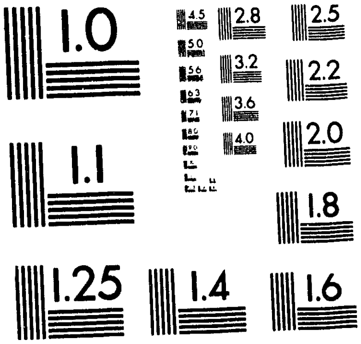
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REMEDIATION OF HEAVY-METAL-CONTAMINATED SOIL USING CHELANT EXTRACTION: FEASIBILITY STUDIES*

by

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ABSTRACT

This paper reports the results of a laboratory investigation conducted to determine the efficacy of using chelating agents to extract heavy metals (Pb, Cd, Cr, Ba, Cu, and Zn) from soil, the primary focus being on the extraction of lead from the soil. This study utilized soil from various ranges (rifle range, handgun range, and hand grenade range) at the Grafenwöhr Training Area in Germany. This paper summarizes the results from the batch-shaker studies and emphasizes the columnar extraction studies. The chelating agents studied included ethylenediaminetetraacetic acid (EDTA) and citric acid, in addition to water. Concentrations of the chelants ranged from 0.01 to 0.05 M; the suspension pH was varied between 3 and 8. Results showed that the removal of lead using citric acid and water was somewhat pH-dependent.

For the batch-shaker studies, the results indicated that EDTA was more effective at removing Cd, Cu, Pb, and Zn than was citric acid (both present at 0.01 M). EDTA and citric acid were equally effective in mobilizing Cr and Ba from the soil. Heavy metals removal was slightly more effective in the more acidic region (pH ≤ 5). Chelant extraction appears to be a promising alternative for removing heavy metals from soils; heavy-metals removal generally exceeded 70%.

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The columnar extraction studies (using 0.05 M EDTA or citric acid) indicated lower heavy-metal removals (typically ≤ 20%) than those achieved during the batch extraction studies. Very small amounts of heavy metals (≤ 1.7%) were mobilized with five pore volumes of water. Use of EDTA resulted in the greatest removal of lead; the maximum removal was 50.6%, with an average removal of 17.6%. EDTA was more effective at removing Cd, Cr, Pb, and Fe than was citric acid, while citric acid was more effective at removing Cu and Zn than was EDTA. Because only a relatively small percentage of heavy metals was mobilized in the columnar extraction studies, in-situ heavy-metal mobilization employing chelant extraction does not represent a viable remediation technique to clean up the surficial contamination at the Grafenwöhr Training Area; however, chelant extraction employing batch treatment offers some promise.

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INTRODUCTION

Military training exercises during the past several decades at the Grafenwöhr Training Area (GTA) have required the firing of a wide range of weapons and weapon systems on a number of firing ranges and target areas. The types of weapons used during these live-fire exercises extend from small arms and hand grenades to artillery, tanks, and helicopter gun-ships. One environmental consequence of these firing exercises has been the deposition of potentially large quantities of heavy metals, such as lead (Pb), copper (Cu), zinc (Zn), and explosive residue onto the soils of firing ranges and target areas at GTA. Thus, it is expected that elevated concentrations of some heavy metals could be incorporated into food webs through uptake by vegetation. It is also possible that significant quantities of heavy metals could be introduced into the local surface waters and/or leached from the soil into groundwater supplies. These conditions could provide an effective mechanism for transporting heavy metals to surrounding nonmilitary areas, thus producing significant adverse environmental impacts that could affect the local German population. The type, degree, and extent of heavy-metal and explosive-residue contamination from current and past training exercises need to be determined, and the probability of off-site transport of heavy-metal contaminants must be evaluated.

This investigation was performed to provide the U.S. Army with documentation of the type, degree, and extent of heavy-metal and explosive-residue contamination on three types of training ranges and their environs at the Grafenwöhr Training Area in Germany. Current and past training exercises requiring the use of small arms and other munitions have resulted in the deposition of some heavy metals onto the soils of training ranges. Potential contamination of the local environment by the introduction of heavy metals into the local surface waters or groundwater supplies was assessed.

This particular portion of the study first addressed whether the heavy metals associated with the various firing ranges leach appreciably into the groundwater system. Second, this study determined the effectiveness of chelant extraction for remediation of the heavy-metal-laden soils.

BACKGROUND

Site Description

Three firing ranges (a handgun range, a rifle range, and a hand grenade range) were studied at the Grafenwöhr Firing Range.

The handgun range is used for handgun practice, mainly by military police units; the range has 10 firing points, with a 7-m-high (23-ft-high) earthen berm about 55 m (180 ft) from the firing line. There are nine pop-up targets for each firing point; the first eight targets are at distances ranging from 10 m (32.8 ft) to 30 m (99 ft), and the ninth is at 50 m (165 ft) from the firing line. A ditch runs parallel with the berm between the eighth and ninth targets and is designed to remove runoff water from the berm and range. The area around the targets is covered with grass that is mowed short, and the ditch and berm are covered with a mixture of grasses and low shrubs. There are a number of spent slugs on the soil surface and on the berm. A tower behind the firing line is used for observation and safety control during firing exercises. The area on both sides behind the range is forest. The area directly behind the berm has tall grass and shrub cover and is part of the impact area.

The rifle range is used by combat troops to check the accuracy of their rifle sights before rifle qualification on another range. This range has 10 pads for firing from the prone position and 10 pits for firing from the standing position.

There is a single small, fixed target 25 m (82 ft) from each firing pad, and the firing pits are located about 5 m (16.4 ft) behind each firing pad. The area between the firing pads and the targets is mowed grass; the 3-m (10-ft) earthen berm generally lacks vegetative cover. There are no spent slugs on the soil surface and none evident in the berm soil, but there is a depression (bullet pocket) in the berm behind each target. There is a shallow depression between the targets and the base of the berm for drainage. A tower behind the firing line is used for observation and safety control during range operations. The area behind the berm and to the right of the range is forested, and a parking lot is to the left.

The hand grenade range is used to provide combat troops with practical experience in the use of high-explosive hand grenades. This range consists of an open oval area about 50 m (165 ft) by 75 m (245 ft), surrounded by an earthen berm approximately 1 m (3 ft) high. The area inside the berm is barren and level except for a number of craters (up to 1 m in depth) resulting from grenade detonations; some of the deeper craters contain standing water. There are two concrete and two log bunkers along the outer edge of the berm for the protection of the grenadier and the instructor during training exercises. Several other, larger concrete structures are located in the area for the protection of troops during training exercises. There is some evidence of damage to the signs, structures, and trees outside the berm. The area outside the berm has grass cover, and the surrounding area is forested.

For the handgun and rifle ranges, sampling locations were selected to represent different degrees of suspected heavy-metal and explosive-residue contamination. Sampling locations included berms behind targets (bullet pockets), other parts of the berm, areas between the firing line and targets, and areas behind the firing range and outside the training area. Sediment samples were taken from range drainage. The sampling depths were 0-15 cm (0-6 in.), using a 2.5-cm soil probe, and 15-30 cm (6-12 in.).

For the hand grenade range, 14 surface soil samples were collected within the berm area (only surface samples were collected within the berm area, because grenade fragments and explosive residues were not expected to penetrate the soil to an appreciable depth). Samples were collected using a stainless steel spoon. Sampling locations included the bottoms, sides, and areas between grenade craters. Additional samples were collected from the berm and outside the berm to provide background levels of heavy metals in the native soils (collected using the soil probe for 0-15-cm and 15-30-cm depths).

Field measurements utilized a portable x-ray fluorescence spectrum analyzer at the data collection points. The device contains a 0.025-Ci ^{109}Cd-sealed source and was calibrated for lead in soil by the manufacturer. The detection limit for lead in soil for this device is ~50 mg/kg, using the standard 60-s measurement time. A validation standard was used to check the consistency of the device before use, periodically during the day, and at the end of each day to ensure that the instrument was operating properly in the field. Field measurements were made using a 60-s time period to collect the spectrum. Data recorded in the x-ray fluorescence analyzer were transferred to a portable computer, and backup copies of the data were placed on a computer disk at the end of each work day.

Before a measurement was made, vegetation was removed without disturbing the soil surface and a 60-s measurement was made in the cleared data collection point. If the surface measurement indicated lead was present above the detection limit of the instrument, several centimeters of soil were removed, and a second measurement was made on the bottom of the excavation. If this reading also indicated lead was present, additional soil was excavated and another measurement was made. This process was repeated until a reading below the detection limit was observed. Multiple readings were taken over a broad range of lead concentrations and used as replicates to determine the precision of the device. The range number, transect number, location on the transect, depth of treading, replicate number, and lead concentration of each measurement were recorded in a notebook. More than 200 x-ray fluorescence measurements were made. A majority of the x-ray fluorescence measurements from the hand grenade range were below the instrument detection limit for lead.

Soil samples from both the initial and primary collections were analyzed in two different laboratories at Argonne National Laboratory (ANL), using several different procedures. The Analytical Chemistry Laboratory (ACL) at ANL used the inductively coupled plasma atomic-emission spectroscopy (ICP-AES) procedure to analyze the samples for arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni), tin (Sn), and zinc (Zn). Samples were also digested using the U.S. Environmental Protection Agency (EPA) Method 3050A (acid digestion of sediments, sludges, and soils), followed by measurement using EPA Method 6010 for ICP-AES. Mercury concentration in selected soil samples was determined by cold vapor atomic absorption (CVAA) according to EPA Method 7471 (soil) by ACL. The analytical laboratory of the Reclamation Engineering and Geosciences Section of the Energy Systems Division at ANL analyzed selected soil samples using the toxicity characterization leaching procedure (TCLP); this method was used to characterize the samples for Ba, Cd, Cr, Cu, Pb, Sn, and Zn. The TCLP data were used to group together samples that had similar heavy-metal concentrations, in order that adequate sample volumes could be used in the batch-shaker flask and continuous columnar extraction experiments.

Previous Studies Involving Extraction of Heavy Metals from Contaminated Soils

Using ethylenediaminetetraacetic acid (EDTA), hydroxylamine hydrochloride, and citrate buffer, Ellis et al. [1] demonstrated the sequential treatment of soil contaminated with Cd, Cr, Cu, Pb, and Ni. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the soil iron oxide-manganese oxide matrix, releasing bound metals, and also reduced insoluble chromates to Cr(II) and Cr(III) forms; and the citrate removed the reduced insoluble Cr and additional acid-labile metals. In single-shaker extractions, using a 0.1 M solution of EDTA was much more effective in metal removal than using a 0.01 M solution. A pH of 6.0 was chosen as optimal because it afforded slightly better Cr removal than that obtained at pHs of 7 or 8. EDTA was the best single extracting agent for all metals; however, hydroxylamine hydrochloride was more effective for removal of Cr. Results of the two-agent sequential extractions indicated that EDTA was much more effective in removing metals than were the weaker agents. The results of the three-agent sequential extraction showed that, compared to bulk untreated soil, this extraction removed nearly 100% of the Pb and Cd, 73% of the Cu, 52% of the Cr, and 23% of the Ni. Overall, this technique was shown to perform better than three separate EDTA washes, better than switching the order of EDTA and hydroxylamine hydrochloride treatment, and much better than simple water washes. The EDTA washing alone can be used effectively, however; the technique resulted in only a slight decrease in overall removal efficiency. Lead was easily removed by the EDTA and was also effectively removed by citrate; Cd was easily removed by EDTA and was also effectively removed by the hydroxylamine hydrochloride; Cu was only removed by the EDTA. Although Ni removal was poor with EDTA alone, the treatment with all three agents showed no better removal.

Hsieh et al. [2,3] studied soil washing for removal of Cr from soil. Chromium was selected for their study because of its prevalence in contaminated sites in northern New Jersey. In the first portion of their study, they investigated the effect of Cr concentration, the type of soil, and pH on Cr adsorption [2]. Sand did not adsorb Cr(III); pH and the quantity of sand had no effect on Cr(III) adsorption. Both Cr(III) and Cr(VI) adsorb onto kaolinite and bentonite clay, with Cr(III) being more prone to adsorption. The amount of Cr adsorbed was proportional to the concentration of Cr added to the soil. After reaching the maximum adsorption, the soil adsorbed no more Cr. Kaolinite had less adsorption capacity for Cr than did bentonite. Cr(VI) had a higher adsorption at low pH. Cr(III) precipitated above pH 5.5. Results from preliminary soil washing experiments indicated that the amount of Cr washed out from the soil was proportional to the number of washings performed and the amount of extracting agents used (sodium hypochlorite and EDTA were used as the extracting agents).

Hsieh et al. [3] observed that Cr washout was related to pH; the efficiency increased with increasing pH and then decreased. The optimal pH was approximately 10.4. They also noted that after some period of time, depending on pH and particle size, Cr was released from the soil again. Approximately 20 to 50% of the Cr in the soil samples was in the free form and could be removed by washing with water alone. The researchers observed that the washing process for different size fractions of the soil followed second-order kinetics. The rate constants for the various size fractions did not vary significantly, which they concluded indicated that the washing time was not dependent on particle size for the extractant used. Removal efficiency was observed to be related to particle size, with the -40 to +70 mesh size fraction giving the maximum efficiency, followed by the -70 to +200 mesh size fraction.

Hessling et al. [4] investigated soil washing techniques for remediation of Pb-contaminated soils at battery recycling facilities. Three wash solutions were studied for their efficacy in removing Pb from these soils: (1) tap water alone at pH 7, (2) tap water plus anionic surfactant (0.5% solution), and (3) tap water plus a 3:1 molar ratio of EDTA to toxic metals at pH 7-8. Tap water alone did not appreciably dissolve the Pb in the soil. Surfactants and chelating agents, such as EDTA, offer good potential as soil washing additives for enhancing the removal of Pb from soils. There was no apparent trend in soil or contaminant behavior related to Pb contamination (predominant Pb species), type of predominant clay in the soil, or particle size distribution. The authors concluded that the applicability of soil washing to soils at these types of sites must be determined on a case-by-case basis.

Elliott et al. [5] performed a series of batch experiments to evaluate extractive decontamination of Pb-polluted soil using EDTA. They studied the effect of EDTA concentration, solution pH, and electrolyte addition on Pb solubilization from a battery-reclamation-site soil containing 21% Pb. The heavy-metals concentrations in the soil were determined to be 211,300 mg Pb/kg (dry weight); 66,900 mg Fe/kg; 1383 mg Cu/kg; 332 mg Cd/kg; and 655 mg Zn/kg. A nine-step chemical fractionation scheme was used to speciate the soil Pb and iron (Fe). The study indicated that increasing EDTA concentration resulted in greater Pb release. Recovery of Pb was generally greatest under acidic conditions and decreased modestly as the pH became more alkaline. Even in the absence of EDTA, a substantial increase in Pb recovery was observed below pH 5. As the pH became more alkaline, the ability of EDTA to enhance Pb solubility decreased because hydrolysis was favored over complexation by EDTA. The researchers observed that EDTA can extract virtually all of the nondetrital Pb if at least a stoichiometric amount of EDTA is employed. When increased above the stoichiometric requirement, the EDTA was capable of effecting even greater Pb recoveries; however, the Pb released with each incremental increase in EDTA concentration diminished as complete recovery was approached. The researchers also investigated the release of Fe from the soil by EDTA. The Fe release increased markedly with decreasing pH. Although the total Fe was nearly 1.2 times the amount of Pb in the soil, only 12% of the Fe was dissolved at pH 6 using 0.04 M EDTA, compared with nearly 86% dissolution of the Pb [6]. Little of the Fe was brought into solution during the relatively short contact time of the experiments (5 h). The iron oxides retained less than 1% of the total soil Pb [6].

Elliott et al. [5] observed that Pb recovery increased by nearly 10% in the presence of $LiClO_4$, $NaClO_4$, and NH_4ClO_4. They attributed this increase to an enhanced displacement of Pb^{++} ions by the univalent cations and the greater solubility of Pb-containing phases with increased ionic strength. Below pH 6, calcium and magnesium salts also enhanced Pb recovery. Above pH 6, however, Pb recovery decreased due to a competition between Ca or Mg and Pb for the EDTA coordination sites. Their research [5,6] provided no evidence that the suspension pH must be raised to at least 12 to prevent Fe interference in soil washing with EDTA to effectively remove Pb.

EPA conducted a series of laboratory bench-scale soil washing studies using water, EDTA, or a surfactant to treat soils from metal recycling sites [7,8]. Soil washing did not remove significant quantities of Pb from any of the soil fractions. The Pb was not concentrated in any particular soil fraction; rather, it was distributed among the fractions. EDTA was more effective in removing Pb than were either the surfactant or water washes. Data from the U.S. Bureau of Mines indicate that the effectiveness of EDTA in removing Pb varies with the species of Pb present [9].

In previous work involving extraction of Pb from soil containing approximately 70% silt and clay, Peters and Shem [10] removed 58 to 64% of the Pb using EDTA over the entire pH range ($4.9 \leq pH \leq 11.3$). In their study, the soil was spiked with lead nitrate solutions, resulting in initial Pb concentrations of 500 to 10,000 mg/kg soil. The chelants studied included EDTA and nitrilotriacetic acid (NTA). The removals of Pb using water and NTA as extractants were both pH-dependent, whereas the removal of Pb using EDTA was pH-insensitive over the pH range investigated ($3 \leq pH \leq 12$). Extraction with water alone removed a maximum of 7.55% for pH ~ 4. The initial Pb concentration had little effect on the metal removal efficiency for the EDTA system. The applied EDTA concentration over the range of 0.01 to 0.10 M also had little effect on the removal efficiency of Pb from the soil. For soils containing a greater fraction of sand (sand > 78%), the removal efficiency of Pb from the soil typically exceeded 85%. Peters and Shem [11] noted that the adsorptive behavior of the soil containing a high silt and clay fraction differed significantly from the sandy soil. Previous studies have indicated that heavy metals are preferentially bound to clays and humic materials [12].

Peters and Shem [10] observed that extraction of Pb with EDTA was rapid, reaching equilibrium within a contact time of 1.0 h; extraction of Pb with NTA was slower, requiring a contact of approximately 3.0 h to reach equilibrium. The order of Pb-removal efficiency for the various extractive agents was as follows: EDTA >> NTA >> water [10]. The maximum Pb removals observed for this high clay and silt soil were 68.7, 19.1, and 7.3%, respectively, for the cases of EDTA, NTA, and water used as the extractive agents on the Pb-contaminated soil [13].

PURPOSE

The purpose of this phase of the project was two-fold: (1) to investigate the leaching potential of Pb (and other heavy metals) from soil samples obtained from Grafenwöhr Training Area and (2) to investigate the potential to extract the heavy metals from the contaminated soil by using chelating agents. The primary heavy metal of interest was Pb; other heavy metals of interest included Cu, Zn, Cd, Cr, and Ba.

EXPERIMENTAL PROCEDURE

Batch-Shaker Test

Two to three batches (~200 g each) of contaminated soil obtained from the Grafenwöhr Training Area were air-dried in a hood. The analytical procedures used to characterize the soils are listed in Table I. Characteristics of groundwater from an industrial-water and a drinking-water well near the firing range are summarized in Table II. Characteristics of the soils used in this study are summarized in Table III. As is indicated in these tables, the groundwater was slightly acidic, with low conductivity and total organic carbon concentration. The drinking-water well also showed no major heavy-metal contamination (with the possible exception of manganese, which may have been due to natural background levels). The soil characterization indicated the soil generally was slightly alkaline, had a low carbon content (<2.2%), had a low cation-exchange capacity, and generally was of a sandy nature.

Soil was weighed in nominal 5-g portions using a top-loading balance and placed in plastic shaker containers (with lids). To each of these containers was added a 50-mL solution of one of the following:

- Deionized water -- pH adjusted to be in the range of 3 to 7
- 0.01 M and 0.05 M EDTA solution
- 0.01 M and 0.05 M citric acid solution

These conditions created a matrix of samples; each combination of Pb-contaminated soil and type and concentration of extracting fluid was tested. In total, there were 108 samples, plus approximately 25% additional spot replicates.

Samples were shaken for a period of nominally 3 h at the low setting on an Eberbach shaker table. This time requirement was determined from a previous study to be adequate for equilibrium conditions to be achieved [10]. Following this agitation, the samples were centrifuged in plastic Nalgene centrifuge tubes equipped with snap-on caps, filtered using No. 42 Whatman filter paper, and stored in glass vials maintained at pH<2 (prepped using ultrapure HNO_3) to await atomic-absorption spectroscopy (AAS) analysis. At least 10 mL of sample was collected for the AAS analysis. The AAS was calibrated using AAS standards for Pb, Cd, Cu, Cr, Zn, and Ba. The analyses were performed in accordance with the procedures described in Standard Methods [18].

Data collected in these studies included the following: operating temperature, extractant type and concentration, heavy metals concentration on the soil before treatment (and after treatment, as determined by calculation), heavy-metals concentration in the extract solution after treatment, pH of the solution before and after treatment, and batch shaking time.

Column Flooding Experiments

Aluminum columns with a fixed glass wall were hand-packed with dry soil (which had been passed through an 850-μm sieve (ASTM mesh #20) and retained by a 75-μm sieve (ASTM mesh #200).

Soil that passed through the 75-μm sieve was discarded; the fine soil might otherwise plug the flow through the soil columns. The weight of the soil contained in the soil column was measured. The heavy-metal concentrations in the various soil portions contained in the column were calculated on the basis of the TCLP data collected by the Reclamation Engineering and Geosciences Laboratory. Solutions were pumped through the columns using a Cole-Parmer Masterflex pump. The volume of solution necessary to initially saturate the soil was noted; this volume was assumed to approximate one pore volume of liquid in the column.

Deionized water was used initially to saturate the soil. The resulting leachate was drained, collected, and analyzed by AAS (after prepping with HNO_3). The heavy-metal concentration of the soil was determined by mass-balance calculations on the soil portions used in performing a column experiment. Since a columnar flow experiment involved the use of approximately 300 g of material, various soil samples had to be grouped together in order to have a sufficient quantity of sample to perform the experiment. The portion of this experiment in which the deionized water column was flushed enabled the determination of the easily desorbed portion of the Pb (and other heavy metals) from the soil. The deionized water flushing also provided an indication of the severity of the problem at the Grafenwöhr Training Area, in terms of the potential for Pb to leach into groundwater supplies.

The contaminated soil columns were then flooded with a wash solution, again operated in an upflow mode. The solution contained one chelant (either EDTA or citric acid) at concentrations determined as being optimal from results of the batch-shaker tests. Each pore volume of liquid was collected, acid-preserved and stored, and analyzed by AAS analysis, as described in the batch-shaker test procedure.

Data collected during these columnar flow experiments included columnar solution feed flow rates, operating temperature, extractant type and concentration, pH (before and after treatment), heavy metal removed from the soil (determined by mass balance on the soil and total heavy-metal concentration in the eluate solution), pore volume, and the efficiency of removing the heavy metals from the soil column.

RESULTS AND DISCUSSION

Characterization of the Untreated Soil

Several national governments, including that of the United States, have developed guidelines and/or regulations defining hazardous levels of heavy-metal contamination in soils and groundwater. In 1988, the Netherlands published the "Dutch list," which gave three categories of heavy-metal concentration: Category A -- Baseline Concentration, Category B -- Detailed Investigation Needed, and Category C -- Remedial Investigation Needed. As of this date, Germany has not established standard action or cleanup levels by national law for heavy-metal-contaminated soils and groundwater. However, the Bavarian state government has generally adopted the Dutch list as guidelines for assessing heavy-metal contamination. Table IV [19] lists the concentrations of heavy metals on the Dutch list for the three categories in soil and groundwater that are included in this investigation.

Prior to performing the chelant extraction experiment, the untreated soil was characterized using ICP-AAS and TCLP techniques.

Characterization of Soil Treated Using Chelant Extraction

Results of the AAS analyses for the contaminated soils treated using chelant extraction (using either 0.01 M citric acid or 0.01 M EDTA) are listed in Table V for the elements of interest in this phase of the research, namely, Pb, Cu, Cd, Cr, Ba, and Zn. The results are also compared with the Dutch list standards in Table V. The numbers marked in boldface are above the standards for Category C; those above the standards for Category B are underlined. The results indicate that the most severe treatment problem involves Cd contamination, with lesser problems presented by Ba and Zn contamination, using both citric acid and EDTA as chelants. The residual concentrations were calculated on the basis of the initial heavy-metal concentration on the untreated soil, subtracting the amount of heavy metal contained in the chelant solution after treatment (based on AAS analyses). Due to the nature of using grab samples to determine the residual concentrations in the untreated and treated soils, several sample analyses exhibited analytical concentrations that had higher estimated quantities of heavy metals extracted into the chelant solution. For those cases, the residual concentrations were arbitrarily assigned a residual concentration of ~0 mg/kg. The results presented are for the case of a chelant concentration of 0.01 M. No attempt was made to optimize the most effective chelant concentration. Rather, the goal of these studies was to determine whether chelant extraction would offer potential as a cleanup technique. In order to assess this, the results of the residual metal concentrations (before and after chelant extraction treatment) were compared. The results are presented in Tables VI and VII. Table VI presents the results for the case of Pb, Cd, and Cu, while Table VII presents the results for Cr, Ba, and Zn.

The results from Tables VI and VII indicate that although the chelant extraction technique did not meet all the Dutch standards, it did reduce the heavy-metal concentrations in these soils quite effectively. Very few soils would fall under Class C criteria after treatment. The concentration of heavy metals in the soils was substantially lower for the chelant-extracted soils than for the untreated soil. The two major heavy metals of concern are Cd and Ba; the treatments did not effectively meet the Dutch guidelines, although the concentrations were indeed lowered with respect to the untreated soil). Again, it should be pointed out that no attempt was made to optimize the concentration of chelant to obtain the maximum removal of heavy metal. The concentration of citric acid and EDTA was maintained at 0.01 M. To obtain the maximum removal of heavy metals from solution, chelant concentrations in the range of 0.05-0.10 M should be investigated.

Batch-Shaker Studies

Figures 1a through 1f present the solubilization data of the heavy metals Cd and Pb, extracted into solution using either 0.01 M citric acid or EDTA, while Figures 2a through 2f present the solubilization data for Ba, Cu, and Zn using the same two chelant solutions. The chelant concentration was held constant at 0.01 M during these experiments. The soil tested involved soil samples from the hand grenade range. Figures 1 and 2 indicate that EDTA was about ten times (~10x) more effective at mobilizing Pb, nearly equal to ~4x more effective at mobilizing Cd, nearly equal to ~5x more effective at mobilizing Zn, and ~2x-10x more effective at mobilizing Cu, compared to extraction with citric acid. EDTA and citric acid were nearly equally effective at removing Ba and Cr from the soil. Figures 1 and 2 generally indicate that as the pH was lowered, the solubilization of the heavy metals increased. Furthermore, the data in Figures 1 and 2 indicate the following trends in terms of solubilization of the heavy metals of interest:

Citric Acid: Ba > Zn > Cu > Cd > Pb > Cr

EDTA: Ba ~ Cu > Zn > Pb > Cd > Cr

The amount of heavy metal solubilized was determined on the basis of the AAS analyses and the volume of the chelant solution applied to the soil samples in the batch-shaker tests. The initial and final concentrations of heavy metals in the hand-grenade-range samples are shown in Figures 3 and 4 (for soil samples S037, S038, S039, S041, S044, and S049) for the cases of citric acid and EDTA extraction, respectively. The data shown in Figures 3 and 4 indicate the following heavy-metal-mobilization information (over the entire pH range studied):

	Citric Acid Extraction						EDTA Extraction					
	Pb	Cd	Cr	Cu*	Ba	Zn	Pb	Cd	Cr	Cu*	Ba	Zn
Maximum Metal Removed, %	100	100	100	~100	100	100	100	100	100	100	100	100
Minimum Metal Removed, %	15	2	69	100	11	3	100	22	70	100	11	7
Average Metal Removal, %	57	39	85	100	52	42	100	69	85	100	56	65
Mean Removal at Low pH (pH<6), %	61	56	85	100	75	41	100	81	85	100	77	64
Mean Removal at High pH (pH>7), %	59	14	85	100	47	48	100	54	85	100	36	61

The data confirm the information presented earlier; EDTA extraction generally performs slightly better than citric acid extraction, with average heavy-metal removals ranging from 56 to 100% and 39 to 100% for EDTA and citric acid extraction, respectively. The data shown in Figures 3 and 4 indicate that chelant extraction (performed batch-wise) does offer promise as a remediation technique to clean up these soils. However, the proper chelant concentration needs to be determined from optimization studies in order to obtain the maximum amount of heavy-metal removal from these soils.

Columnar Studies

In the columnar studies, deionized water and chelating agent solution were percolated through the soil columns. As indicated in the "Approach" section, five pore volumes of water were first passed through the soil column, after which approximately eight pore volumes of chelant solution (0.05 M) were passed through. The chelant solution concentration was increased to 0.05 M to improve the removal efficiency of heavy metals from the soil. Because a limited quantity of soil samples was available, several soil samples were combined in order to provide the approximately 300 g of soil needed to perform the columnar flow experiment. Results of the columnar flow studies are shown in Figures 5 through 9 for Pb, Cd, Cu, Fe, and Zn, respectively. Results from these experiments are summarized below:

	Heavy Metal					
	Pb	Cd	Cr	Cu	Zn	Fe
Average Removal, %						
Deionized Water	0.31	3.72	1.60	3.72	1.69	0.03
Citric Acid	4.25	11.1	2.37	8.96	10.6	0.39
EDTA	17.6	13.0	2.80	1.41	4.87	0.51
Removal Range, %	0.0-50.6	0.1-34.7	0.5-6.6	0.0-16.0	0.5-24.0	0.0-0.5
Most Effective Treatment Method	EDTA	(a)	(a)	CIT	CIT	(a)

[a] Both EDTA and citric acid (CIT) are equally effective at removing this heavy metal.

SUMMARY AND CONCLUSIONS

The results of this feasibility/treatability study indicate the following:

Batch-Shaker Studies:

- EDTA was more effective than citric acid (both present at 0.01 M) at removing Cd, Cu, Pb, and Zn.
- EDTA and citric acid were equally effective in mobilizing Cr and Ba from the soil.
- The batch-shaker method showed that chelant extraction offers promise as a remediation technique for on-site clean-up of contaminated soil.
- Heavy-metals removal was slightly more effective at pHs in the range of 5-6 (compared to pH > 7).

Columnar Flooding Experiments:

- In terms of mobilization of heavy metals, deionized water was the least effective leaching solution used; the maximum solubilization achieved was 3.72% for Cd.
- Extraction with deionized water indicates that all of the heavy metals are very tightly bound to the soil; the quantity of heavy metals leached into solution generally was less than 1.7% of the total heavy metals contained in the soil sample.
- The deionized-water extraction results indicate that the heavy metals are very stable in the soils at Grafenwöhr Training Area and do not represent a serious threat to the groundwater system.
- EDTA (0.05 M) had the greatest removal of Pb, with a maximum removal of 50.6% and an average removal of 17.6%.
- EDTA (0.05 M) was more effective at removing Cd, Cr, and Fe than were 0.05-M citric acid or distilled water;

the average removals were 13.0, 2.8, and 0.5%, respectively, for these three heavy metals.

- Citric acid (0.05 M) was more effective at mobilizing Cu and Zn than were either EDTA (0.05 M) or deionized water; the average percentages of Cu and Zn mobilized using citric acid were 8.96 and 10.59%, respectively.
- The amount of heavy metals mobilized from these soils constitutes a relatively low percentage (typically <20%).
- Due to the relatively small percentage of heavy metals mobilized in the columnar flow studies, in-situ heavy-metal mobilization employing chelant extraction probably does not represent a viable remediation technique to clean up the soils at Grafenwöhr Training Area, although chelant extraction employing batch treatment offers some promise.

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NOTATION

AAS	Atomic-absorption spectroscopy
ACL	Analytical Chemistry Laboratory
ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
As	Arsenic
Ba	Barium
BOD_5	Biological Oxygen Demand (5-day)

Cd	Cadmium
CEC	Cation exchange capacity
CIT	Citric acid
Co	Cobalt
Cr	Chromium
Cu	Copper
CVAA	Cold vapor atomic absorption
DOE	U.S. Department of Energy
EDTA	Ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
Fe	Iron
GTA	Grafenwöhr Training Area
Hg	Mercury
HNO_3	Nitric acid
ICP-AES	Inductively coupled plasma atomic-emission spectroscopy
$KMnO_4$	Potassium permanganate
$LiClO_4$	Lithium perchlorate
Mg	Magnesium
$NaClO_4$	Sodium perchlorate
Ni	Nickel
ND	Not detected
NH_4-N	Ammonia nitrogen
NH_4ClO_4	Ammonium perchlorate
NTA	Nitrilotriacetic acid
Pb	Lead
pH	$-\log[H^+]$
Sn	Tin
TCLP	Toxicity characteristics leaching procedure
USCS	Unified Soil Classification System
Zn	Zinc

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Table I. Analytical Procedures or Methods for Determining Physical/Chemical Characteristics of Fill Samples

Soil Parameter	Method
Cation Exchange Capacity	EPA 9081[a] Methods of Soil Analysis (Part 8)
Particle Size Characterization:	
Size Gradation - sieving	ASTM D2487-85[b]
Particle Size Analysis - hydrometer	ASTM D422-63[c]
Particle Size Analysis	U.S.C.S.[a]
Soil pH	EPA 9045[d] Methods of Soil Analysis (Part 9)
Organic Carbon	Methods of Soil Analysis (Part 29)

[a] Particle size classifications are in accordance with the Unified Soil Classification System.

[b] Source: Ref. 14.

[c] Source: Ref. 15.

[d] Source: Ref. 16.

Table II. Characteristics of the Industrial-Water and Drinking-Water Wells at Grafenwöhr, Germany (adapted from Ref. 17)

Contaminant	Industrial-Water Well No. 118	Drinking-Water Well No. 6
Organics (mg/L):		
Dichloromethane	ND[a]	ND
trans-1,2-Dichloroethene	ND	ND
cis-1,2-Dichloroethene	ND	ND
Trichloromethane	0.0024	ND
1,2-Dichloroethane	ND	ND
1,1,1-Trichloroethane	ND	ND
1,2,2-Trichloroethane	ND	ND
1,2,3-Trichloroethane	ND	ND
Tetrachloromethane	ND	ND
1,2-Dichloropropane	ND	ND
1,2-Dichloropropane	ND	ND
Trichloroethylene	ND	ND
Tetrachloroethylene	ND	ND
1,1,1,2-Tetrachloroethane	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND
Hexachloroethane	ND	ND
Inorganics (mg/L):		
Iron	0.14	0.02
Manganese	0.01	5.3
Mercury	ND	ND
Chromium	4	ND
Cadmium	0.001	0.008
Nickel	ND	0.01
Lead	0.01	ND
Copper	0.08	ND
Zinc	0.08	0.54
Arsenic	ND	ND
Boron	0.10	0.22
Sodium	2	26
Potassium	4	14
Calcium	5	110
Magnesium	2	28
Anions (mg/L):		
Chloride	5	24
Fluoride	ND	ND
Sulfate	18	190
Phosphate	ND	ND
Cyanide	ND	ND
Nitrate	4	49

Table II. (Cont.) (adapted from Ref. 17)

Contaminant	Industrial-Water Well No. 118	Drinking-Water Well No. 6
Anions (mg/L):		
Nitrite	0.02	0.02
Ammonium (NH_4-N)	0.1	20
Other Characteristics (mg/L, except as noted):		
pH (dimensionless)	5.27	6.18
Conductivity (μs/cm)	13.0	12.7
Total Organic Carbon	0.4	18
BOD_5	1.8	5.0
$KMnO_4$ Demand	1.1	37
Total Suspended Solids	6	11
Total Dissolved Solids	25	740
Residue	5	445
Buffer Capacity (mmol/L)	0.15	2.9

[a] ND = Not Detected.

Table III. Physical and Chemical Characteristics of Soils Collected[a]

Range	Depth (cm)	Soil pH	% Carbon	CEC (g mole/kg)	Soil Texture (g/kg)			Textural Class
					Sand	Silt	Clay	
Handgun	0	5.8	1.99	12.43	750	180	70	Sandy Loam
Rifle	15	7.1	2.20	17.57	690	210	100	Sandy Loam
Rifle	7	7.4	0.78	7.47	770	160	70	Sandy Loam
Rifle	0	7.1	1.19	6.23	810	120	70	Loamy Sand
Rifle	60	7.7	0.23	1.69	800	130	70	Loamy Sand
Hand Grenade	0	8.7	0.31	4.85	750	130	120	Sandy Loam
	10	8.0	0.37	4.69	800	130	70	Loamy Sand
Detection Limits		0.1	0.01	0.05	10	10	10	

[a] Analyzed in the Reclamation Engineering and Geosciences Laboratory at ANL.

Table IV. "Dutch List" of Heavy Metals with Category Contamination Levels for Soil and Groundwater

Heavy Metal	Concentration in Soil (mg/kg)			Concentration in Groundwater (µg/L)		
	Category A*	Category B*	Category C*	Category A*	Category B*	Category C*
Arsenic (As)	--	30	50	--	30	100
Barium (Ba)	200	400	2000	50	100	500
Cadmium (Cd)	--	5	20	--	2.5	10
Chromium (Cr)	--	250	800	--	50	200
Cobalt (Co)	20	50	300	20	50	200
Copper (Cu)	--	100	500	--	50	200
Lead (Pb)	--	150	600	--	50	200
Mercury (Hg)	--	2	10	--	0.5	2
Nickel (Ni)	--	100	500	--	50	150
Tin (Sn)	20	50	300	10	30	150
Zinc (Zn)	--	500	3000	--	200	800

Source: Ref. 19.

*Category A: Baseline Concentration.
Category B: Detailed Investigation Needed.
Category C: Remedial Investigation Needed.

Table V. Results of Chelant Extraction from Treated Soil (Batch Studies)

Sample No.	pH	Element Concentration, (mg/kg)					
		Pb	Cd	Cu	Cr	Ba	Zn
Citric Acid							
R111 -S037	5.92	9.06	17.3	~0	0.140	204	902
	6.41	10.2	19.4	~0	0.140	637	624
	7.70	10.2	**21.1**	~0	0.139	684	780
R111 -S038	6.24	8.04	17.8	~0	0.140	119	1380
	6.74	12.8	**22.0**	~0	0.140	532	1480
	7.73	12.8	**25.1**	~0	0.139	665	1350
R111 -S039	6.30	10.4	**31.6**	~0	0.140	338	413
	6.32	10.5	**46.3**	~0	0.139	618	562
	7.42	9.31	**62.9**	~0	0.139	718	568
R111 -S041	5.86	~0	3.08	~0	~0	~0	141
	6.50	0.26	**39.9**	~0	~0	490	129
	7.60	0.28	**40.2**	~0	~0	534	109
R111 -S044	6.43	1.51	11.7	~0	~0	119	153
	6.75	1.51	15.5	~0	~0	499	300
	7.26	0.28	14.0	~0	~0	348	4.82
R111 -S049	3.26	~0	~0	~0	~0	16.2	~0
	5.16	~0	~0	~0	~0	17.7	~0
	7.09	~0	~0	~0	~0	15.7	~0
EDTA							
R111 -S037	6.72	~0	11.2	~0	0.140	243	861
	7.11	~0	11.3	~0	0.140	633	902
	7.23	~0	15.4	~0	0.140	613	906
R111 -S038	6.88	~0	10.9	~0	0.139	233	1390
	6.98	~0	15.1	~0	0.140	598	465
	7.20	~0	15.0	~0	0.139	797	997
R111 -S039	6.40	~0	0.48	~0	0.139	46.7	223
	6.85	~0	10.8	~0	0.138	550	343
	7.19	~0	16.7	~0	0.139	628	381
R111 -S041	6.21	~0	~0	~0	~0	30.6	~0
	6.89	~0	~0	~0	~0	246	~0
	7.43	~0	3.02	~0	~0	417	~0
R111 -S044	6.70	~0	2.96	~0	~0	121	~0
	7.32	~0	7.79	~0	~0	340	29.7
	7.85	~0	9.44	~0	~0	474	83.5
R111 -S049	3.18	~0	~0	~0	~0	15.0	~0
	5.08	~0	~0	~0	~0	17.7	~0
	7.10	~0	~0	~0	~0	0.70	~0
Soils (mg/kg):							
Category A	--	--	--	--	--	200	--
Category B	--	150	5.0	100	250	400	500
Category C	--	600	20	500	800	2000	3000

Table VI. Comparison of Lead, Cadmium, and Copper Concentrations in the Treated and Untreated Soils

Sample No.	pH	Element Concentration (mg/kg)					
		Pb		Cd		Cu	
		Untreated	Treated	Untreated	Treated	Untreated	Treated
Citric Acid							
R111 -S037	5.92	112	9.06	**31.1**	17.3	276	~0
	6.41	112	10.2	**31.1**	19.4	276	~0
	7.70	112	10.2	**31.1**	**21.1**	276	~0
R111 -S038	6.24	152	8.04	**32.3**	17.8	370	~0
	6.74	152	12.8	**32.3**	**22.0**	370	~0
	7.73	152	12.8	**32.3**	**25.1**	370	~0
R111 -S039	6.30	90.6	10.4	**94.6**	**31.6**	**1560**	~0
	6.32	90.6	10.5	**94.6**	**46.3**	**1560**	~0
	7.42	90.6	9.31	**94.6**	**62.9**	**1560**	~0
R111 -S041	5.86	70.1	~0	**32.5**	3.08	364	~0
	6.50	70.1	0.26	**32.5**	**39.9**	364	~0
	7.60	70.1	0.28	**32.5**	**40.2**	364	~0
R111 -S044	6.43	70.7	1.51	**73.6**	11.7	322	~0
	6.75	70.7	1.51	**73.6**	15.5	322	~0
	7.26	70.7	0.28	**73.6**	14.0	322	~0
R111 -S049	3.26	26.0	~0	1.0	~0	11.0	~0
	5.16	26.0	~0	1.0	~0	11.0	~0
	7.09	26.0	~0	1.0	~0	11.0	~0
EDTA							
R111 -S037	6.72	112	~0	**31.1**	11.2	276	~0
	7.11	112	~0	**31.1**	11.3	276	~0
	7.23	112	~0	**31.1**	15.4	276	~0
R111 -S038	6.88	152	~0	**32.3**	10.9	370	~0
	6.98	152	~0	**32.3**	15.1	370	~0
	7.20	152	~0	**32.3**	15.0	370	~0
R111 -S039	6.40	90.6	~0	**94.6**	0.48	**1560**	~0
	6.85	90.6	~0	**94.6**	10.8	**1560**	~0
	7.19	90.6	~0	**94.6**	16.7	**1560**	~0
R111 -S041	6.21	70.1	~0	**32.5**	~0	364	~0
	6.89	70.1	~0	**32.5**	~0	364	~0
	7.43	70.1	~0	**32.5**	3.02	364	~0
R111 -S044	6.70	70.7	~0	**73.6**	2.96	322	~0
	7.32	70.7	~0	**73.6**	7.79	322	~0
	7.85	70.7	~0	**73.6**	9.44	322	~0
R111 -S049	3.18	26.0	~0	1.0	~0	11.0	~0
	5.08	26.0	~0	1.0	~0	11.0	~0
	7.10	26.0	~0	1.0	~0	11.0	~0
Soils (mg/kg):							
Category A	--	--	--	--	--	--	--
Category B	--	150	150	5.0	5.0	100	100
Category C	--	600	600	20	20	500	500

Table VII. Comparison of Chromium, Barium, and Zinc Concentrations in the Treated and Untreated Soils

Sample No.	pH	Element Concentration, (mg/kg)					
		Cr		Ba		Zn	
		Untreated	Treated	Untreated	Treated	Untreated	Treated
Citric Acid							
R111 -S037	5.92	34.8	0.140	97.3	204	**5680**	902
	6.41	34.8	0.140	97.3	**637**	**5680**	624
	7.70	34.8	0.139	97.3	**684**	**5680**	780
R111 -S038	6.24	41.8	0.140	115	119	691	1380
	6.74	41.8	0.140	115	**532**	691	1480
	7.73	41.8	0.139	115	**665**	691	1350
R111 -S039	6.30	27.7	0.140	94.8	338	976	413
	6.32	27.7	0.139	94.8	**618**	976	562
	7.42	27.7	0.139	94.8	**718**	976	568
R111 -S041	5.86	44.4	~0	164	~0	703	141
	6.50	44.4	~0	164	**490**	703	129
	7.60	44.4	~0	164	**534**	703	109
R111 -S044	6.43	25.8	~0	92.0	119	48.6	152
	6.75	25.8	~0	92.0	**499**	48.6	299
	7.26	25.8	~0	92.0	348	48.6	4.82
R111 -S049	3.26	16.3	~0	61.0	16.2	--	~0
	5.16	16.3	~0	61.0	17.7	--	~0
	7.09	16.3	~0	61.0	15.7	--	~0
EDTA							
R111 -S037	6.72	34.8	0.140	97.3	**243**	**5680**	861
	7.11	34.8	0.140	97.3	**633**	**5680**	902
	7.23	34.8	0.140	97.3	**613**	**5680**	905
R111 -S038	6.88	41.8	0.139	115	233	691	1390
	6.98	41.8	0.140	115	**598**	691	465
	7.20	41.8	0.139	115	**797**	691	997
R111 -S039	6.40	27.7	0.139	94.8	46.7	976	223
	6.85	27.7	0.138	94.8	**550**	976	343
	7.19	27.7	0.139	94.8	**628**	976	381
R111 -S041	6.21	44.4	~0	164	30.6	703	~0
	6.89	44.4	~0	164	246	703	~0
	7.43	44.4	~0	164	**417**	703	~0
R111 -S044	6.70	25.8	~0	92.0	121	48.6	~0
	7.32	25.8	~0	92.0	340	48.6	29.7
	7.85	25.8	~0	92.0	**474**	48.6	83.5
R111 -S049	3.18	16.3	~0	61.0	15.0	--	~0
	5.08	16.3	~0	61.0	17.7	--	~0
	7.10	16.3	~0	61.0	0.70	--	~0
Soils (mg/kg):							
Category A	--	--	--	200	200	--	--
Category B	--	250	250	400	400	500	500
Category C	--	800	800	2000	2000	3000	3000

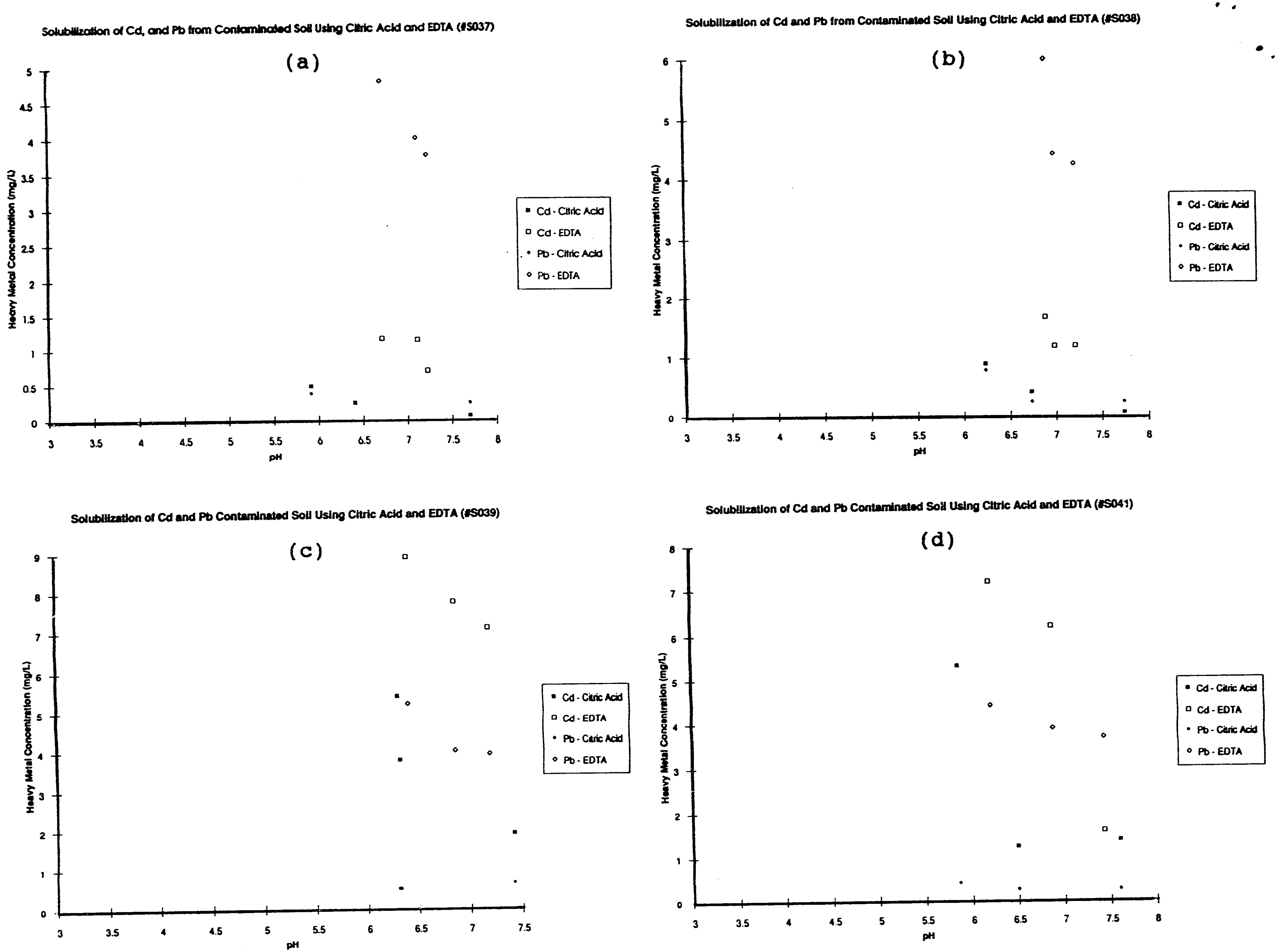
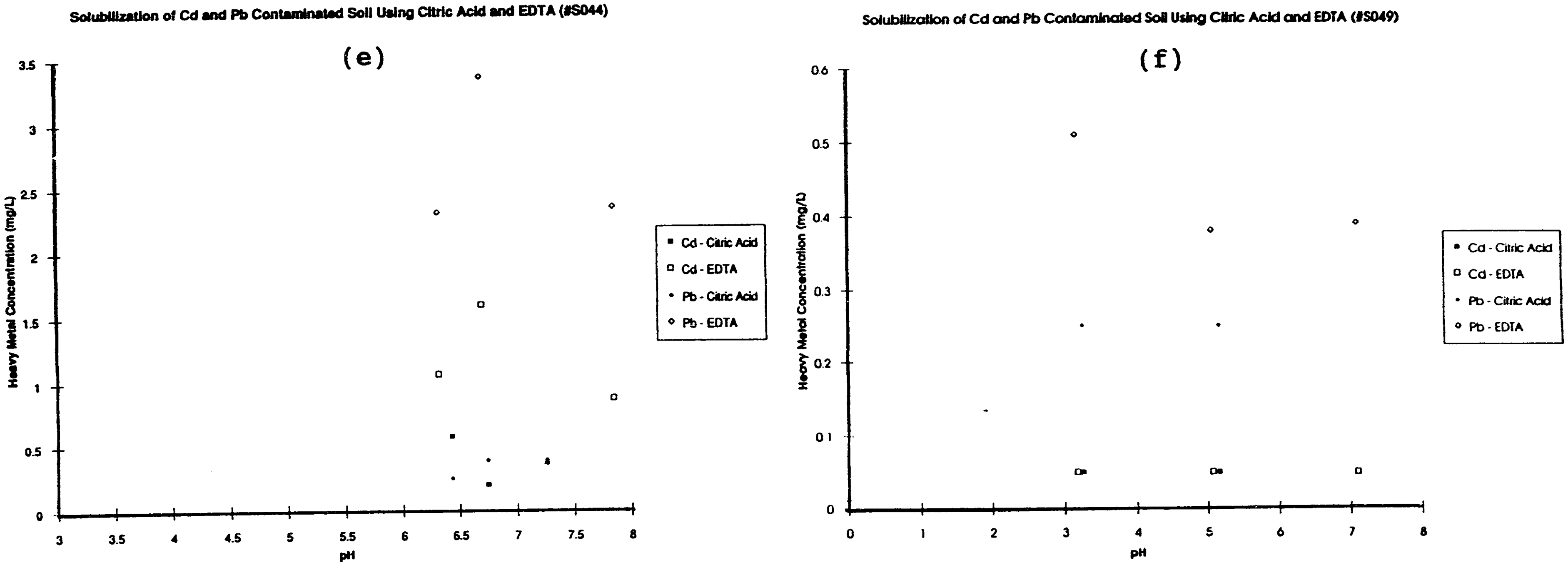


Figure 1. Solubilization of heavy metals (cadmium and lead) using 0.01 M citric acid and 0.01 M EDTA from contaminated soil samples: (a) S-037, (b) S-038, (c) S-039, and (d) S-041.


Solubilization of Cd and Pb Contaminated Soil Using Citric Acid and EDTA (#S044)

Solubilization of Cd and Pb Contaminated Soil Using Citric Acid and EDTA (#S049)

Figure 1. (Cont.) Solubilization of heavy metals (cadmium and lead) using 0.01 M citric acid and 0.01 M EDTA from contaminated soil samples: (e) S-044 and (f) S-049.

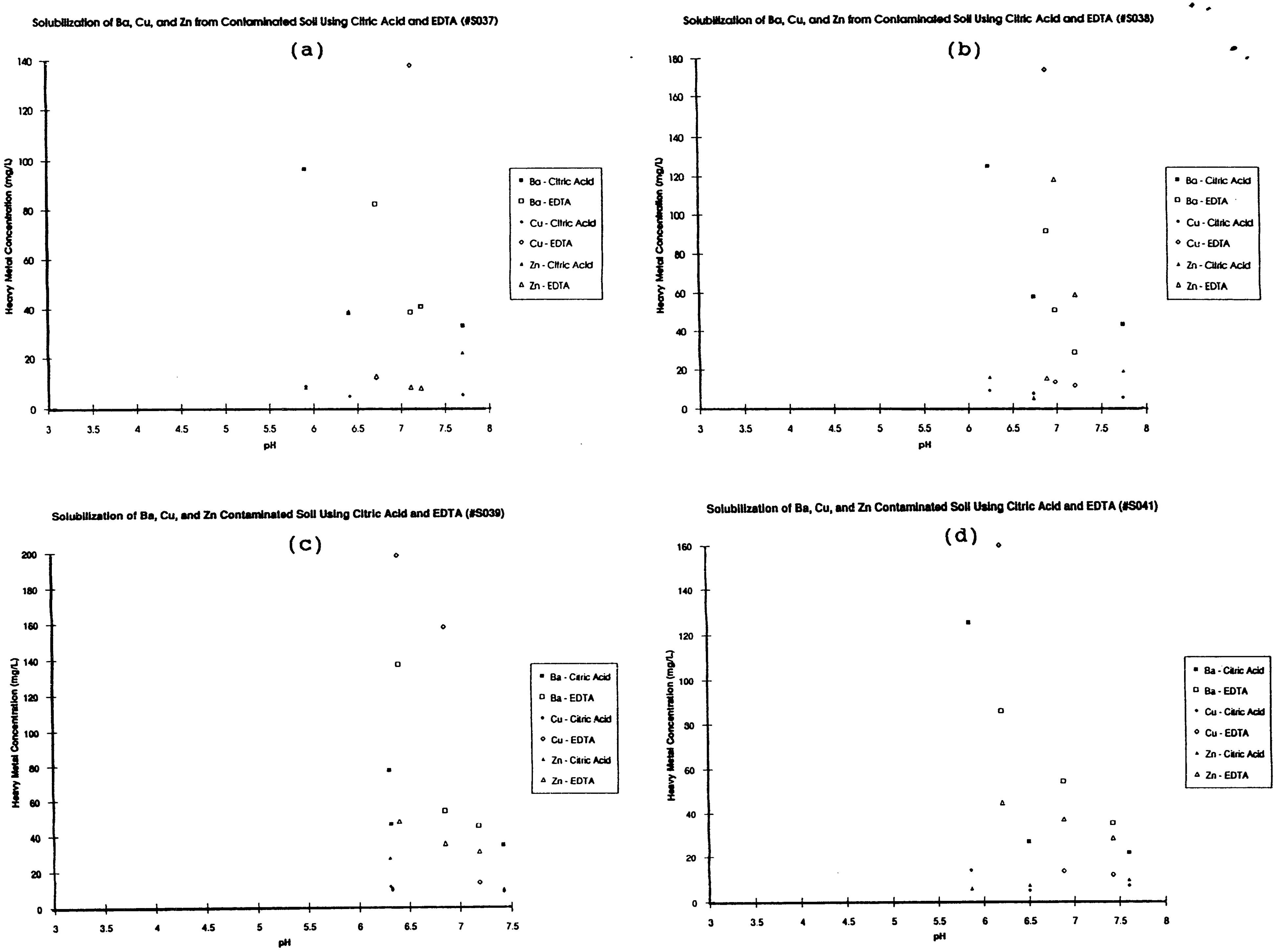


Figure 2. Solubilization of heavy metals (barium, copper, and zinc) using 0.01 M citric acid and 0.01 M EDTA from contaminated soil samples: (a) S-037, (b) S-038, (c) S-039, and (d) S-041.

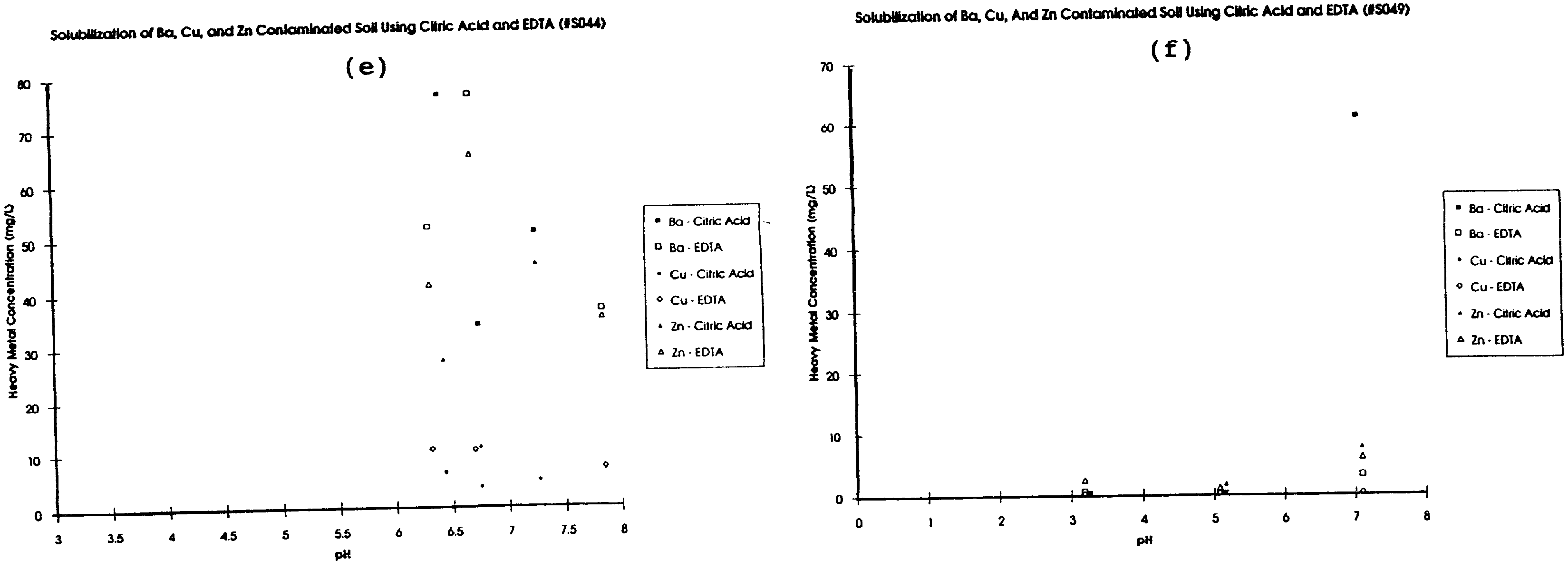


Figure 2. (Cont.) Solubilization of heavy metals (barium, copper, and zinc) using 0.01 M citric acid and 0.01 M EDTA from contaminated soil samples: (e) S-044 and (f) S-049.

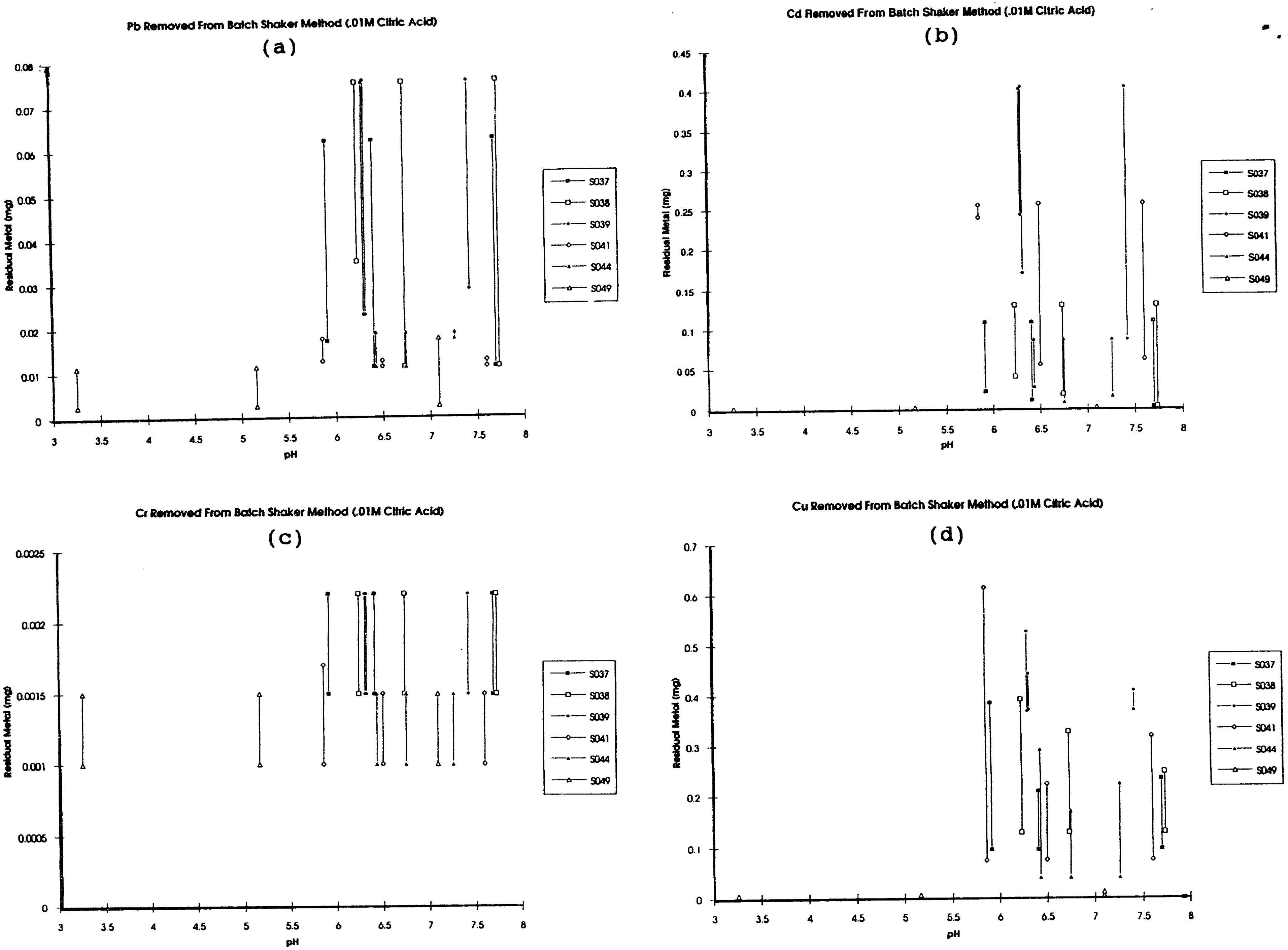


Figure 3. Initial and final heavy-metal concentrations from six soil samples as a function of pH for batch chelant extraction with 0.01 M citric acid for (a) Pb, (b) Cd, (c) Cr, and (d) Cu.

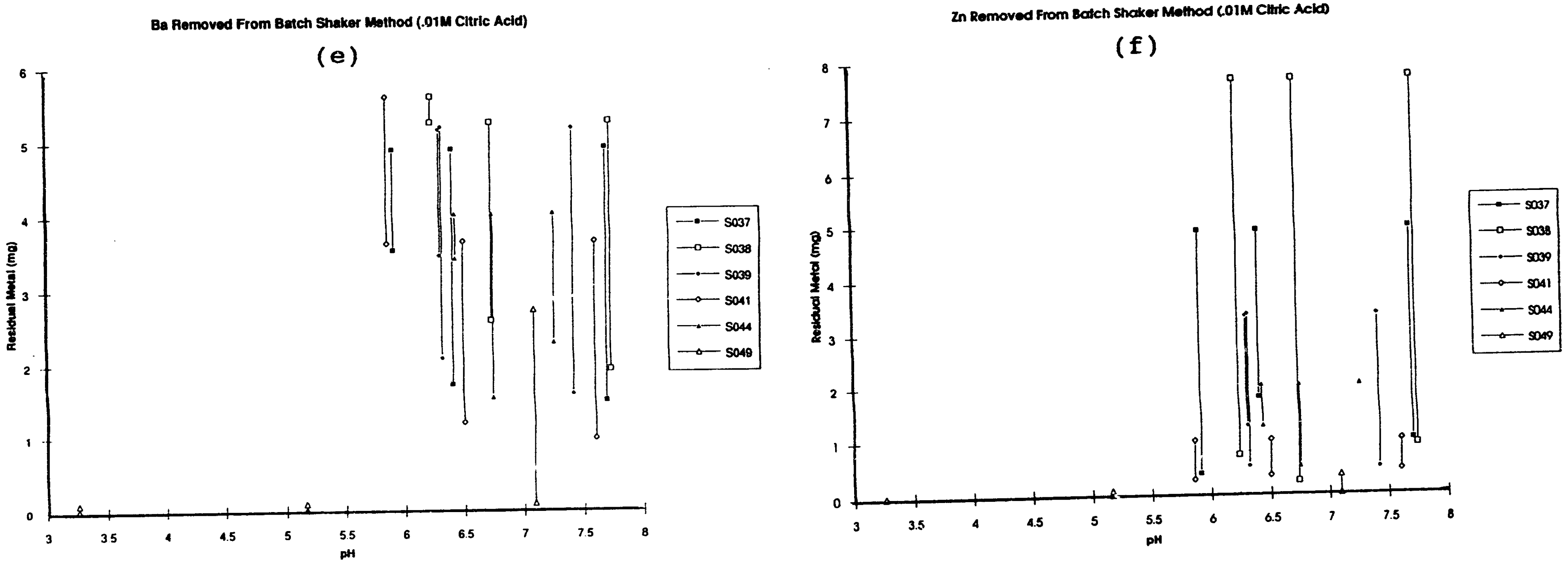


Figure 3. (Cont.) Initial and final heavy-metal concentrations from six soil samples as a function of pH for batch chelant extraction with 0.01 M citric acid for (e) Ba and (f) Zn.

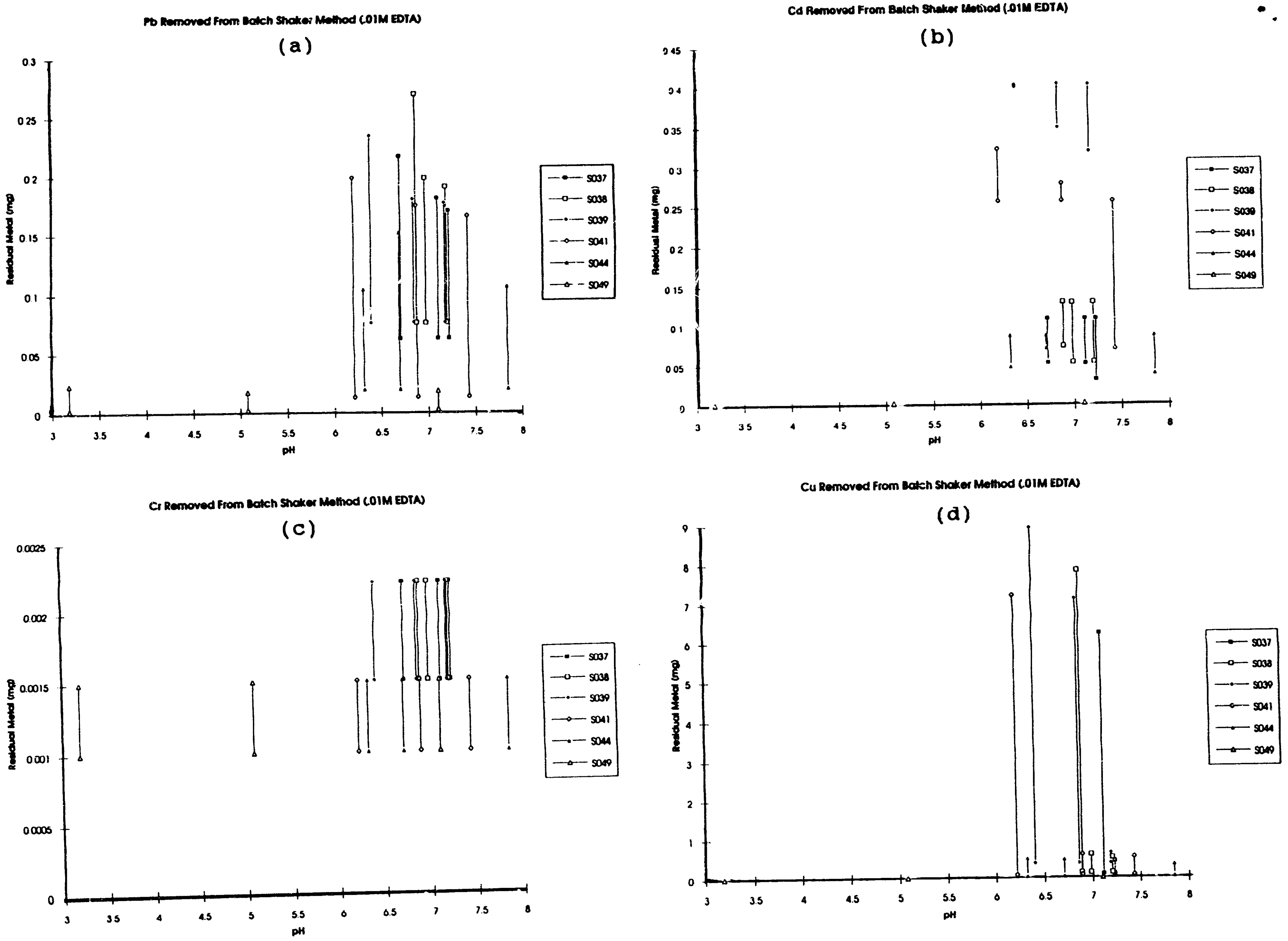


Figure 4. Initial and final heavy-metal concentrations from six soil samples as a function of pH for batch chelant extraction using 0.01 M EDTA for (a) Pb, (b) Cd, (c) Cr, and (d) Cu.

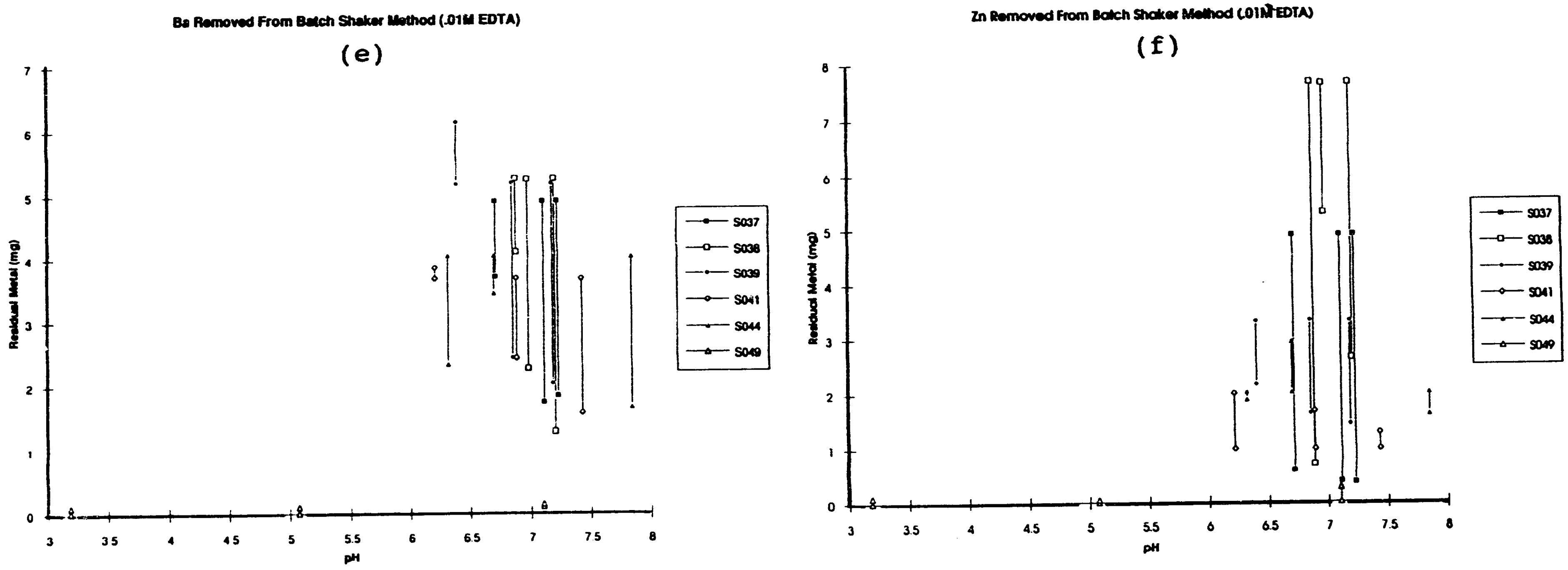


Figure 4. (Cont.) Initial and final heavy-metal concentrations from six soil samples as a function of pH for batch chelant extraction using 0.01 M EDTA for (e) Ba and (f) Zn.

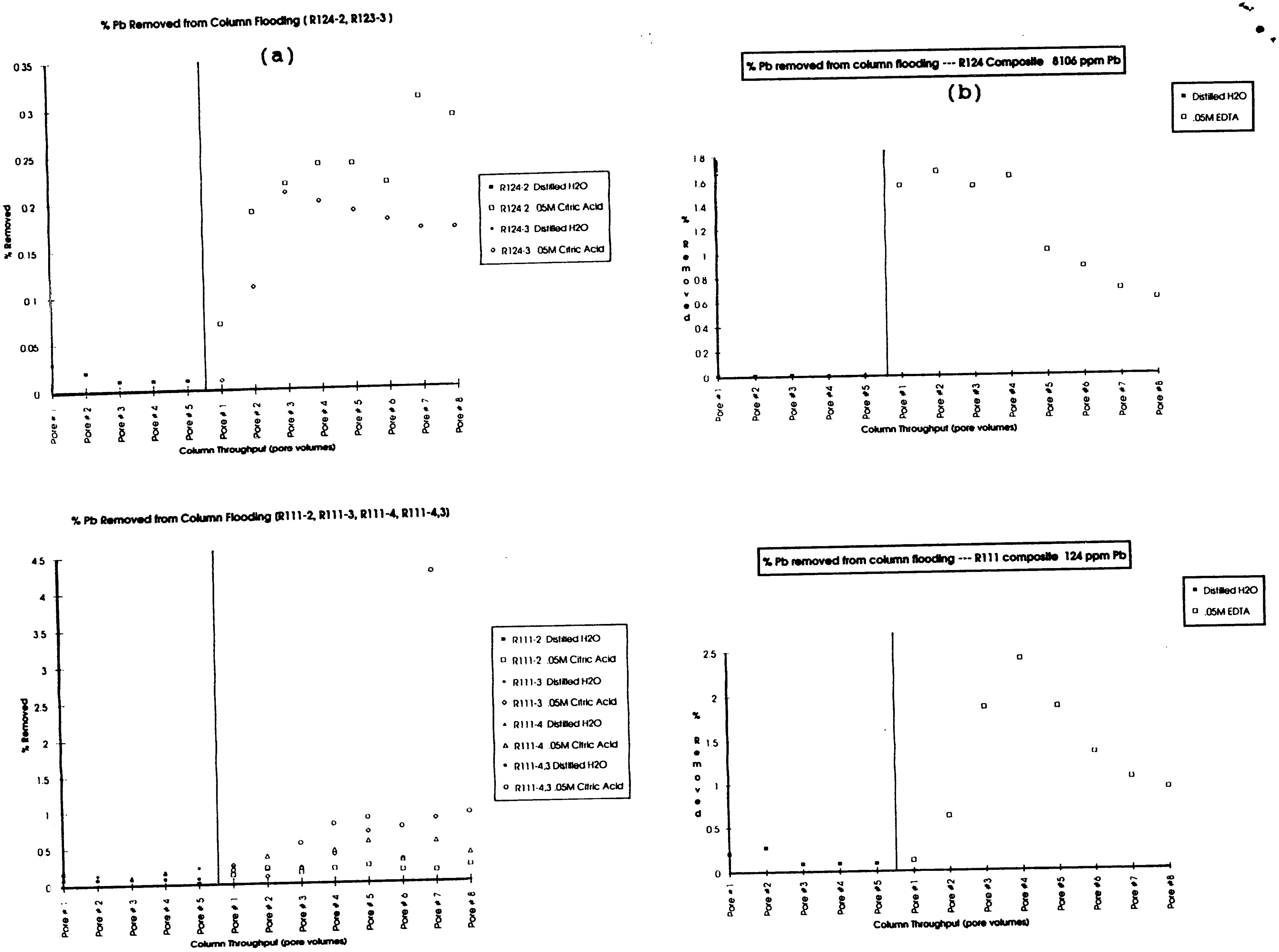


Figure 5. Columnar extraction of lead from contaminated soil using (a) 0.05 M citric acid or (b) 0.05 M EDTA.

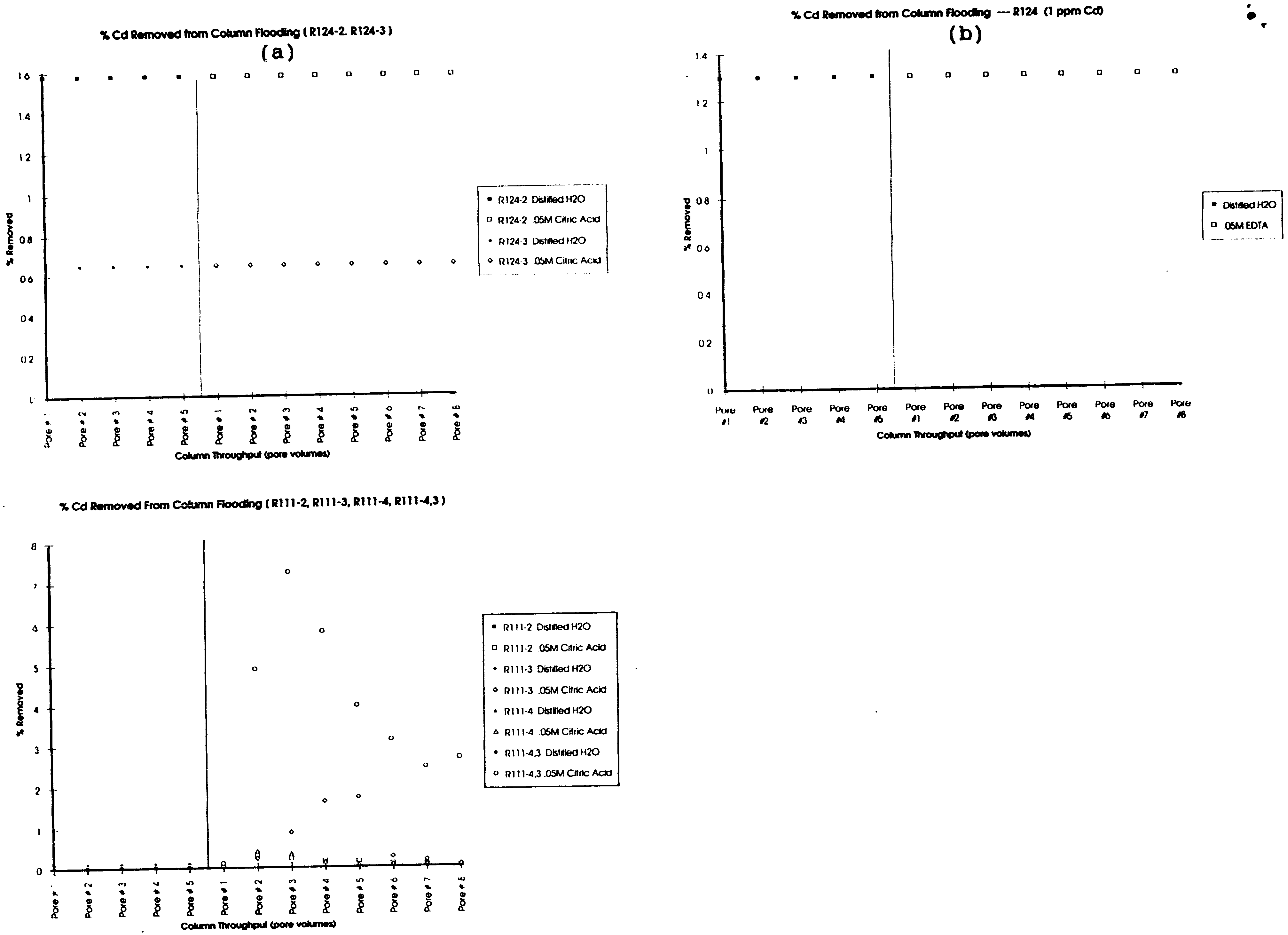


Figure 6. Columnar extraction of cadmium from contaminated soil using (a) 0.05 M citric acid or (b) 0.05 M EDTA.

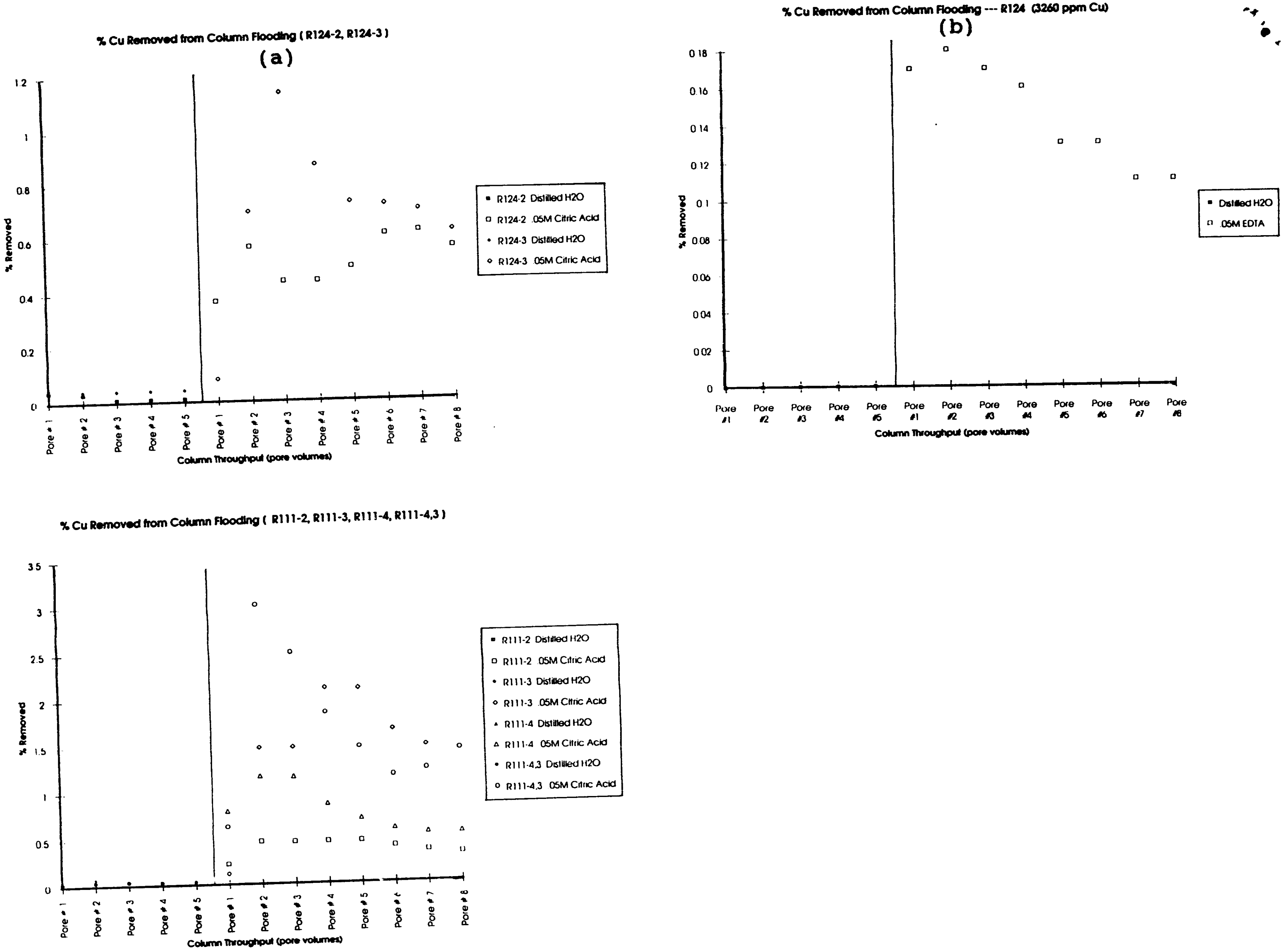


Figure 7. Columnar extraction of copper from contaminated soil using (a) 0.05 M citric acid or (b) 0.05 M EDTA.

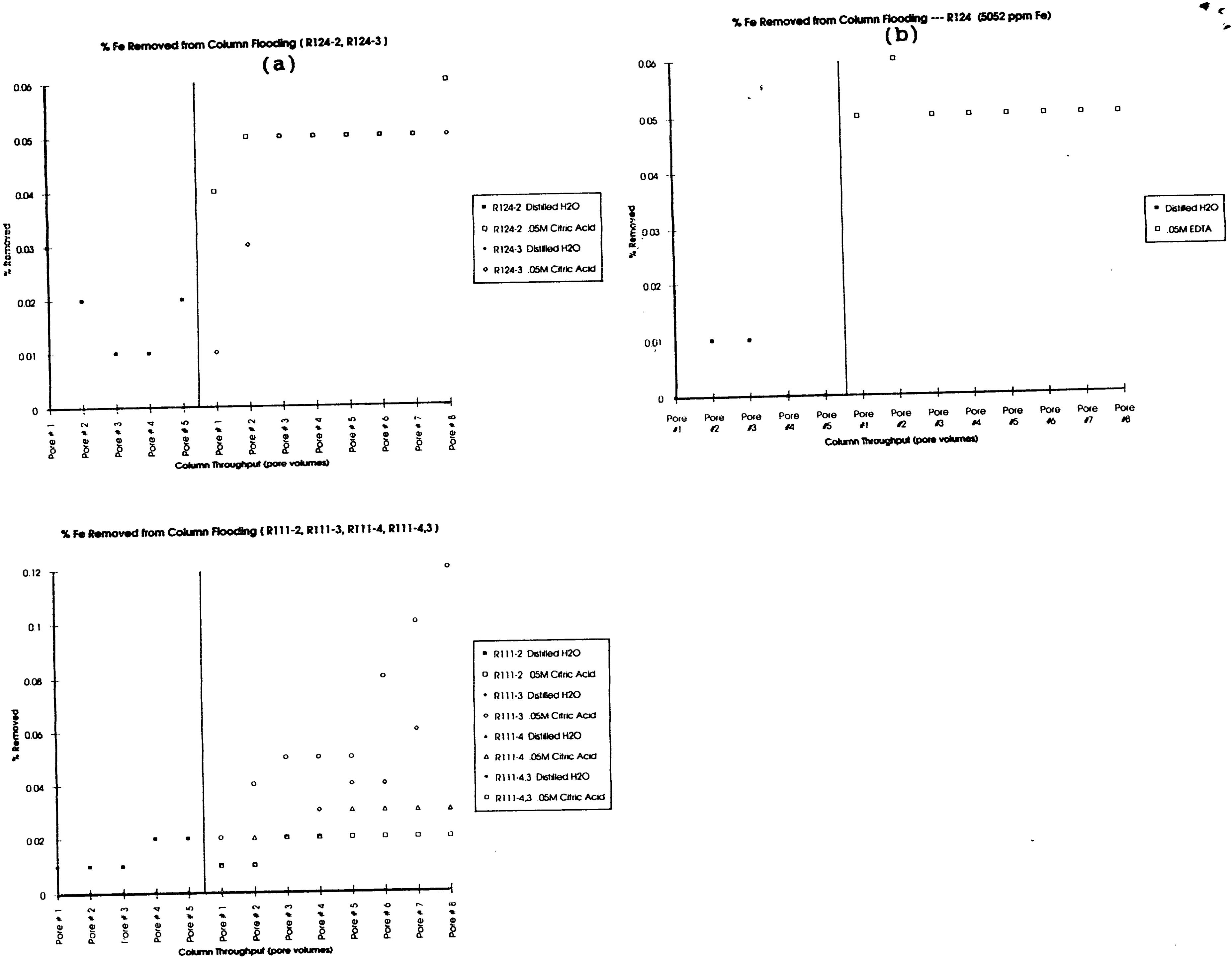


Figure 8. Columnar extraction of iron from contaminated soil using (a) 0.05 M citric acid or (b) 0.05 M EDTA.

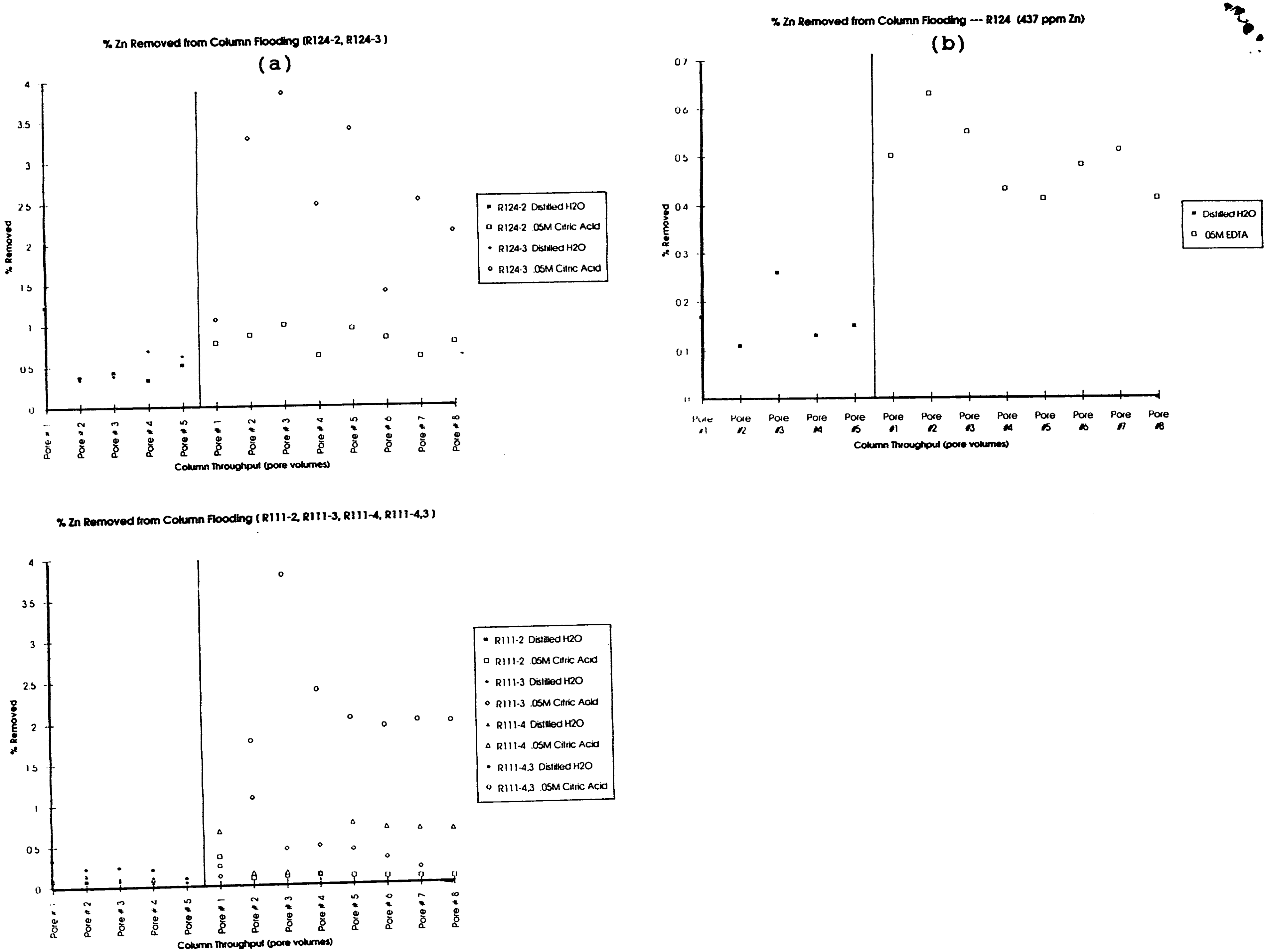


Figure 9. Columnar extraction of zinc from contaminated soil using (a) 0.05 M citric acid or (b) 0.05 M EDTA.

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