractions by EDTA.