

LEAD EXTRACTION FROM EXCAVATED SOIL

by

ROBERT A. EVANGELISTA  
Roy F. Weston, Inc.  
Response Engineering and Analytical Contract  
Edison, New Jersey 08837

and

ANDRE P. ZOWNIR  
Environmental Response Team  
U.S. Environmental Protection Agency  
Edison, New Jersey 08837

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Robert A. Evangelista  
Roy F. Weston, Inc.  
Response Engineering and Analytical Contract  
Edison, New Jersey 08837

Andre P. Zownir  
Environmental Response Team  
U.S. Environmental Protection Agency  
Edison, New Jersey 08837

### ABSTRACT

The Environmental Response Team (ERT) of the U.S. Environmental Protection Agency provides expertise and consulting in engineering studies, sampling and assessment, and alternative technologies. The ERT evaluated the specific methodologies being used for soil remediation at the Lee Farm site located in Woodville, WI. To achieve this goal, the ERT performed bench-scale engineering studies to determine the feasibility of soil washing with ethylenediaminetetraacetic acid (EDTA) to remove lead contamination resulting from a former battery reclamation operation.

Contaminated soil from the soil averaged 50,280 ug./g. total lead and 65 mg/l Extraction Procedure Toxicity (EP Tox) lead. To facilitate materials handling and soil/liquid separation, the soil was classified into three fractions prior to soil washing: oversized, coarse, and fine. These three fractions comprised approximately 25%, 50%, and 25% of the whole soil, respectively.

Soil washing of the coarse fraction with 20% (w/w) EDTA reduced lead 95-97% with a total lead concentration of 656-3411 ug./g. remaining in the treated soil. Soil loadings (the percentage of soil in the extraction mixture) of 25 and 45% were used and the increase did not significantly reduce extraction efficiency. The EDTA polish rinse, following the EDTA extraction step adversely affected treatment compared with a EDTA-free (water) rinse by increasing Extraction Procedure Toxicity (EP Tox) lead and not reducing total lead in the treated soil. The 45-minute extraction step was shortened to 15 minutes for subsequent experiments because the lead uptake by EDTA was occurring more rapidly than expected. Sequential extractions, where an extraction solution was repeatedly exposed to contaminated soil, were performed to replicate field conditions. These experiments found that the EDTA solution still reduced lead significantly after eleven sequential extractions.

In conclusion, this study found that EDTA is an effective extraction agent for lead contaminated soil to meet EP Tox criteria and soil washing is an emerging technology applicable to a wide range of contaminants in soil.

#### KEY-WORDS INDEX

Soil washing, chelation, lead extraction, EDTA, ethylenediaminetetraacetic acid.

#### INTRODUCTION

The Environmental Response Team (ERT) was established in 1978 by the U.S. Environmental Protection Agency (U.S. EPA) in accordance with its disaster and emergency responsibilities under the National Contingency Plan (NCP). The ERT provides expertise and consulting in treatability studies; sampling and assessment;

analytical methods; alternative technology, and personnel training for hazardous waste sites and materials situations. The Emergency Response Division, Office of Emergency and Remedial Response and U.S. EPA-Region V requested the ERT to provide support at the Lee Farm site in Woodville, WI, a former battery recycling site. The purpose was to evaluate the specific equipment and methodologies being used at the site to extract lead from soil.

The processing and disposal of spent lead storage battery cases at the rural site had contaminated the soil with lead and lead compounds. A preliminary excavation and a detailed site survey indicated the presence of approximately 15,000 cubic yards of contaminated material (mostly soil and broken battery casings). As an option to land disposal of this material, the method of choice was soil washing with a chelating agent to extract the lead contaminant.

Early heavy metal chelation efforts have focused on metal availability for plant uptake from soil and extracting metals from sewage sludge (1,2). Limited extraction of excavated soils has had encouraging results. Connick, et al. (3,4) preadsorbed metal salts onto soil contained in columns and rinsed the soil with 0.144 M ethylenediaminetetraacetic acid (EDTA) resulting in a 63, 93, 94, 100, and 86 percent removal of lead, zinc, nickel, cadmium, and copper, respectively. Farrah and Pickering (5) extracted preadsorbed clays to show the effectiveness of EDTA on the strong metal-binding clay fraction. Because metal-soil binding changes with time until an equilibrium is established, the preadsorbed soils used in the previous studies may not be representative of "aged" Superfund site soils (2,4).

For an in-situ extraction of soil at the Western Processing site, Ellis and Fogg (6) used EDTA sequential extraction to reduce lead, nickel, cadmium, copper and chromium by 96, 22, 100, 75, and 52 percent, respectively. The U.S. EPA Office of Research and Development, Releases Control Branch used EDTA in their pilot-scale Soil Washing System at Leeds, AL (7). Other chelating agents have been explored. During bench-scale experiments at Georgia Tech, ammonium pyrrolidinecarbodithioate (APOC), a chelating agent, extracted 95 percent of the lead from the soil (8) and nitrilotriacetic acid (NTA), a chelating agent, was not as effective as EDTA in removing lead (9).

The objective of this study was to explore the feasibility of soil washing with EDTA to remove lead contamination from contaminated soils at the Lee Farm site.

## METHODOLOGY

### Soil Characterization

Particle size distribution of the whole (unclassified) Lee Farm soil was determined by sequential screening. Sieve sizes from 0.25 in. (6.35 mm.) to #325 (0.044 mm.) were used (Figure 1). Whole soil was initially screened on a 0.25 in. mesh, then the minus 0.25 in. soil fraction was placed in a #4 stainless steel, 8-inch diameter Tyler sieve and gently washed with deionized (DI) water until water leaving the screen ran clear. For soil passing through the sieve, the process was subsequently repeated using the next smaller sieve. Soil remaining on the sieve was dried and weighed. After sequential screening, the minus #325 fraction was further characterized for particle size distribution in a coulter counter. All soil for this study was obtained from the Lee Farm site.

## Analysis

For metals analysis, each soil sample was placed in a Teflon-lined digestion bomb with concentrated nitric acid and heated for one hour at 60°C and 12 hours at 120°C in an oven. After cooling to room temperature, the sample extract solution was analyzed with a Spectra-Scan multi-channel DC Plasma Emission Spectrometer. Water samples were analyzed for metals "as is," i.e., pH levels for metals were not adjusted to pH <2. Nitric acid was not added to the sample since it would cause the EDTA to precipitate. Since there were percent levels of EDTA in the samples, co-precipitation of metal ions could result yielding erroneous results. For Extraction Procedure Toxicity (EP Tox) analysis, Method 1310 was used (10). For EDTA analysis of the extractant, the Oxalate Titration method was used (11).

## Soil Extraction

Whole soil was classified prior to EDTA-chelation experiments. Classification was performed by placing soil into a 5-gallon vessel containing a 0.25-in. mesh and sprayed (at approximately 1 gpm and 25 psi) with DI water. The minus 0.25-in. soil slurry was collected, gently hand-mixed for several minutes to suspend all solids, allowed to settle for 5 minutes, then decanted to remove the liquid fraction containing small, suspended soil particles. After decantation, the remaining, settled particles were resuspended with DI water, settled for 5 minutes, and the liquid decanted. The decanted liquids were combined and the fine particles allowed to settle for 24 hours. This classification technique was modified during the sequential chelation experiments. The modification included wet screening the minus 0.25-in. soil slurry on a #140 sieve until the water ran clear. Both techniques produced three soil fractions: oversized, coarse, and fine (Table 1). The choice of particle size range was based on the anticipated performance of off-the-shelf classification equipment.

Soil washing comprised a four-step process: chelation, a polish rinse, and two water rinses. For chelation, the extractant was a 20 percent (w/w) aqueous solution of Ciba-Geigy Sequestrene<sup>R</sup> 220 tetrasodium EDTA. The 20 percent EDTA concentration was chosen to replicate work previously performed at Lee Farm by PEI Associates from the U.S. EPA. The chelation solution was adjusted to pH 7.0 because the conditional stability constant of the EDTA-lead complex was favored over that of the EDTA-iron complex. The EDTA solution and coarse soil fraction sample was mixed 45 minutes at 100 rpm to suspend the particles. Soil loading (the percent [w/w] of soil in the chelation solution) was varied. After chelation, vacuum filtration in a Buchner funnel was used for soil liquid separation. Next, soil was exposed to three successive rinse steps: a 0, 2, or 5 percent EDTA polish rinse followed by two DI water rinses. Each rinse duration of 20 minutes was followed by solid liquid separation. All experiments were performed at room temperature and ambient pressure.

For the sequential chelations, the 20 percent EDTA chelation solution was repeatedly exposed to new batches of contaminated soil (25% loading). The coarse soil fraction was extracted with the chelation solution for 15 minutes followed by 5 minute 2 percent EDTA polish and two water rinses. Soil-liquid separation occurred between steps. After soil washing, the chelation solution was saved to extract the next sample of contaminated soils until the required number of sequential chelations were performed.

TABLE 1. CLASSIFIED SOIL COMPONENTS

Fraction Nomenclature	Particle Size Range		Mesh Size
	(mm.)	(in.)	
Oversized	6.35	0.25	0.25-in.
Coarse	0.105 - 6.35	0.004 - 0.25	#140 - 0.25-in.
Fine	<0.105	<0.004	<#140

The oversized (plus 0.25-in.) soil fraction was treated with an EDTA-free water wash rather than an EDTA extraction. The wash consisted of spraying the oversized particles with a designated amount of DI water based on a soil/water weight ratio. After spraying, the soil was air dried before EP Tox analysis.

## RESULTS

### Soil Characterization

Whole soil (lot 1) was characterized for metal content, EP Tox lead, and moisture. In addition to lead, other metals were analyzed to determine the presence of other compounds that could compete with lead during chelation. Table 2 lists these results.

Soil particle size distribution varied between two soil sample lots. Wet sieving of these samples (designated lots 1 and 2) produced large differences between lots in the amount of soil greater than #4 sieve (0.187 in./4.76 mm.), (Figure 1). This result shows the difficulty in obtaining homogeneous samples where a large rock or two can significantly affect the proportion of soil retained by the largest screen. These large soil particles (designated oversized) were of special

TABLE 2. WHOLE SOIL CHARACTERIZATION

Sample #	Total Metals (ug./g.)								EP Tox Pb (mg./l.)	Moisture (%)
	Pb	Fe	Ca	Mg	Ni	Zn	Cd	Cu		
1	48,800	25,100	8,960	3,710	19	141	8	102	63.5	12.5
1	45,100	22,700	8,270	3,490	20	108	7	61	68.7	--
2	30,200	13,500	5,410	5,410	26	98	3	54	65.5	12.1
2	89,700	12,500	5,520	3,450	23	120	3	65	--	--
3	46,750	34,020	10,690	5,370	18	83	2	43	43	12.0
4	41,100	30,600	10,600	2,650	--	--	-	--	--	10.4
Average	50,280	23,070	8,240	4,010	21	110	5	65	60.2	11.8



interest since this fraction would be processed in a non-chelation treatment scheme different from the remaining soil. Soil size cutoff between treatment schemes was 0.25 in. The amount of lot 1 soil retained by a 0.25-in. mesh after wet sieving ranged from 19.0 to 28.7 percent and averaged 24.8 percent. This fraction contained rocks, wood, and Bakelite and plastic battery casings.

Large differences between soil lots were found in the amount of the smallest particles. Wet sieving showed 25.5 percent of the soil was smaller than #140 (0.105 mm.), respectively, in lot 1, as opposed to 10.2 percent in lot 2. A coulter counter characterization of the minus 325 mesh fraction (predominantly silt and clay) from wet sieve analysis showed little particle size distribution difference between lots 1 and 2 (Figure 2). Hence, among the smallest particles there is little difference in particle size distribution between lots. However, the amount of the fine fraction soil varies greatly between soil lots. These are the types of non-homogeneity problems to be expected during field treatment.

The concentration of lead in the soil increased as the soil particle size decreased (Figure 3). This result verifies other studies which have been done and is not unexpected. The lead increase observed between the largest and smallest particles was greater than 2.5 orders of magnitude. This phenomenon is due to two major factors: 1) the surface area increases per unit soil weight as the particle size decreases giving lead a greater surface to adsorb; and, 2) the small, alumino-silicate clay particles have a high cation exchange capacity thereby increasing the electro-static attraction between the lead molecules and the soil particles.

## Chelation

Soil was classified prior to soil washing experiments. Two chelation tests with unclassified soil proved unsuccessful because the soil could not be effectively dewatered between the chelation and polish steps in the laboratory scale experiments. Historically, solid-liquid separation step in a soil washing process has been problematical as seen at the following sites: Lee Farm, Woodville, WI; Church of God, Leeds, AL; and Shaffer Equipment, Minden, WV. Therefore, to reduce or eliminate the solid-liquid separation problems associated with a matrix containing a wide distribution of particle sizes as soil, classification was a necessary initial step. Classification produces a soil matrix with a narrow particle size distribution range, therefore, soil-liquid separation can be tailored to the particular soil fraction. In this study the wet screen/settle/decant classification technique was modified to a sequential wet screen technique for the sequential chelation test. The latter technique produced a more uniform soil. Both techniques yielded three soil fractions: oversized, coarse, and fine comprising approximately 25, 50, and 25 percent of the soil, respectively.

Soil washing with EDTA was found to be an effective method of reducing lead contamination. Total lead reduction of 95 to 97 percent and residual concentrations as low as 696 ug./g. were observed after soil washing (Figure 4). The lead reduction was due to the chelating agent and not the aqueous solvent since the control experiment, with EDTA-free chelation and polish steps, did not remove any lead contamination. In addition, the high iron content of the soil was not mobilized by the chelation solution. While determining the effectiveness of chelation, several experimental parameters were explored that affect both residual total lead and EP Tox lead concentrations in the treated soil. These parameters were soil loading during chelation, EDTA concentration in the polish rinse, and reaction time of the soil to the chelation solution.

The increase in chelation soil loadings from 25 to 45 percent did not significantly change the percentage of lead removed from soil. In the 25 percent soil mixture, 97 percent of the lead was removed, while 95 to 97 percent of the lead was extracted from the 45 percent soil/chelant slurry (Figure 4). The chelating ability of fresh extractant did not diminish with greater amounts of contaminant loading.

The EDTA polish rinse was not only ineffective but also detrimental to soil washing. The objective of the EDTA polish rinse was to remove residual lead from the soil after chelation. However, exposing soil to an EDTA polish rinse after chelation did not significantly lower total lead in the treated soil; moreover, soil treated with the polish rinse had a high EP Tox lead content (Figure 5). The polish rinse caused more residual EDTA to remain in the washed soil even after the two subsequent water rinses. This residual EDTA contained chelated and, therefore, mobile lead which was easily extracted during the EP Tox analysis.

During 25 and 45 percent soil loading chelations, the extractant was sampled several times. Figures 6 and 7 show that the lead uptake of the EDTA solution was rapid in the early part of the 45-minute chelation. Consequently, the chelation time may be shortened with little or no adverse results to the treatment. A 15-minute chelation was used subsequent and proved successful.

The sequential chelations were performed to replicate a soil washing process where soil would be added to an extraction vessel in a batch-wise or continuous manner, replicating the field system at the Lee Farm site. This experiment was designed to explore the amount or rate of spent chelant removal from the extraction

vessel and its subsequent replacement with fresh stock. Figures 8 and 9 show that as the chelation number increased, the lead concentration in the extractant increased and the free EDTA concentration decreased. Even at low free-EDTA concentrations, chelation of lead was still occurring. Similarly, after 11 chelations with the same EDTA solution, lead contamination was still being removed from the soil (Figure 10) and the average EP Tox lead concentration in treated soil remained under the 5 ppm legal criteria (Figure 11).

The non-chelation, water-spray technique, used to decontaminate the oversized soil, reduced EP Tox lead concentrations. Since most of the lead contamination was in the small soil particles, the objective of this technique was to remove lead contaminated soil attached to the oversized fraction. To achieve the objective of physically removing the attached soil from the oversized fraction, the use of EDTA was unnecessary and would require additional rinse steps. As the volume of water used to spray increased, the EP Tox lead concentration decreased (Figure 12). After washing, however, the irregular surface of the rocks and battery casings still retained enough contaminated soil to yield excessive levels of EP Tox lead. The EP Tox values were the criteria of cleanliness. To achieve EP Tox levels below the 5 ppm limit, the rocks and casings must be sufficiently washed to remove all adhering soil.

## DISCUSSION

Lead removal from this contaminated soil was successfully accomplished in this study. Following soil washing, the treated soil showed a 95 to 97 percent lead reduction and met the EP Tox criteria of 5-ppm lead. However, residual total lead in the treated soil range from 656 to 3411 ug./g. These values may be too high for soil lying above an aquifer because of potential pollution liability. In addition,

the fine fraction of soil was not treated in this study because of the difficulty with soil/liquid separation (dewatering). This fraction comprised approximately 25 percent of the total soil. Several experimental parameters (soil loading, polish rinse EDTA concentration and chelation duration) were investigated. These have a direct impact on the effectiveness and efficiency of soil washing.

There was no loss in treatment effectiveness when soil loading was increased from 25 to 45 percent. As the soil loading in a system increases, so does the system capacity. Consequently, the higher soil loading explored could nearly double a system's throughput compared to the lower loading.

Decrease in chelation reaction time can increase the soil throughput. The results of lead uptake by the chelant shows the 45-minute reaction time as excessive, hence the sequential chelations had a 15-minute reaction time.

The incorporation of a low (extractant) strength polish rinse following the extraction step into a soil washing scheme reduces the acceptability of the treated soil. After treatment including polish rinse, soil showed no beneficial reduction of residual total lead and exhibited increasing EP Tox lead values with increasing polish EDTA concentrations. The EP Tox procedure is sensitive to the amount of mobile lead with respect to contaminant mobility. During the extraction steps all efforts are focused on mobilizing the lead contaminant with, in this case, a chelation solution. After extraction, the removal of the mobile contaminant (Pb-EDTA complex) through sequential soil-liquid separation and rinsing is of primary concern. The introduction of a polish rinse leaves residual EDTA lead complex in the soil. This highly mobile species is readily picked up in the EP Tox analysis and is a cause of treated soil exceeding the EP Tox limitation.

For the batch or continuous operation of a soil washing process it is necessary to know when or at what rate to add fresh extractant. The addition of fresh chelant is determined by the acceptability of the final product - clean soil. Through pilot or full-scale treatment, it may be possible to predict treated soil quality by measuring the chelant's lead content or the percent of uncomplexed EDTA.

## CONCLUSION

In conclusion, this study showed:

- o EDTA is an effective extraction agent for lead contaminated soil, however, the effectiveness is dependent on allowable lead residuals in soil;
- o High soil loading during chelation does not affect lead extraction effectiveness and will improve process efficiency;
- o The EDTA polish rinse is detrimental to soil washing and should be eliminated or substituted with an additional water rinse;
- o Soil classification, prior to chelation, improved soil-liquid separation after chelation;
- o The 45-minute chelation reaction time can be shortened to 15-minutes;
- o Chelation solutions containing low uncomplexed free-EDTA will substantially reduce the lead content in soil;
- o Additional work should be done to explore optimal chelation time, rate of removal of spent and addition of fresh extractant, material handling, and the regeneration of the chelant;
- o Finally, soil washing is an emerging technology applicable to a wide range of contaminants in soil.

## ACKNOWLEDGEMENT

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FIG.1  
 SOIL PARTICLE SIZE DISTRIBUTION  
 WET SIEVE ANALYSIS

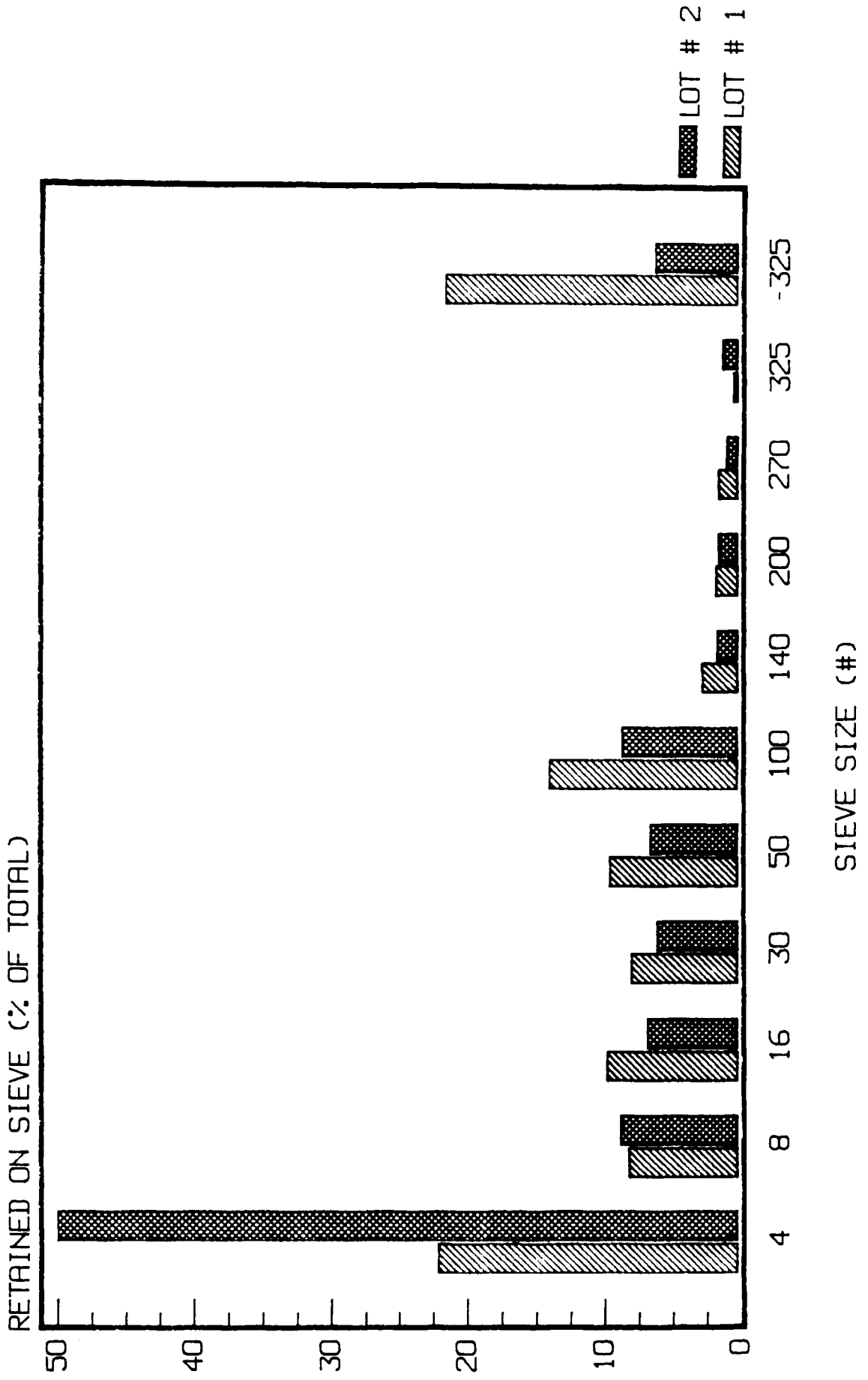




FIG. 2  
COULTER COUNTER ANALYSIS OF THE  
MINUS 325 MESH SOIL FRACTION

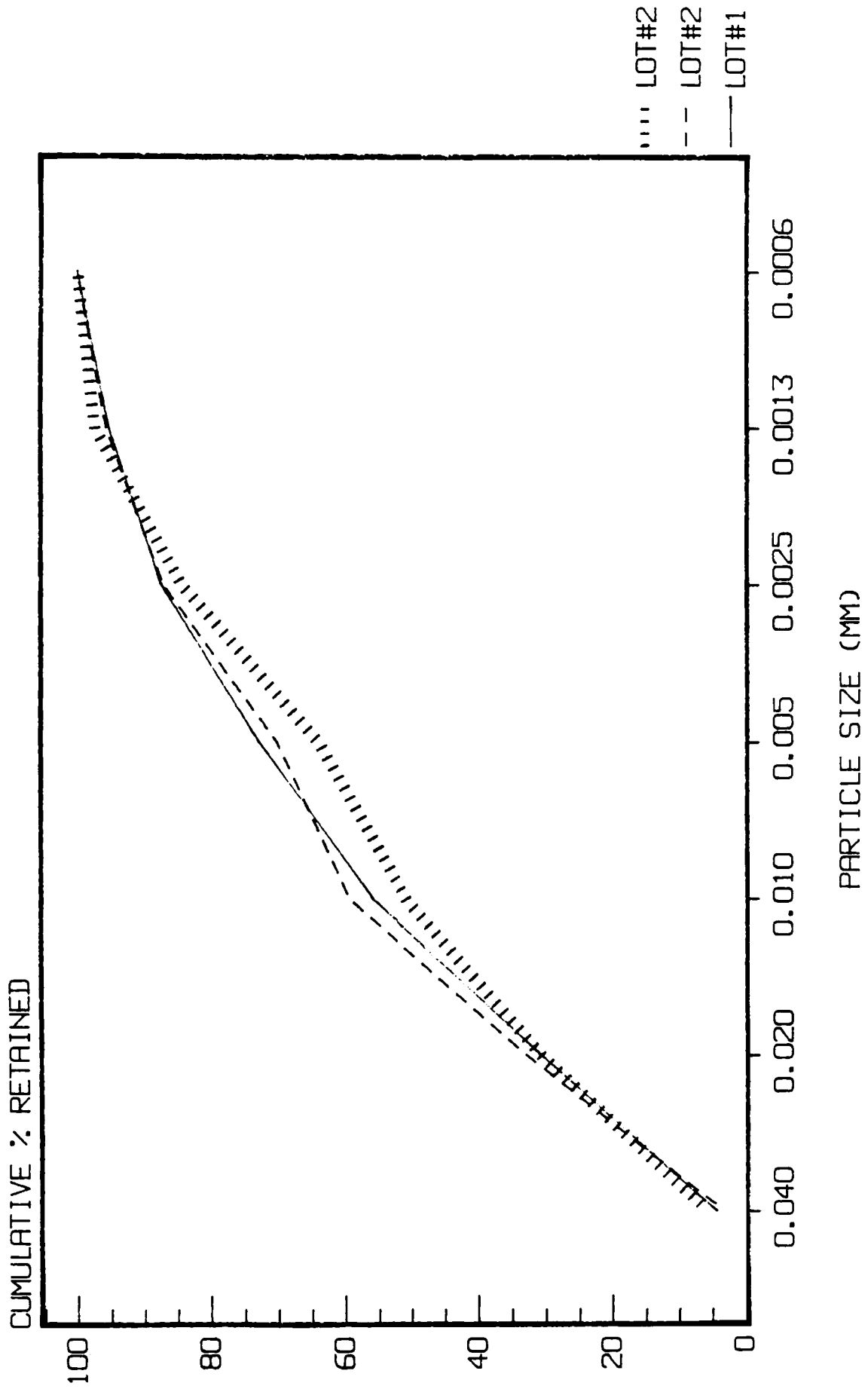


FIG. 3  
LEAD DISTRIBUTION IN SOIL BY  
PARTICLE SIZE FRACTIONS

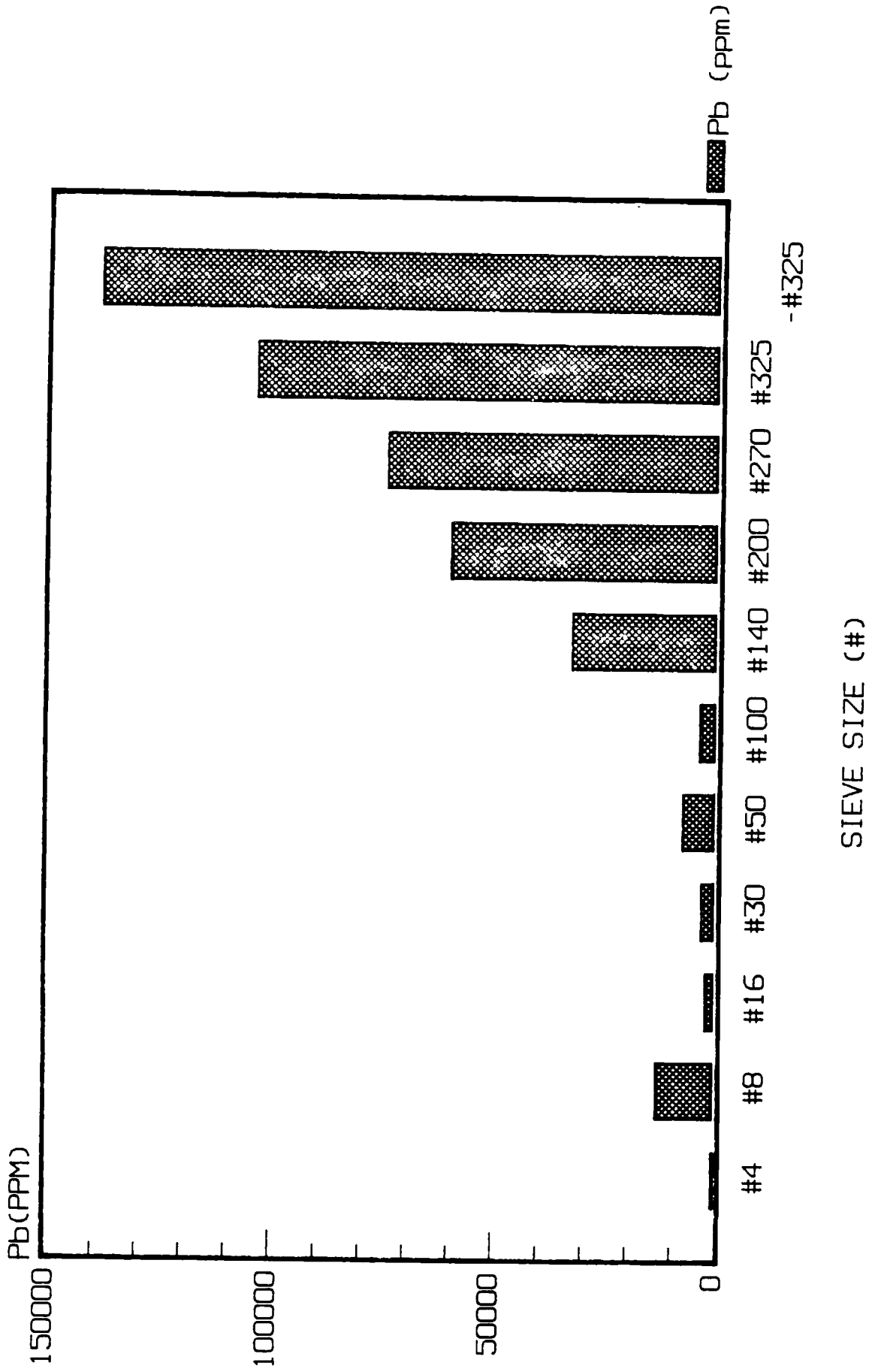


FIGURE.5 THE EFFECT OF POLISH RINSE EDTA CONCENTRATION ON RESIDUAL LEAD AND EP TOX CONCENTRATIONS

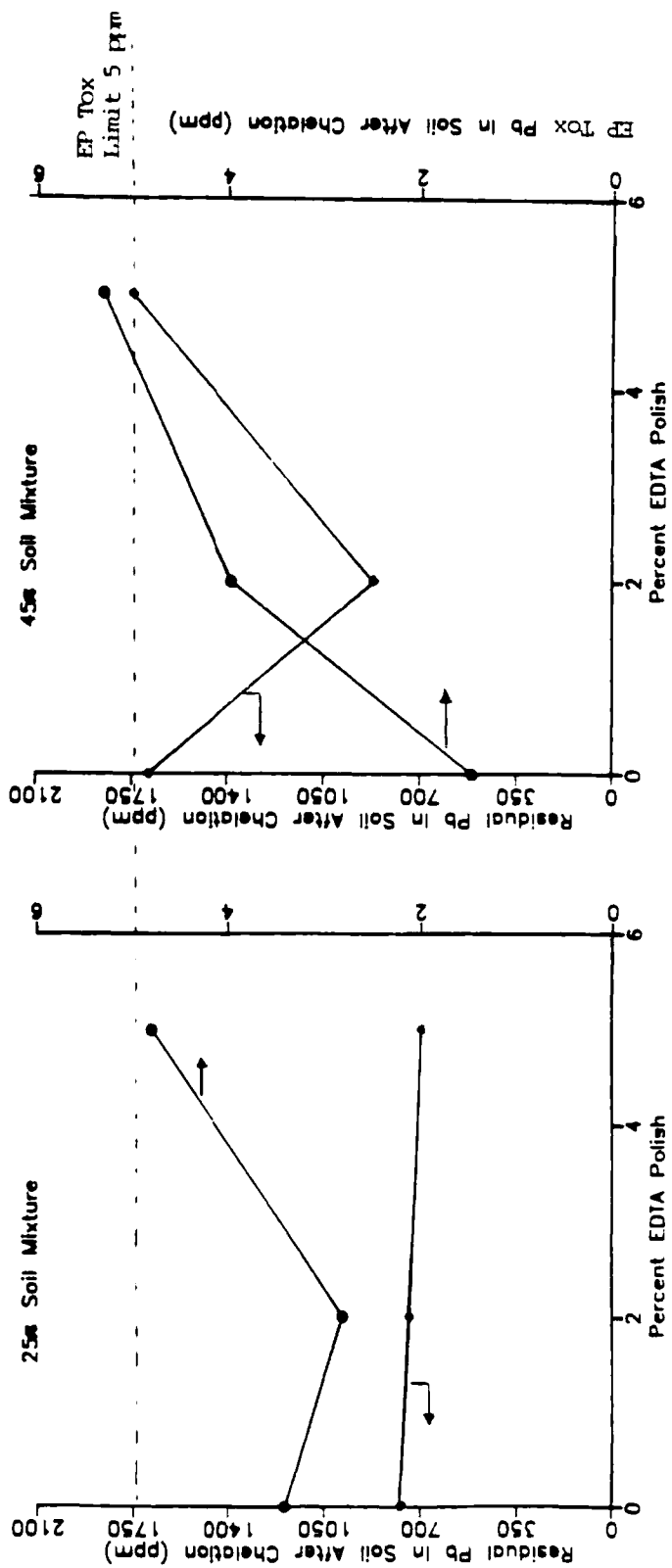


FIGURE.6 CHELATION SOLUTION LEAD UPTAKE  
25% SOIL MIXTURE

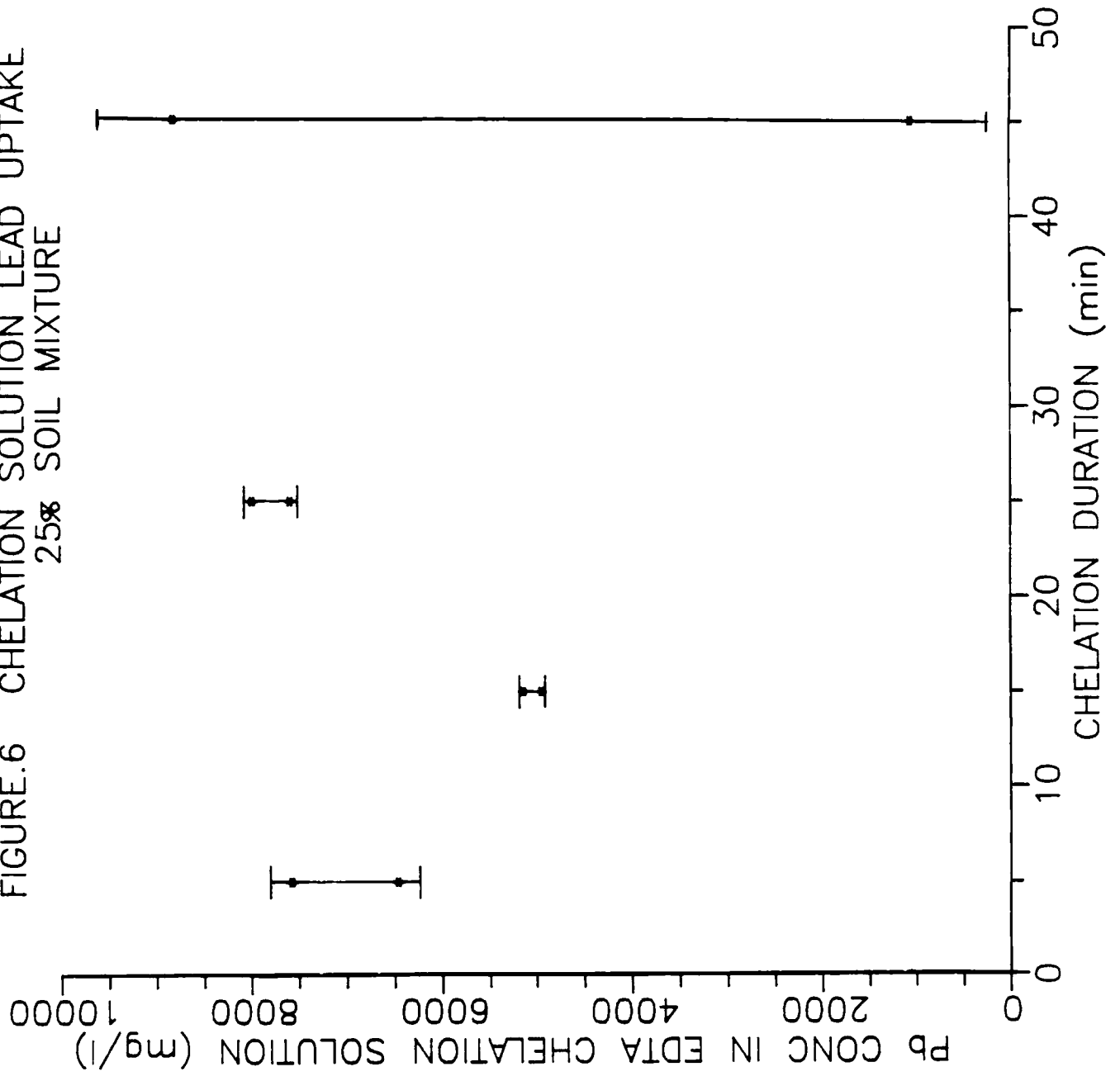


FIGURE 7. CHELATION SOLUTION LEAD UPTAKE  
45% SOIL MIXTURE

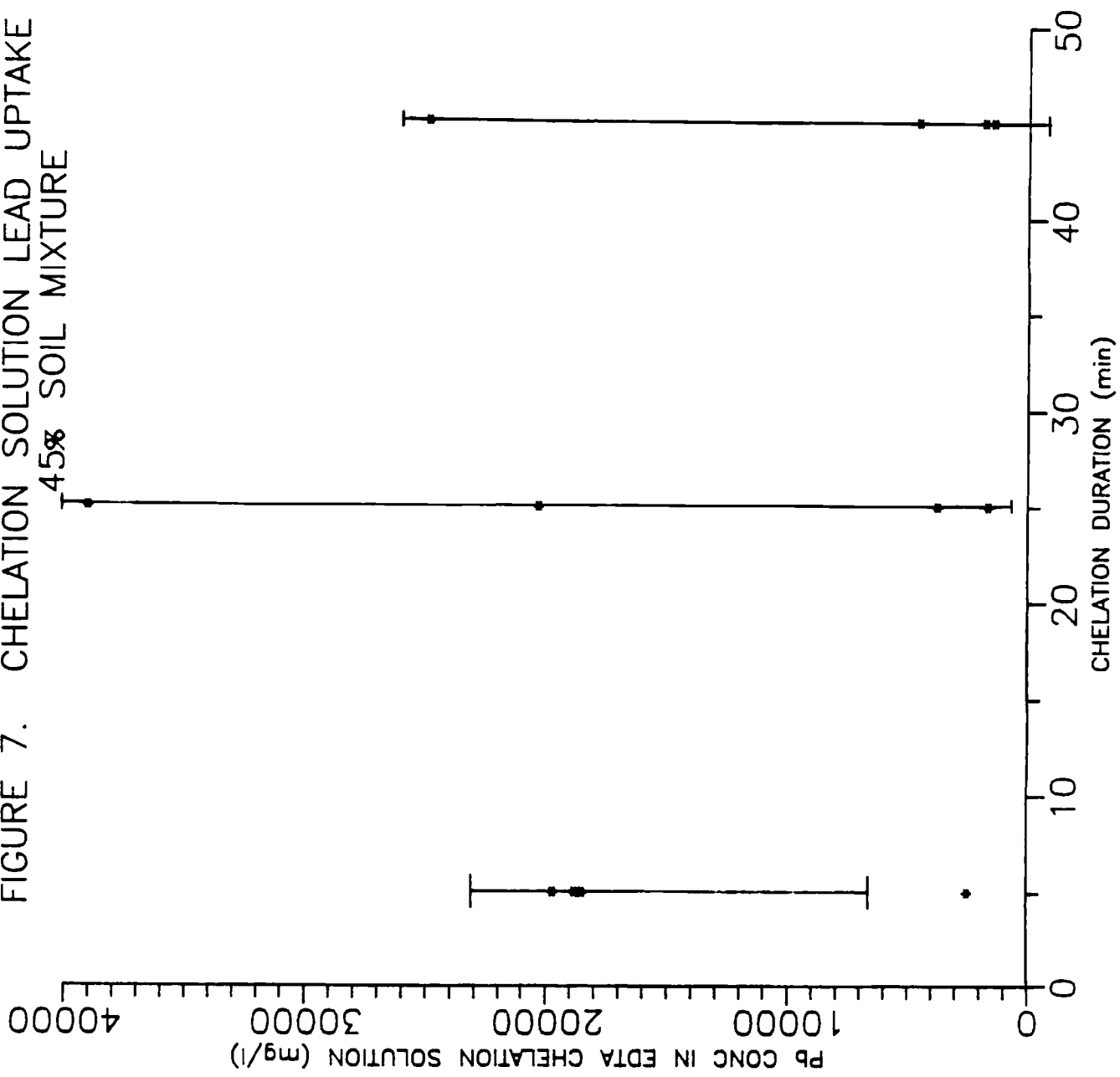


FIG.8  
RESIDUAL LEAD CONCENTRATION IN CHELATION  
SOLUTION DURING SEQUENTIAL CHELATIONS

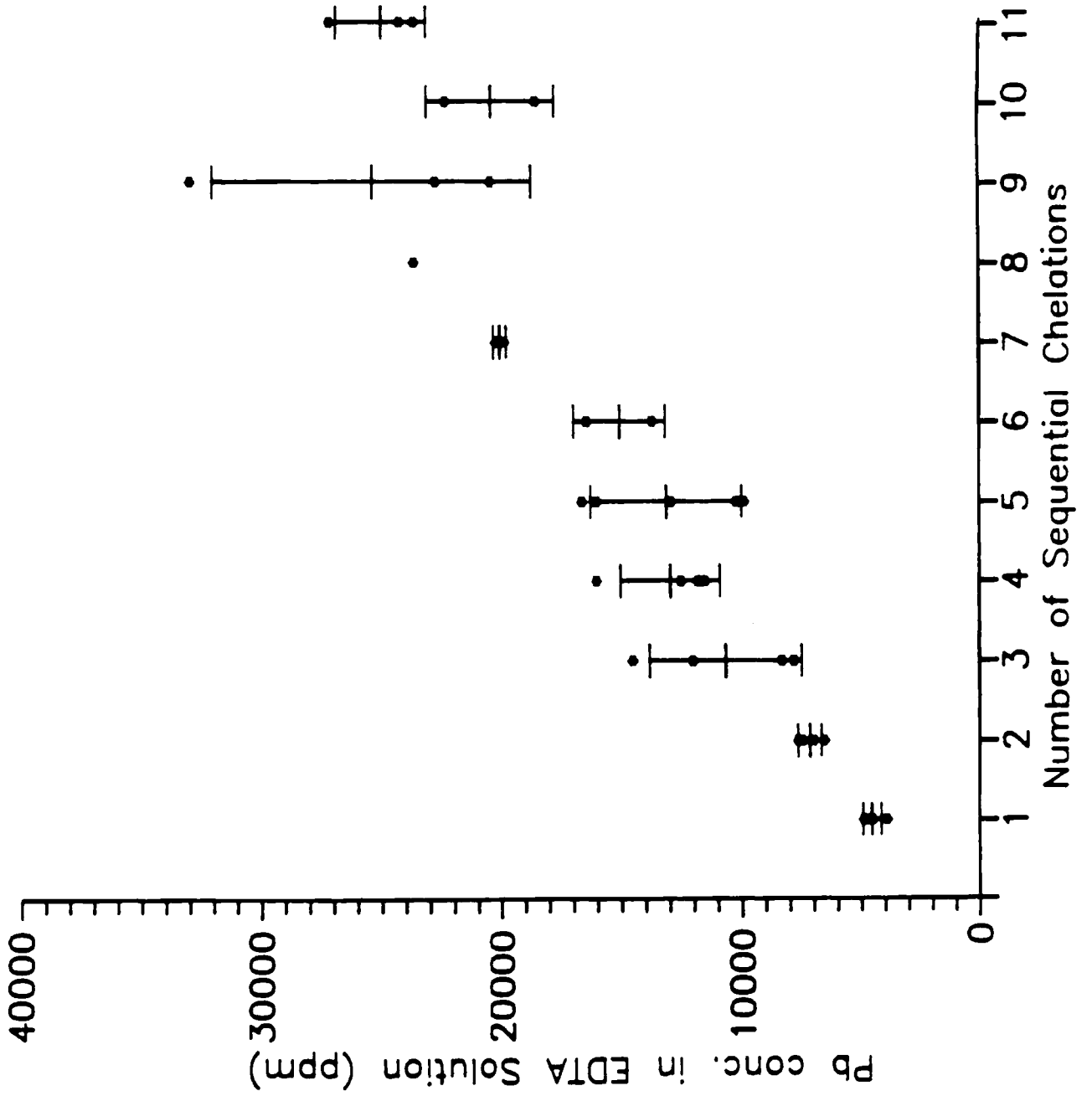


FIG.9  
FREE EDTA CONCENTRATION IN CHELATION  
SOLUTION DURING SEQUENTIAL CHELATIONS

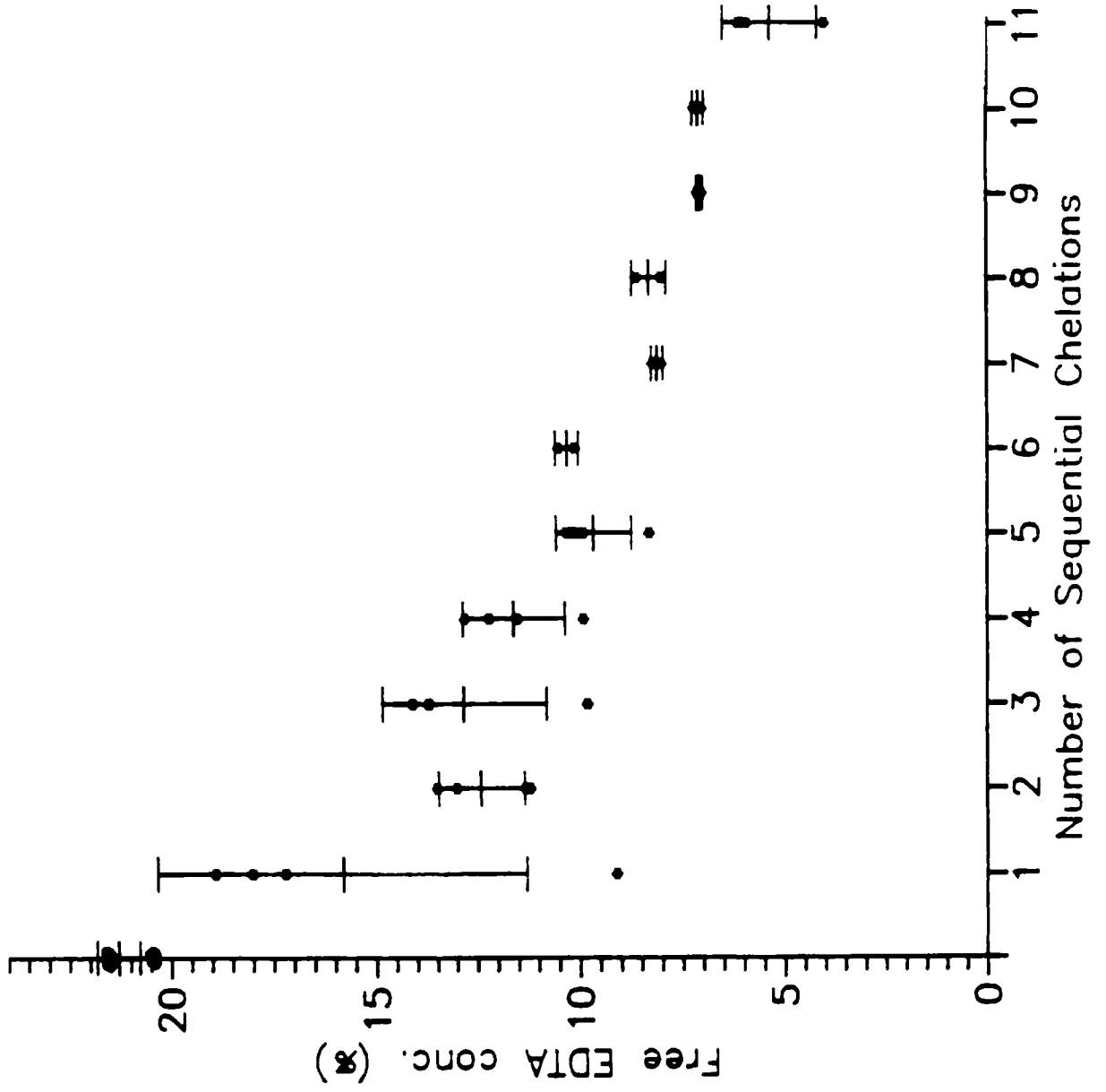


FIG.10  
RESIDUAL LEAD CONCENTRATION IN SOIL  
DURING SEQUENTIAL CHELATIONS

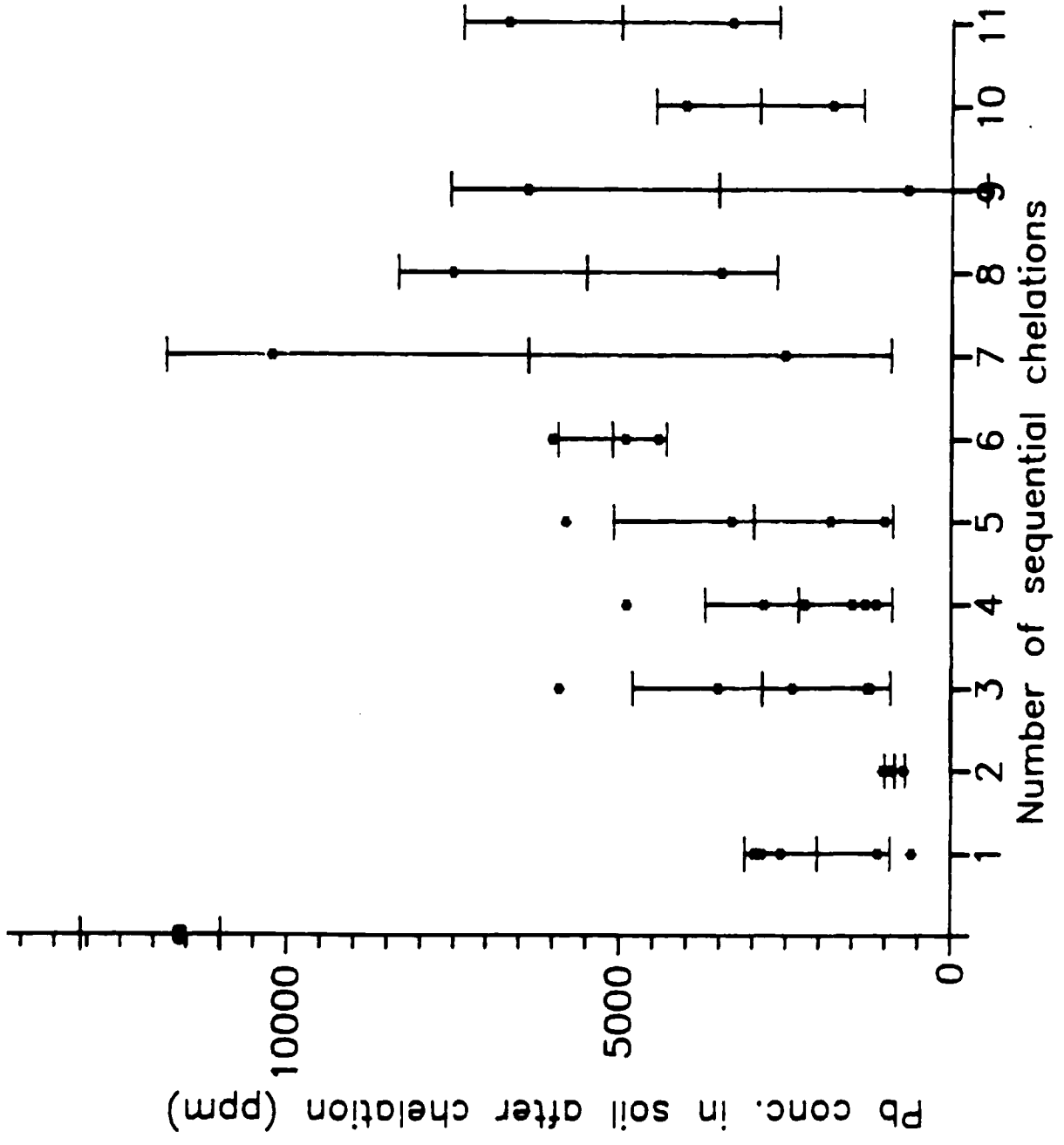




FIGURE 11. EP TOX LEAD IN SOIL AFTER EXTRACTION

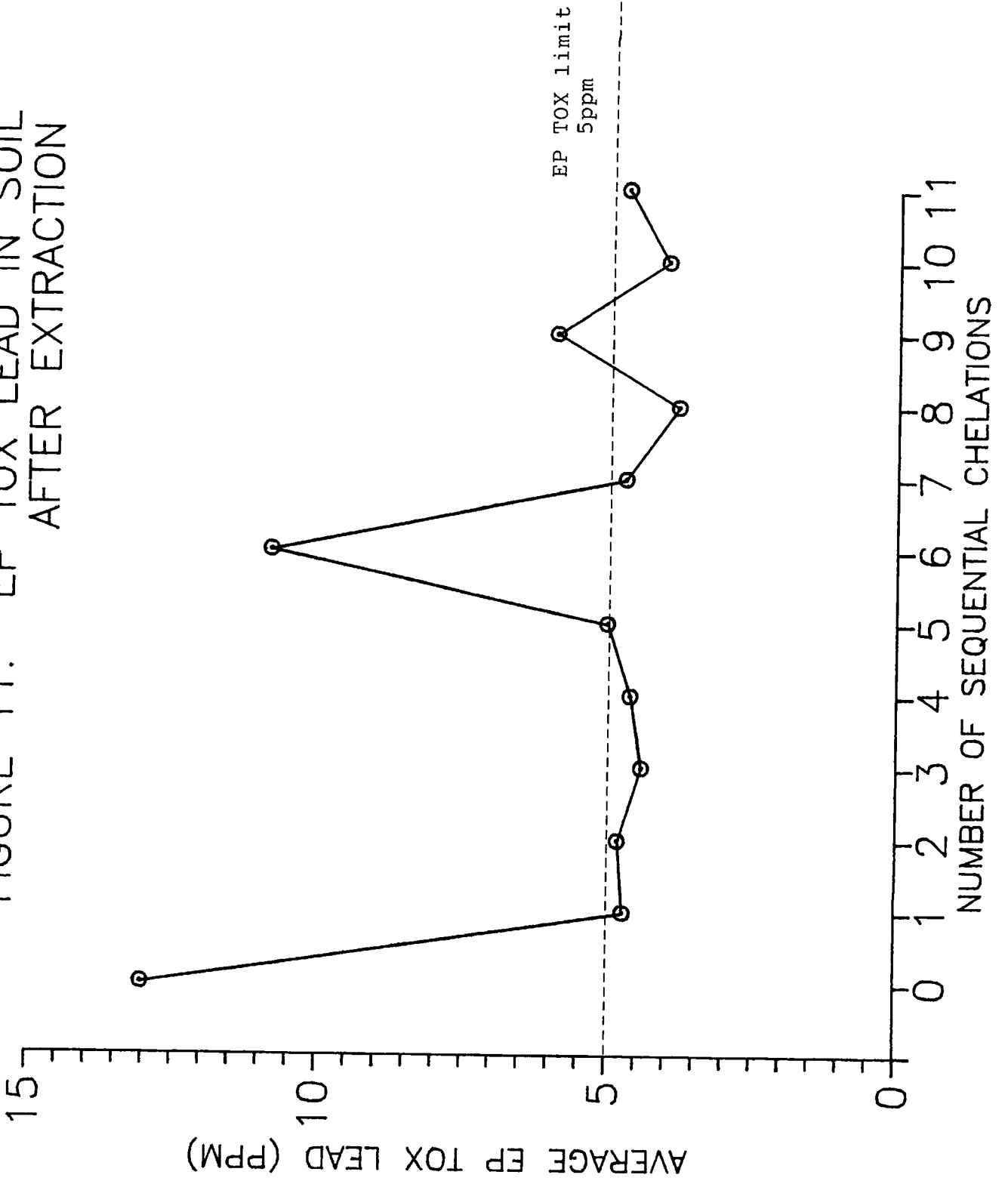
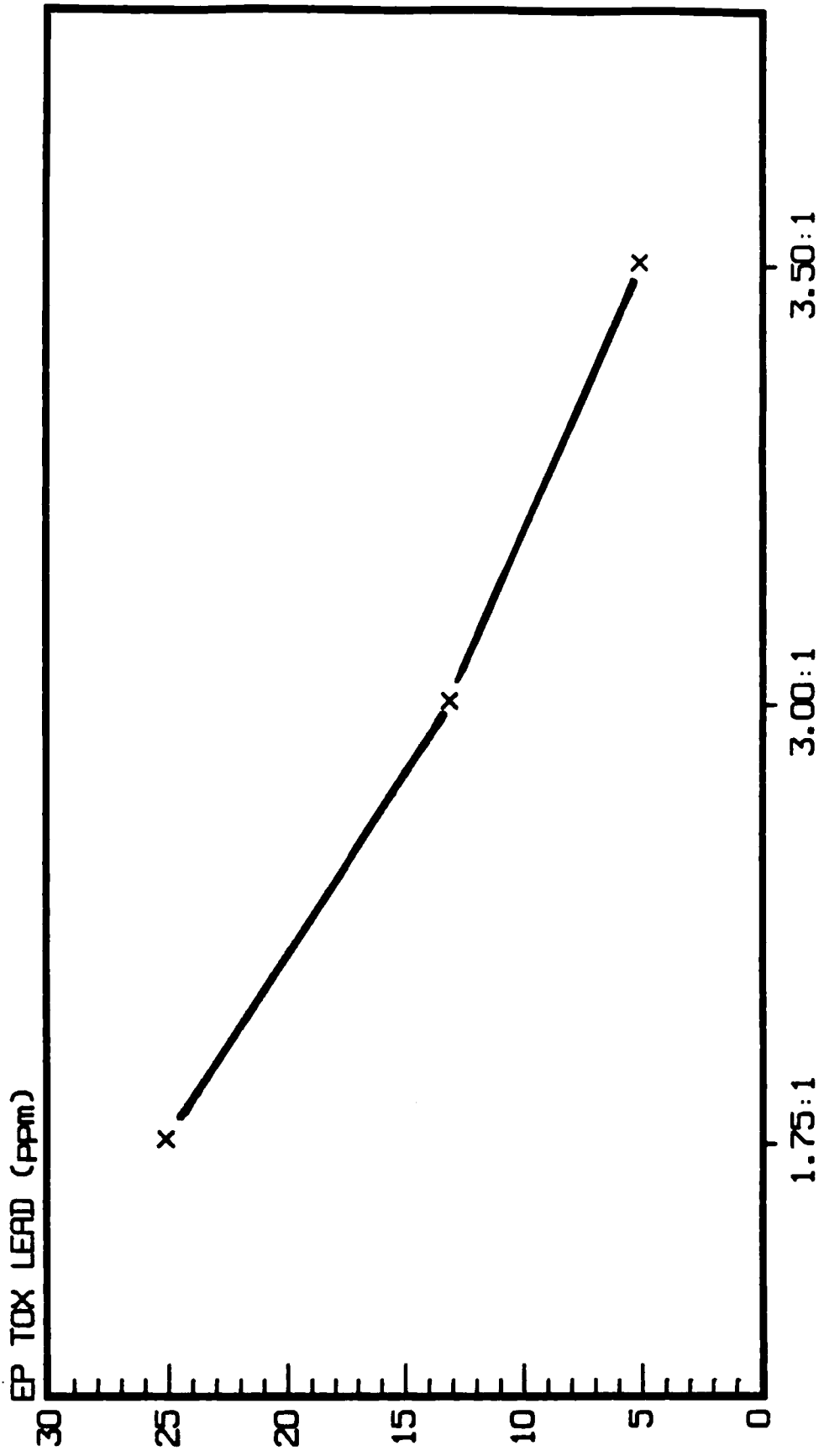


FIGURE. 12  
THE EFFECT OF SPRAY VOLUME ON THE  
EP TOX Pb CONCENTRATION  
OVERSIZED (+1/4 IN) MATERIAL



WATER : SOIL RATIO