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USE OF A CHELATING AGENT TO DETERMINE THE METAL AVAILABILITY FOR LEACHING FROM SOILS AND WASTES

Andrew C. Garrabrants and David S. Kosson
Department of Chemical and Biochemical Engineering
Rutgers, the State University of New Jersey
Piscataway, NJ, USA 08855-0909

ABSTRACT

Use of the available content of elements, or availability, as the thermodynamic driving force for release can provide a more realistic assessment of leaching potential than total elemental content. Availability is often measured by an extraction procedure using a high liquid-solid (LS) ratio and pH control at levels which maximize solubility within the limits of a reasonable release scenario (e.g., pH 4.0 for cations and pH 8.0 for oxyanions). An alternative extraction procedure using ethylene diamine tetraacetic acid (EDTA) as a chelating agent was evaluated to eliminate the need for rigorous pH control and provide a single extraction step method. The availability of As, Cd, Cu, Mn and Pb in four materials, representing both treated and untreated soils and wastes, were tested using the EDTA procedure. The approach of a Dutch availability test, NEN 7341, and total elemental content were used as a basis for comparison of results.

INTRODUCTION

Accurate determination of inorganic contaminant leachability from soils and waste is essential for risk assessment and hazardous waste management decision-making. An often misleading estimate of inorganic leachability from wastes and soils is to measure the total constituent concentration in the solid phase and assume that mass release continues until depletion. A protocol that accurately determines the mobile, or available, fraction of a constituent in a solid matrix is important for assessment and release models. The resulting measure of "availability" can be viewed as (i) the potentially mobile content of an element or (ii) the element content which serves as the thermodynamic source or driving force for release. In the latter context, availability has been used in conjunction with solubility data and observed diffusivities from monolith leach tests to estimate contaminant release for a variety of environmental scenarios (1-3).

In past experimentation, these fixed and mobile fractions have been referred to as "detrial" and "non-detrial" fractions, respectively, and have been quantified by a number of sequential extraction techniques with increasingly aggressive extractants (4-6). The non-detrial, or available, fraction has been observed to include water soluble, exchangeable, and specifically or physically absorbed constituents (7). The available fraction of the total constituent concentration, therefore, refers to that amount that is leachable from the solid phase, excluding that which is immobilized by incorporation into glassy, amorphous, or geologically stable mineral forms (8). Theoretically, measurement of the available fraction should be carried out under conditions that permit complete solubilization of the elements of concern in mineral phases which could solubilize under credible extreme environmental scenarios. For example, a standardized availability test, NEN 7341 (9), uses pH 4.0 and 7.0 as conditions for solubilization of potential toxic cations and oxyanions, respectively. A large fraction of solubilization is anticipated by use of reduced particle size (e.g., $\leq$ 300 μm) and high liquid-solid ratio (e.g., 50 ml/g) for each extraction step. This approach has been criticized because the specified time intervals can be insufficient to approach complete solubilization or equilibrium and, despite high LS ratios, mass release of some low solubility constituents may be limited by saturation of the aqueous phase (1, 10). Suggested alternative approaches to measurement of the available fraction have included smaller particle sizes, longer extraction intervals, and long-term leaching to depletion (1, 10, 11).

Development of a readily implemented test to measure availability requires that (i) fractional solubilization be maximized over the range of environmentally significant pH values, (ii) extractions be completed in a short time frame (e.g., 48 hours) and (iii) sample preparation, manipulations and specialized equipment needs should be minimized. The approach explored in this paper is the use of a chelating agent at neutral pH in a single step extraction to achieve the above objectives. By using a chelating agent during extraction to relax metal solubility limitations in the extraction fluid, it is hypothesized that a rigorous estimate of the maximum constituent fraction available for release can be measured.

OBJECTIVES AND EXPERIMENTAL DESIGN

The specific objectives of the work presented here were to (i) optimize a chelation extraction procedure to determine the availability of inorganic constituents from wastes and soils using a single waste, (ii) evaluate the application of the optimized test to several waste types, and (iii) compare the results of the chelation procedure to the total elemental content and the availability measured using the approach described by NEN 7341 (9). The experimental factors evaluated during test method optimization were (i) liquid-solid ratio at two levels (50 and 100 ml/g), (ii) chelating agent concentration at three levels (50, 100 and 150 mM) and (iii) contact time at three levels (18, 24 and 48 hours). An extraction pH of 7.0 ± 0.5 was selected to maximize solubility of anions simultaneously with increasing solubility of cations through chelation. The availability of arsenic, lead, cadmium, copper and manganese was determined in this study. Arsenic and manganese represent those elements that are capable of speciation as oxy-anions. Lead, arsenic and cadmium are common toxic cations in many soils and waste. Manganese and copper are important plant nutrients that may be toxic to plant life at high soil concentrations.

The release of a constituent with time is an asymptotic process, and for a given LS ratio the system can be considered at equilibrium when no significant time effect on the liquid phase concentration is observed. The required contact time to reach equilibrium is dependent on the particle radius due to mass transfer rate limitations in larger particles. Since short testing times are desirable, the diameter of the solid material particles must be small enough to minimize mass transfer rate constraints. However, particle size reduction usually requires a grinding or milling process that can be cumbersome or impractical. NEN 7341 suggests that three to four hour contact times are adequate to achieve equilibrium for particles of ≤300 μm maximum diameter (9). Fällman et al. (10) have shown that some low solubility metals may be mass transfer constrained within this time interval and recommended that a minimum 24 hour contact time with size reduction to ≤ 125 μm diameter particles. For this study, a maximum particle size of 300 μm was used based on preliminary testing and system modeling which indicated that equilibrium conditions could be achieved in less than 48 hours (10).

Ethylene diamine tetraacetic acid (EDTA) was chosen as the chelating agent because of a high affinity for a wide range of cationic metals (12). EDTA is a tetraprotic acid (H_4Y) having four dissociation constants [pKa of 2.00, 2.67, 6.16 and 10.26, yielding H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-} respectively (13)]. At pH 7.0 ± 0.5, the primary form of EDTA will be the singly protonated acid (HY^{3-}). Below a pH of 6.16, the doubly protonated form of EDTA exists with stability constants that differ from the above form by several orders of magnitude. Table 1 presents the metal-complex stability constants for many common metals with the protonated forms of EDTA prevalent at near-neutral pH along with solubility constants for each metal hydroxide form. The large stability constants illustrate that the presence of EDTA can significantly increase metal solubility, often by many orders of magnitude, by formation of soluble metal-chelates. The extraction potential of EDTA concentrations at or less than 100 mM have been studied in releation to remediation of contaminated soils (7, 13-16). For this optimization, EDTA concentrations higher than those previously reported in literature also were investigated

Initial optimization of the test procedures was carried out using municipal solid waste incinerator (MSWI) combined air pollution control residue and bottom ash (17). This waste type offers measurable quantities of many metal contaminants, and therefore the effectiveness of the test parameters can be evaluated for a number of constituent behaviors. For the comparison portion of this study, four wastes were studied that are representative of common waste types with differing physical and chemical properties. In addition to the MSWI combined ash, two different field contaminated soils and a contaminated soil treated by solidification/stabilization (S/S) were tested. The total concentration of principle contaminants for each waste is summarized in Table 2.

EXPERIMENTAL METHODS

Prior to sample extraction for measurement of availability, each sample was titrated with sodium hydroxide solution in the presence of the desired EDTA concentration to determine the quantity of sodium hydroxide required to achieve a final pH of 7.0±0.5. Aliquots of base were added to 2 g samples of particle size reduced material and agitated for 24 hours in a reciprocating shaker. Separate titrations at LS ratios of 50 ml/g dry and 100 ml/kg dry were conducted to mimic test conditions. For the optimization study, eighteen extraction conditions were conducted in duplicate. A 4 g sample of MSWI combined ash was put into each of thirty-six 500 ml HDPE extraction vessels. One of three EDTA concentration leachants was added to each extraction vessel at the proper volume for each LS ratio (i.e., 50 and 100 ml/kg dry). The required equivalents of sodium hydroxide was added to achieve a final solution pH of 7.0±0.5. When all of the extractions were setup, the 36 bottles were arranged in a random order on a reciprocal shaker for the required contact time applicable for each extraction (i.e., 18, 24, or 48 hours).

After the appropriate contact time, six extractions representing the two desired LS ratios at three EDTA concentrations were removed from the tumbler. Each extraction was allowed to settle for 10 minutes to segregate solid and liquid phases. Approximately 5 ml of the supernatant was removed from each extract so that the pH of the leachate could be measured. The remainder of each the leachate was filtered by vacuum through a 0.45 μm pore size polypropylene filtration membrane held in a polycarbonate filtration apparatus. The samples were not acid-preserved prior to analysis to prevent precipitation of EDTA salts at very low pH.

All aqueous solutions were prepared with de-ionized water. Aqueous solutions of EDTA were mixed at the three concentrations (e.g., 50, 100, 150 mM) using ACS certified disodium, dihydrate salt of EDTA (Sigma Chemical Co., St. Louis, MO). 10 N sodium hydroxide solution (Fisher Scientific, Bridgewater, NJ) was used to adjust for solution pH as necessary. All extractions were carried out in 500 ml high density polyethylene (HDPE) bottles. Extraction slurries were filtered through polycarbonate filter membrane holders and 0.45 μm pore size polypropylene filtration membranes (Fisher Scientific, Bridgewater, NJ).

A sequential extraction approach similar to NEN 7341 was used as a comparison to the EDTA procedure. A 10 g test sample was sequentially extracted in DI water at a LS ratio of 50 ml/g under static pH conditions. For the two extractions, the solution pH was maintained at pH values of 7.0 and 4.0, respectively, with a pH controller that delivered 0.5 N nitric acid into the reaction vessel. After the first extraction contact time of four hours at a pH of 7.0, the sample was filtered through a 0.45 μm pore size polypropylene membrane and an analytical sample preserved. The solid was returned to the reaction vessel and extracted with an additional 50 ml/g of DI water at a pH of 4.0 for three hours. At the end of the second interval, the extract was filtered and another analytical sample was preserved for chemical analysis. The samples were analyzed separately and the released constituent masses for each extract were combined to determine the availability. For materials without sufficient acid neutralization capacity, a parallel batch procedure was used to yield one extract at each solution pH. Since these were parallel extractions, the released masses were not combined to determine constituent availability.

All of the extraction samples were analyzed within one week after generation. A Varian Model 640 flame atomic absorption spectrophotometer was used to analyzed the preserved samples for As, Cd, Cu, Pb, and Mn. All analytical samples were analyzed using the same bulk standard and performance check solution.

DATA REDUCTION AND STATISTICAL DESIGN

Availability was calculated from the analytical data by multiplying the leachate concentration by the appropriate LS ratio,

$$AVL_{i,x} = (C_{i,x})(LS_i) \qquad \text{Equation 1}$$

where:

- $AVL_{i,x}$ is the availability of constituent "x" for treatment "i" [mg/kg dry],
- $C_{i,x}$ is the concentration of constituent "x" for treatment "i" [mg/l], and
- LS_i is the liquid-solid ratio for treatment "i" [ml/g dry].

For the statistical design of the procedure optimization, the primary experimental factors were (i) the concentration of leachant EDTA at three levels (50, 100, and 150 mM), (ii) the LS ratio at two levels (50 and 100 ml/g dry) and (iii) the contact time for each extraction at three levels (18, 24, 48 hours). Figure 1a shows a schematic representation of the experimental design with shaded blocks indicating the treatment combinations that were conducted. The availability values of Cd, Cu, Pb and Mn were optimized examining leverage and prediction plots using the statistical software JMP (18).

The MSWI combined ash samples were particle size reduced and homogenized, then stored in air-tight containers for over five years (17). Since the consistency of homogenization, handling and storage of the replicates could not be verified over this time interval, a Split-Split Plot Blocking Design using replication as a blocking factor was used to minimize significant blocking effects. The whole plot factor for the design was EDTA concentration, the split plot factor was the LS ratio, and contact time was the split-split plot factor. Thirty-six extractions were needed to complete the full factorial.

For the comparison study, the applicability of the optimized treatment combination for a number of wastes types was evaluated and compared to values obtained using the NEN 7341 approach. The applicability of the optimized EDTA procedure was evaluated by comparison to additional extractions performed in parallel by increasing each experimental factor separately. Also, a combined increase of all factors was performed to show if there was significant change in availability due to interactions amongst the factors. Figure 1b shows a schematic representation of this experimental design. To validate that a maximum mass release was extracted, the solid material recovered from the optimized extractions was extracted a second time at the same conditions and the additional mass release was determined. In order to compare the EDTA Availability values derived from each of the five extractions shown in Figure 1b, a oneway ANOVA was conducted using JMP (18) The hypothesis tested was the equality of replicate mean values between extraction conditions within some experimental error.

RESULTS AND DISCUSSION

The objective of the optimization was to statistically determine the optimal combination of experimental factors (i.e., EDTA concentration, LS ratio, and contact time) to maximize the measured availability of Pb, Cu, Cd, and Mn in MSWI combined ash. Once the availability was evaluated for each treatment and response variable, the data residuals were analyzed to determine the significant factors for the availability response of each constituent.

There was no significant effect of EDTA concentrations greater than 50 mM on the availability of Pb, Cu, Cd, and Mn. This is consistent with previous work (13, 15) where EDTA concentrations greater than approximately 10 mM did not result in an increased extraction of Pb, Cu, Mn, and Zn from contaminated soils. The availability data from the optimization study showed an obvious replicate effect for Pb, Cd, and Mn while the availability of Cu did not display a trend due to replication. Since the replication effect was strong enough to outweigh variance due to the experimental factors, the significant factors had to be identified for each constituent response within each replicate. Figure 2 shows two leverage plots for LS ratio on Cu availability that illustrate the difference between a significant factor and a factor that does not have a significant effect on the sample mean. Each leverage plot illustrates how the standard least square model changes when a factor is removed from the model fit. The tested factor is significant if the 95% confidence curves (shown as dashed lines) intersect the sample mean shown on the leverage plot. The main effects (i.e., EDTA concentration, LS ratio and contact time) were found to influence only the availability of copper in one replicate of the MSWI ash. All other constituents showed no significant main effect or interactions other than replication.

Although the main effects were not found to be significant, an optimized combination of experimental factors was found by maximizing the predicted availability responses for all four constituents. Figure 3 presents the prediction profiles from the screening model showing two sets of trends in availability (response variable) as a function of the three experimental factors. In each trend set, the response value extremes for each constituent are shown on the vertical axis while high and low factor values (e.g., EDTA concentration, LS ratio and contact time) are shown on the horizontal axis. The current value for the predicted availability response and factors are shown respectively as gray horizontal and vertical lines. The lines and markers within the plot show how the trend in the predicted response value changes when the current factor values are changed. Error bars represent the 95% confidence interval around the predicted values. Figure 3 also shows the interaction between LS ratio and EDTA concentration. As the LS ratio is increased from 50 ml/g to 100 ml/g at 50 mM EDTA (i.e., shifting from left to right in the figure) the trend in Cd availability changes from nearly flat to a negative trend as a function of EDTA concentration. From these prediction plots, it is clear that availability increases for all constituents when both LS ratio and contact time are maximized.

Since the only observed effect of increasing the concentration of EDTA within the tested range was on the copper availability for only one replicate, the EDTA concentration was minimized to 50 mM in order to address practical considerations. Excess EDTA in analytical solutions hindered chemical analysis and required additional analytical expense. Thus, an overall optimized combination of treatment factors was determined to consist of EDTA concentration of 50 mM, LS ratio of 100 ml/g, and contact time of 48 hrs.

For the comparison study, the objectives were (i) to compared EDTA extraction availability to that determined by NEN 7341 and (ii) to check that the combination of experimental factors optimized for the MSWI combined ash also was applicable for other waste types. There was no statistical difference in extraction means as a result of increasing the experimental factors. Only a replicate effect for Soil 2 was observed to be significant. Therefore, it can be concluded that the variance in availability brought about by sampling, handling, analytical and other experimental errors outweigh the variance as a result of the experimental factors.

In general, the mean EDTA extraction availability values were higher for all material than NEN 7341 availability values. This implies that either the liquid phase of NEN 7341 extractions was solubility-constrained or dilute EDTA solution was able to dissolve a large fraction of the solid phase mineral. Chelators are much less aggressive towards solid phase mineralization than strong acids or caustics (19). For example, the dissolution of Fe oxide phase with EDTA is kinetically controlled and can take up to three months (14). Thus, it was concluded that NEN 7341 was solubility-limited for all constituents in the tested materials.

Figures 4a-4e compare the mass releases measured by NEN 7341 and the EDTA extraction to the total concentration for each constituent and all materials. The fraction of the total constituent that was removed with each technique is presented in Table 3.

Arsenic: Figure 4a shows that only 13% and 8% of the total arsenic for the untreated and S/S treated Soil 2, respectively, was removed under NEN 7341 conditions. In the EDTA extractions, 100% of the arsenic in both materials was found to be available. There was no apparent decrease in the fraction of As that was available as a result of the treatment process of Soil 2 and only the dilution effect on the total concentration by the addition of Portland cement was observed.

Copper: The releases of copper from the tested materials were all significantly less than the total Cu concentration regardless of the extraction technique (Figure 4b). This shows that some of the copper may be incorporated in detrial mineral phases. In general EDTA was able to remove approximately 40-60% of the total copper whereas only 20% was found to be available by the NEN 7341 approach.

Lead: Figure 4c shows that 100% of the total concentration[1] was available by the EDTA extraction for all but the S/S treated soil. The fixation effect due to treatment of this material reduced the available fraction of Pb to 64% over the untreated sample. When the NEN 7341 approach was used to determine available Pb in the treated and untreated Soil 2, the lead concentration in the extract was less than the analytical detection limit. NEN 7341 data would indicate that all of the lead present in Soil 2 is unavailable for release. The discrepancy between NEN 7341 and EDTA availability values may be explained by the speciation of Pb in the soil. If the speciation of lead in the solid is such that lead solubility at pH 4 is negligible, there would be no detected lead availability following the NEN 7341 approach.

Manganese: The increase in Mn availability determined by EDTA extraction over NEN 7341 is shown in Figure 4d. The chelation extraction was able to remove approximately 50% of the total manganese concentration from each sample while NEN 7341 availability values were between 15 and 25%. The available fractions of Mn that were determined show that a dignificant fraction of Mn is speciated in detrial phases in the tested materials.

Cadmium: The total cadmium concentrations for both soils were below the detection limit, therefore the total content value was reported as the detection limit. EDTA availability values for Cd in these samples, as well as the S/S Treated Soil, were greater than 100% of the reported total concentration (Figure 4e). In the MSWI combined ash, Method 3050 dissolution ()and atomic absorption spectrophotometry were used to measure the total cadmium concentration. The ability of NEN 7341 to predict Cd

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[1] as measured by x-ray fuorescence (20)

availability was variable amongst the tested materials with the best parity to EDTA availability in the MSWI combined ash and S/S Treated Soil 2 (e.g., 100% of the reported total Cd by EDTA versus 65-70% by NEN 7341) and the least parity for the untreated Soil 2 (e.g., 100% of the reported total Cd by EDTA versus only 13% of the total Cd detected). The fixation effect of S/S treatment on Soil 2 is shown by the EDTA availability values that decrease with treatment by more than the dilution factor. The NEN 7341 approach availability value shows that Cd becomes more available when the soil is treated.

As a protocol, a single batch extraction (such as the EDTA extraction) under conditions that can remove the available fraction of many material constituents is more desirable than a two-step sequential extraction. The EDTA extraction technique yields a more rigorous availability value than NEN 7341 for the constituents from each of the four tested wastes. Examination of constituent mass release stemming from the second challenge of the solid phase from the optimized EDTA extraction test conditions show that the available fraction was quantified in one extraction. More than 94% of the available As, Cd and Cu was removed in the first extraction as well as greater than 88% of the available Pb and Mn. The mass of each constituent that was removed in the subsequent optimal extraction were found to be on the order of the confidence interval of the mean availability values.

CONCLUSION

Since a fraction of inorganic constituents in the solid phase (e.g., Mn, Cu, etc.) may be immobilized in amorphous or geologically stable mineral forms, a rigorous determination of the available fraction is important. One approach to measure the available constituent fraction involves static pH extractions in a two-step sequence to solubilize both cations and anions. One such standardized method, NEN 7341, has been criticized for physical limitations that can result in a saturated liquid phase. In this study, an alternative protocol using chelating agents to relax the solubility limitation for some low solubility constituents was developed. Ethylene diamine tetraacetic acid (EDTA) is a common chelating agent that forms water soluble complexes, or chelates, with many metals resulting in an increased release from the solid phase.

Optimization of the experimental factors (e.g., EDTA concentration, liquid to solid, or LS, ratio, and the extraction contact time) showed that no significant difference in the availability of each lead, copper, cadmium and manganese from a mixture of municipal solid waste incinerator bottom ash and APC residue. Examination of leverage and prediction plots showed that the overall maximum availability of the four constituents, however, could be measured at long time intervals and high LS ratios. The concentration of EDTA did not have a significant effect on the maximizing the availability values. An optimized EDTA extraction procedure was developed using 50 mM EDTA at a LS ratio of 100 ml/g and a contact time of 48 hours.

The applicability EDTA technique as a protocol was tested on four materials representing common waste types. These wastes included contaminated soils and S/S treated wastes. For all of the tested wastes, the availability of As, Cd, Cu, Pb and Mn as determined by EDTA extraction were found to be significantly higher than the constituent availability following the NEN 7341 approach. The constituents that showed the greatest difference between the extraction techniques were As, Cd and Pb. These constituents were completely available as measured by extraction with EDTA in all the tested materials, whereas the NEN 7341 approach showed that a large fraction of each constituent was unavailable for release. In fact, the available fraction of lead in one soil for both untreated and solidification/stabilization forms was found to be undetectable by the NEN 7341 approach, illustrating that solid phase speciation can influence the results of pH dominated tests. Manganese and copper were found to be considerably less available in the tested materials than As, Pb and Cd by both techniques.

By the increasing each of optimization parameter (e.g., EDTA concentration, LS ratio and contact time) the constituent availability values were found to be insensitive to deviations from the optimized EDTA procedure. A second sequential extraction at the optimized conditions proved that approcimately 90% of the available fraction was removed in a single batch extraction for most constituents. Thus, the available fraction of the tested constituents was measured in a single extraction at near-neutral pH.

Table 1. Metal-complex stability constant with EDTA for common metals (13) compared to solubility constants for metal hydroxides (21).

Metal (Cation)	log K_{MEDTA}	log K_{MHEDTA}	log K_{MOH}
Cadmium (Cd^{2+})	16.5	2.9	-14.3
Chromium (Cr^{2+})	23.0	2.3	na
Copper (Cu^{2+})	18.8	3.0	-13.8
Iron (Fe^{2+})	14.3	2.8	-16.3
Iron (Fe^{3+})	25.1	1.4	-38.6
Lead (Pb^{2+})	18.0	2.8	-19.8
Manganese (Mn^{2+})	14.0	3.1	-12.7
Nickel (Ni^{2+})	18.6	3.2	-15.3
Zinc (Zn^{2+})	16.5	3.0	-16.2

na - information was not available

Table 2. Mass concentrations measured by total constituent analysis, EDTA extraction and NEN 7341 approach.

	Availability [mg/kg]				
	As x±95%c.i.	Cd x±95%c.i.	Cu x±95%c.i.	Pb x±95%c.i.	Mn x±95%c.i.
MSWI Ash					
Total Conc.	nt	31	2,140^{m}	1,220^{m}	2,130
EDTA	nt	28	1,480	1,460	1,180
NEN 7341	<25^{d}	20	403	465	375
Field Soil 1					
Total Conc.	5.8±0.5	<5^{d}	54±1	690^{x}±3	930±30
EDTA	nt	<10^{d}	23±3	690±20	130±10
NEN 7341	nt	<5^{d}	<12.5	274	23
Field Soil 2					
Total Conc.	20,000±1500	<104^{d}	14,300±10	1,520^{x}±5	357±15
EDTA	24,000±4000	180±8	8,790±300	1,800±100	170±10
NEN 7341	2,560	13	1,550	<25^{d}	49
S/S Soil 2					
Total Conc.	14,250^{c}	<60^{c}	10,230^{c}	1,100^{c}	480^{c}
EDTA	14,000±900	83±8	3,780±40	700±40	250±20
NEN 7341	1,100	41	2,140	<25^{d}	110

All total concentrations by NAA (20) except where noted:

d - Value below detection limit, availability value at detection limit reported

nt - not tested

m - Method 3050 (22)

c- calculated from Soil 2 and OPC NAA data

x - X ray fluorescence method

Table 3. Available constituent extracted by EDTA method and NEN 7341 compared to total concentration

Avail./Total [%]	MSWI Comb. Ash	Field Soil 1	Field Soil 2	S/S Treated Soil 2
Arsenic				
EDTA Avail.	nt	nt	100	99
NEN 7341	nt	nt	13	8
Cadmium				
EDTA Avail.	90	na	100^t	100^t
NEN 7341	65	na	13^t	70^t
Copper				
EDTA Avail.	69	43	61	37
NEN 7341	19	23^a	11	21
Lead				
EDTA Avail.	100	100	100	64
NEN 7341	38	40	2^a	2^a
Manganese				
EDTA Avail.	55	14	48	52
NEN 7341	18	2	14	23

nt - not tested

na - not applicable, all values below detection limits

a - availability value below detection limit, availability value of detection limit reported

t - total concentration value below detection limit, detection limit reported

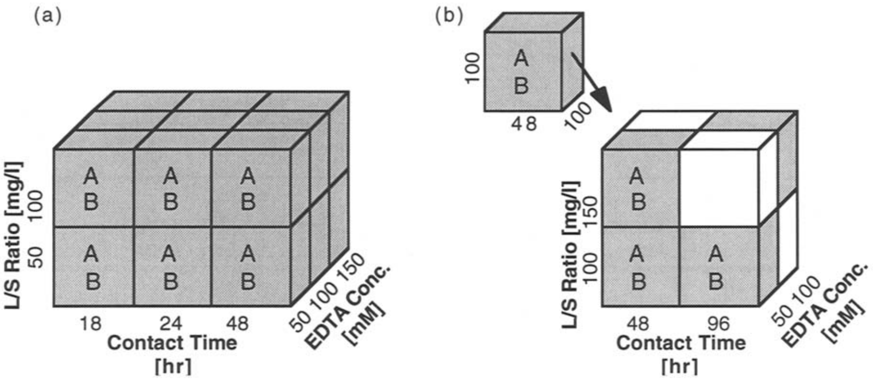
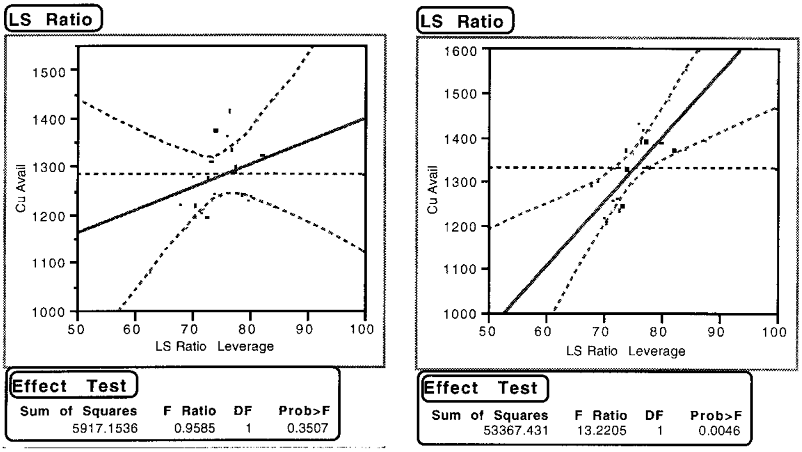


Figure 1. EDTA extraction experimental design for (a) method optimization study and (b) comparison to NEN 7341 study.



Sum of Squares	F Ratio	DF	Prob>F
5917.1536	0.9585	1	0.3507

Sum of Squares	F Ratio	DF	Prob>F
53367.431	13.2205	1	0.0046

Figure 2. JMP (18) leverage plots for LS ratio on Cu availability from MSWI combined ash replicate B and C, respectively. Significant factors are represented by 95% confidence intervals intersecting sample mean values and Prob>F of less than 0.05.

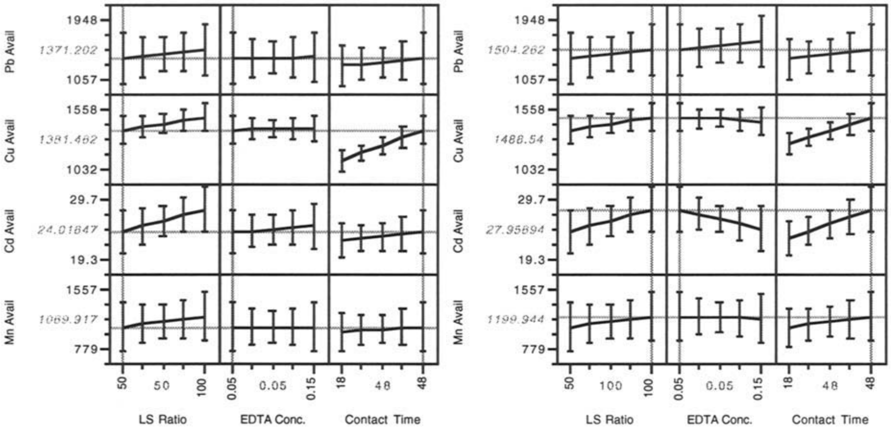


Figure 3. JMP (18) screening model profiles for the availability values of Pb, Cu, Cd, and Mn as a function of experimental factors LS ratio, EDTA concentration, and contact time.

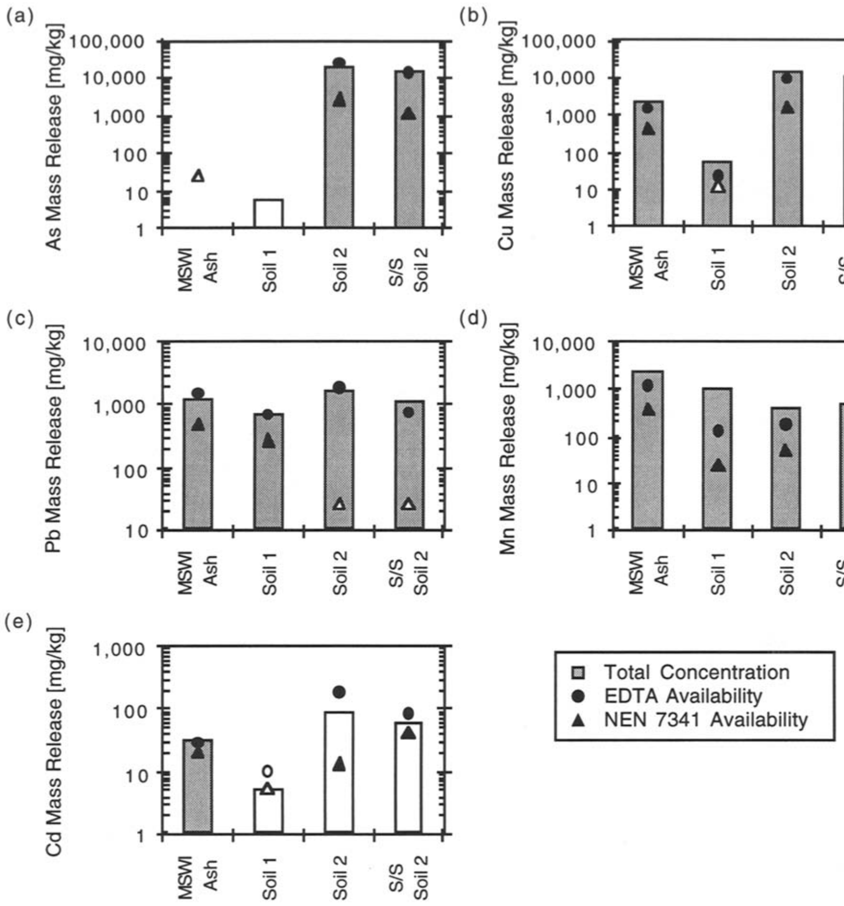


Figure 4. Release of (a) arsenic, (b) copper, (c) lead, (d) manganese and (e) cadmium from four materials as determined by EDTA Availability and NEN 7341 Availability. Values compared to total concentration measured by NAA or XRF (20). Unfilled items indicate that detection limit values were reported.

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