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**Evaluation of a Sequential Leach Procedure for the Determination
of Metal Partitioning in Deep Sea Sediments**

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ABSTRACT

Two chemical leach techniques are evaluated for the purpose of determining potential labile metal partitioning in deep sea sediments. Although results from batch leach techniques compare favorably with results from a sequential leach technique (deviations $\pm 15\%$ of the amount present), there are potential advantages in using a sequential technique because of reduced needs for multiple subsamples, and because of improved detection of errors in the sequential method as a result of reduced sample and data transfer errors.

INTRODUCTION

Selective chemical leaching techniques have been used by soil scientists and geochemists for a number of years to determine the quantity of potential labile metals in the soils or sediments or to infer the probable mineral phases found in these materials, (Chester and Hughes, 1967; Tessier et. al., 1979; Malo, 1977). Problems in obtaining unambiguous results for selective extraction of both major element components and trace metal constituents have been identified by Rendell et. al. (1980), Tipping et.al. (1985) and Rapin et. al. (1986). However, in spite of analytical and interpretative difficulties, selective leaching techniques have been gaining ever increasing use in geochemistry laboratories.

In this report we evaluate two procedures which have been used in our laboratory for determining metal partitioning in deep sea sediments:

1. The current procedure is referred to as a 'sequential' leach method. After a weak acid leach, the residue is recovered and subjected to two successive reducing leaches of increasing strength. Finally, the residue is subjected to total decomposition.
2. An earlier procedure referred to as a 'batch' leach method, utilized a weak acid leach and a separate 'batch' hydroxylamine hydrochloride leach (which include the weak acid). The easily reducible metals were determined by difference in results between the above two 'batch' leaches.

Results obtained from analyses of the above leachates for Fe, Mn, Ca, Zn, Cu and Ni will be compared to the total concentrations of these metals in the sediments. These total concentrations will be determined by a total decomposition procedure.

EXPERIMENTAL

Sampling. Sediment samples (obtained using the long corer developed by the University of Rhode Island) were collected from the Southern Nares Abyssal Plain (Buckley, 1984). Subsamples (n=68) were taken from the Bedford Institute of Oceanography core 84-046-18, between the depths of 150 cm and 1050 cm. The core subsamples were stored in a nitrogen atmosphere at 10 °C following pore water extraction by centrifugation. Sediments were subsequently freeze dried and pulverised in an agate mortar.

Sequential leach Procedure. This procedure was adapted from procedures which are described in Chester and Hughes (1968) and Tessier et. al. (1979). The four stages of this procedure include weak acid leachable metals (bound as carbonates or oxyhydroxides), easily reducible metals (bound to Fe-Mn oxides or as oxide coatings on other minerals), moderately reducible metals (strongly bound as mature oxides) and residual metals (considered to be mainly in the mineral lattice).

1. **Weak acid leachable metals** (bound as carbonates or oxyhydroxides). One g of unwashed freeze dried sediment was added to a 50 mL 'Falcon Blue Max' centrifuge tube. To this tube was added 20 mL of 25 % (v/v) acetic acid. Subsequently, this mixture was shaken for 30 s and allowed to settle for 24 h before the leachate was decanted into test tubes and saved for later atomic absorption analyses of Fe, Mn, Ca, Zn, Cu and Ni.

2. **Easily reducible metals** (bound to Fe-Mn oxides or as oxide coatings on other minerals). The residue from the previous leach (which remained in the original reaction vessel) was washed twice with 50 mL portions of deionized water. Each wash was vigorously shaken for 30 s and was followed by centrifugation at 3000 rpm for 0.5 h before the wash water was decanted. A 20 mL portion of 1 M hydroxylamine hydrochloride (pH 2.9) was added to the residue and shaken vigorously for 30 s and allowed to settle

for 24 h before the leachate was decanted into test tubes and saved for later atomic absorption analyses.

As a result of subsequent experiments the 1 M solution of hydroxylamine was decreased to 0.25 M. This change was made because the 1 M solution sometimes caused the atomic absorption atomization assembly to clog.

3. **Moderately reducible metals** (strongly bound as mature oxides. The residue from the previous leach was washed once in the same manner as that described above. The residue was then leached with 20 mL of 0.04 M hydroxylamine hydrochloride in 25 % (v/v) acetic acid. The samples were vigorously mixed for 30 s before being heated (90 °C) in a covered water bath for 24 h. The leachate was allowed to settle for 24 h before the leachate was decanted into a test tube for later atomic absorption analyses.

4. **Residual metals.** The residue from the previous leach was washed once (see above) and was then dried in the open centrifuge tube at 60 °C for 48 h. A 0.5 g portion of the dried residue was then subjected to a total decomposition procedure which is described in Buckley and Cranston (1971). See below, section on 'Total Decomposition Procedure'.

The results for the total analyses of the leached sediment residue must be adjusted so that they are representative of the metals concentrations in the original sediment sample (1 g). These adjusted concentrations are representative of the nonlabile concentrations in the sediments which are not recovered by either of the three leach media.

For example,

$$\text{FeR} = \text{FeTR} * (\text{residue wt.}) / (\text{initial sample wt.})$$

where FeTR is the concentration of iron in the residue and FeR is the residual Fe concentration which is proportioned so that it is relative to the mass of the original unleached sample.

Batch Leach Procedure. This procedure was adapted (Cranston, 1974 and MacIntosh et al, 1976) from the procedure described in Chester and Hughes (1968) and it has three stages:

1. Weak acid leachable metal as described in stage 1 of the above sequential leach procedure.
2. Combined leachable metal where the weak acid leach reagents (above stage 1 of sequential leach procedure) and the easily reducible leach reagents (above stage 2 of sequential leach procedure) were combined into a single leach. This combined leach was performed on a separate 1 g sample.
3. Easily reducible metal is computed as the difference between the combined leachable metal (stage 2) and the weak acid leachable metal (stage 1).

Total Decomposition Procedure. The total decomposition method was described in Buckley and Cranston (1971). A washed sample was use for the analyses of Fe, Mn and Ca, and an unwashed sample was used for the analyses of Zn, Cu and Ni. A 0.5 g portion of sample was washed twice with 1 L of deionized water. Each wash was shaken for 30 s and was followed by centrifugation at 3000 rpm for 0.5 h before the wash water was decanted. To a teflon digestion bomb was added 0.5 g of freeze dried sediment, 1 mL of aqua regia (3 portions of concentrated hydrochloric acid to 1 portion nitric acid), and 6 mL of hydrofluoric acid. The bomb was sealed and heated at 80 °C for 24 h (on hot plates in a fume hood). The contents of the bomb (after cooling to 20 °C) were transferred to a vial containing 5.6 g of boric acid. The bomb was rinsed with deionized water and these rinse waters were added to the vial which was than bulked to a total contents mass of 100 g. The sample was set aside for later atomic absorption analyses.

Metal Analyses. All leachate and total decomposition samples were analyzed for Fe, Mn, Ca, Zn, Cu, and Ni utilizing a

Table 1. Analytical results for the sequential leach procedure, the batch leach procedure and the total analyses (-T) for Fe, Mn, Ca, Zn, Cu, and Ni. The sequential -WASq, -HASq, -HHASq and -SUM are the weak acid, hydroxylamine and heated hydroxylamine leaches, and the summation of all three leaches plus the residual concentration, respectively. The residual concentrations are not shown here, however they are the difference between -SUM and the summation of the three leaches. The batch -WA and -HR are the weak acid and hydroxylamine residual (easily reducible metal by difference).

Table with 30 columns: a (Depth, FeT, Fe2ASq, FeHASq, FeHHASq, FeWA, FeHR, Depth, MnT, MnSUM, MnWASq, MnHASq, MnHHASq, MnWA, MnHR, Depth, CaT, CaWASq, CaHASq, CaHHASq) and 30 rows of data.

Varian Model PT975 atomic absorption spectrophotometer. All instrumental parameters were as recommended by the manufacturer and appropriate dilutions were carried out for solutions with very high metal concentrations. Large volumes of the reagents blanks were prepared for the specific leaches and appropriate blank solutions were used for sample dilution and for the preparation of standards. This latter precaution helped avoid analytical problems which could be caused by chemical matrix interferences.

RESULTS AND DISCUSSION

All analytical results for the Fe, Mn, Ca, Zn, Cu and Ni and the mean concentrations (n=68) for each leach fraction are reported in table 1. These results for mean concentrations are also reported in table 2 and figure 1 as the relative % of the mean total concentrations. The mean loss for a specific metal after the completion of the sequential leach procedure is computed as the difference between the mean total concentration and the mean summation for the three leaches plus the residual concentration. Bar graphs for each metal show the comparison between results for the batch leach analyses and the sequential leach analyses (figure 1).

Table 2. Fe, Mn, Ca, Zn, Cu and Ni mean concentrations as a percentage of the specific metals mean total concentrations. Results are reported for both the sequential leach procedure and the batch leach procedure.

metal	-WAsq rel.%	-HASq rel.%	-HHAsq rel.%	-R rel.%	-LOSS rel.%	-WA rel.%	-HR rel.%
Fe	0.3	1.2	9.0	85.4	3.2	0.8	2.5
Mn	9.8	49.3	11.5	15.6	13.8	17.5	52.6
Ca	32.6	15.4	6.2	36.9	8.8	---	---
Zn	1.2	1.8	19.4	73.7	3.9	1.8	4.1
Cu	3.9	12.0	34.6	45.7	3.9	6.3	24.6
Ni	4.2	15.8	20.3	53.9	5.8	7.2	15.2

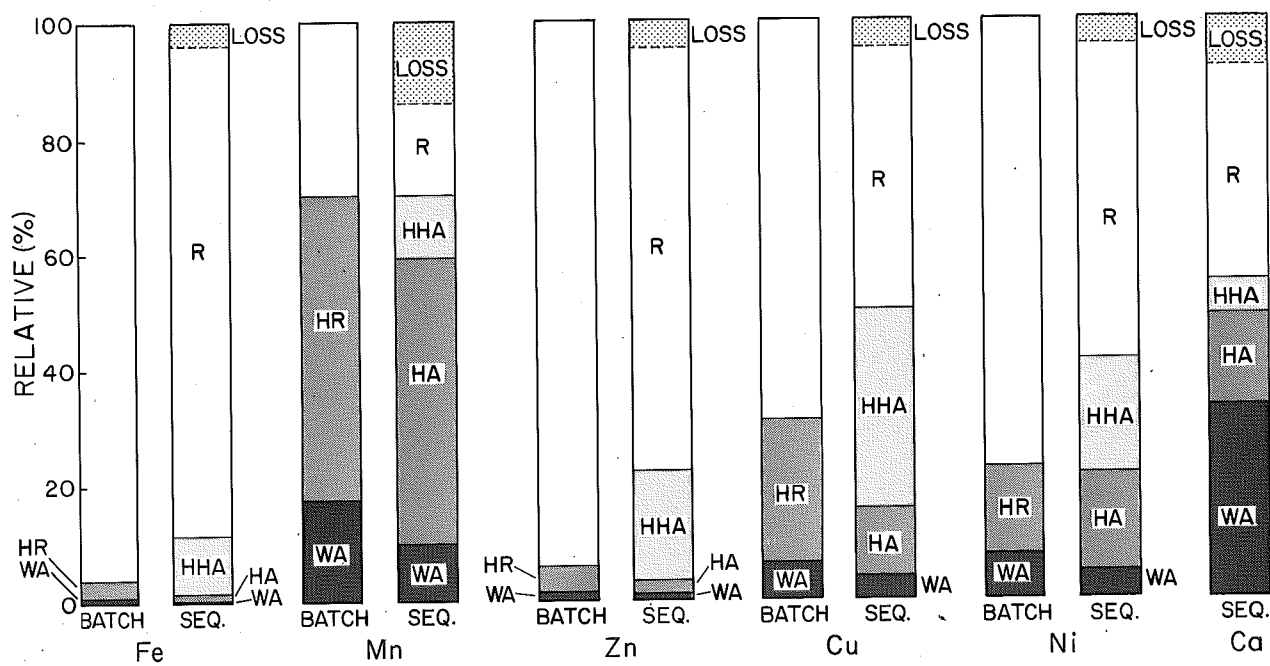


Figure 1. Mean concentrations for each leach fraction are expressed as the relative % of the mean total concentration for each metal.

The batch leach results for both -WA and -HR were higher than the sequential leach results for -WAsq and -HAsq, respectively. This trend was observed for all of the metals which we analyzed: Fe, Mn, Zn, Cu and Ni (batch leach results had not been obtained for Ca). The reason for this decrease in leach recovery is unknown and our records show that the only procedural change is a decrease in the cross sectional area of the reaction vessel. It seems unlikely that this alteration in the procedure would decrease the reaction rate by 40 % to 50 %. The first reaction vessel had a flat bottom with a diameter of 42 mm and a 1 g sample would have covered its bottom to a depth of 0.3 mm. The second reaction vessel had a conical shaped bottom and the diameter at the surface of the 1 g sample was 15 mm with a maximum depth of 9 mm and an average depth of 3 mm. Thus it is apparent that the second reaction vessel had an effective surface area of 1/8 or 13 % of that in first reaction vessel, and that the average depth had increased by a factor of 10. If less than half of the dissolution reaction occurred during the elutriation and mixing stage and the remainder occurred during the 24 h settling stage (most of the settling occurred during the first few minutes), then the decrease in the leached metal concentrations may have been caused by the change in reaction vessel's shape.

The third sequential leach (heated hydroxylamine) recovered additional and relatively large amounts of Fe, Mn, Ca, Zn, Cu and Ni. The sum of the metals concentrations which were obtained for the three sequential leaches exceeded the metals concentrations which were obtained for the combined batch leach using hydroxylamine at pH 2 (see Fig. 1). The additional incremental concentrations recovered by this third sequential leach may include the apparent losses which we noted (above) when we compared the sequential and batch leach results.

We observe a real loss of metal when we compare the mean sequential summation (including the residual metal concentrations) to the mean total metal concentrations. These

losses for Fe, Zn, CU and Ni vary between 3.2 % and 5.8 % of these metals total concentrations. The Mn and Ca losses are 14 % and 9 %, respectively. These losses may be associated with the loss of fine sediment during the sediment washing and residue recovery, which is required by this sequential leach procedure. The greater losses for the Mn and Ca may be caused by a preferential loss of the fine fraction of the sediment in which the concentrations of Mn and Ca may be highest or soluble in the washes.

These metal losses were further assessed by employing least squares linear regression analysis. This analysis was designed to determine the mean trends for the % of Fe, Mn, Ca, Zn, Cu and Ni which were lost during the sequential leach procedure. For each metal the summation was regressed with the measured total concentrations. All regression lines are forced to pass through the origin because as the total concentrations approach '0', then, so must the summation of the concentrations of its component parts approach '0'. The regression constant (slope) is then an approximation of the 'population mean' for the fraction of a metal's total concentration which is recovered by the sequential leach procedure (table 3). The percentage of a specific metal's loss is computed as: (e.g. Fe)

$$\text{FeLOSS} = (1 - \text{slope}) * 100\%.$$

The % of Fe, Mn, Ca, Zn, Cu and Ni losses (resulting from the sequential leach procedure) as calculated from this regression analyses (table 3) were similar to approximations computed from the sample means (table 2). Thus it appears that the sample means are a reasonable approximation of the population means. Also, the analytical results, which we present in this report, are a reasonable representation of the application of our sequential leach procedure to the analyses of deep sea sediments.

Table 3. Comparison of sum total, MeSUM, with the independantly determined total composition, MeT. Regression analyses results for the 95 % confidence interval. A few out-lying points were rejected from the regression analyses as indicated by the reduction in sample number (n) below the initial n=68.

Regression equation	n	% LOSS
FeSUM = 0.96 ±0.01 FeT	65	4
MnSUM = 0.85 ±0.01 MnT	68	15
CaSUM = 0.91 ±0.02 CaT	66	9
ZnSUM = 0.95 ±0.01 ZnT	68	5
CuSUM = 0.96 ±0.01 CuT	66	4
NiSUM = 0.94 ±0.02 NiT	67	6

Stanners et. al. (1988) compared their analytical results for core 48 from Nares Abyssal Plain, of ESOPE expedition, MD-45, 1985, (their sequential leach method is described in Thomas and Chester, 1986) with analytical results for duplicate samples which were obtained using this proposed method (data available in Buckley et. al., 1988b). They concluded that "Despite the fact that different sequential analysis schemes were used by the two groups, for all major trends observed the partitioning results are qualitatively comparable." Also, Buckley et. al. (1988a) reported that data obtained using this proposed method provided a basis for identifying zones of paleo-oxidation in buried turbidites and explaining the remobilization of dissolved Mn and Fe in pore waters extracted from sediments which were collected in Nares Abyssal Plain.

Tabulated results for the sequential leach method and the batch leach method are compared in table 4 (see also, fig. 1). The correlation coefficients, "r", show a high degree of covariances between analytical results for the similar analyses and the values for r^2 show that (except for NiWAsq versus NiWA) most of the variance in Y could be described by the variance in X (72 % to 95). For individual variables the data for this sample

set showed a large variations and the standard deviations were large (e.g. MnWAsq = 188 ± 109 ppm and MnHAsq = 942 ± 871 ppm). We first thought that these variations were due to variation in sediment texture and organic carbon content. However correlation analyses showed that no simple relationship existed between sediment texture and organic carbon and these labile metal fractions.

Table 4. Mean, standard deviation, minimum and maximum values for the sequential leach analytical method and the comparison of this method with the similar results which were determined by the batch leach method.

variables		FeWAsq (ppm)				std. error	r	%r ²	
Y	X	min.	max.	mean	std.dev.	for estimate			
		of Y given X							
FeWAsq	FeWA	98	383	172	± 49	25	.860	74	
FeHAsq	FeHR	204	1444	646	± 284	109	.925	86	
MnWAsq	MnWA	33	560	188	± 109	29	.963	93	
MnHAsq	MnHR	17	3474	942	± 871	138	.988	98	
ZnWAsq	ZnWA	1.0	2.7	1.6	± 0.5	0.2	.861	74	
ZnHAsq	ZnHR	0.6	4.1	2.3	± 0.7	0.3	.874	76	
CuWAsq	CuWA	0.8	6.8	2.7	± 1.4	0.6	.893	80	
CuHAsq	CuHR	1.0	20.8	8.4	± 5.0	1.8	.932	87	
NiWAsq	NiWA	0.1	8.2	2.6	± 2.1	2.1	.132	2	
NiHAsq	NiHR	0.4	35.2	9.8	± 7.3	2.1	.957	92	

To assess the analytical precision for the leach analyses of labile metals we have compared similar results for the sequential leach and batch leach methods. The total variance between the two methods was assessed as the standard error for the estimate of Y given X (table 4). This standard error is the greatest error which we would expect to observe because Y and X were determined for duplicate subsamples by different methods on different days by different analysts. This method for assessment of precision is necessary because we did not conduct replicate analyses of

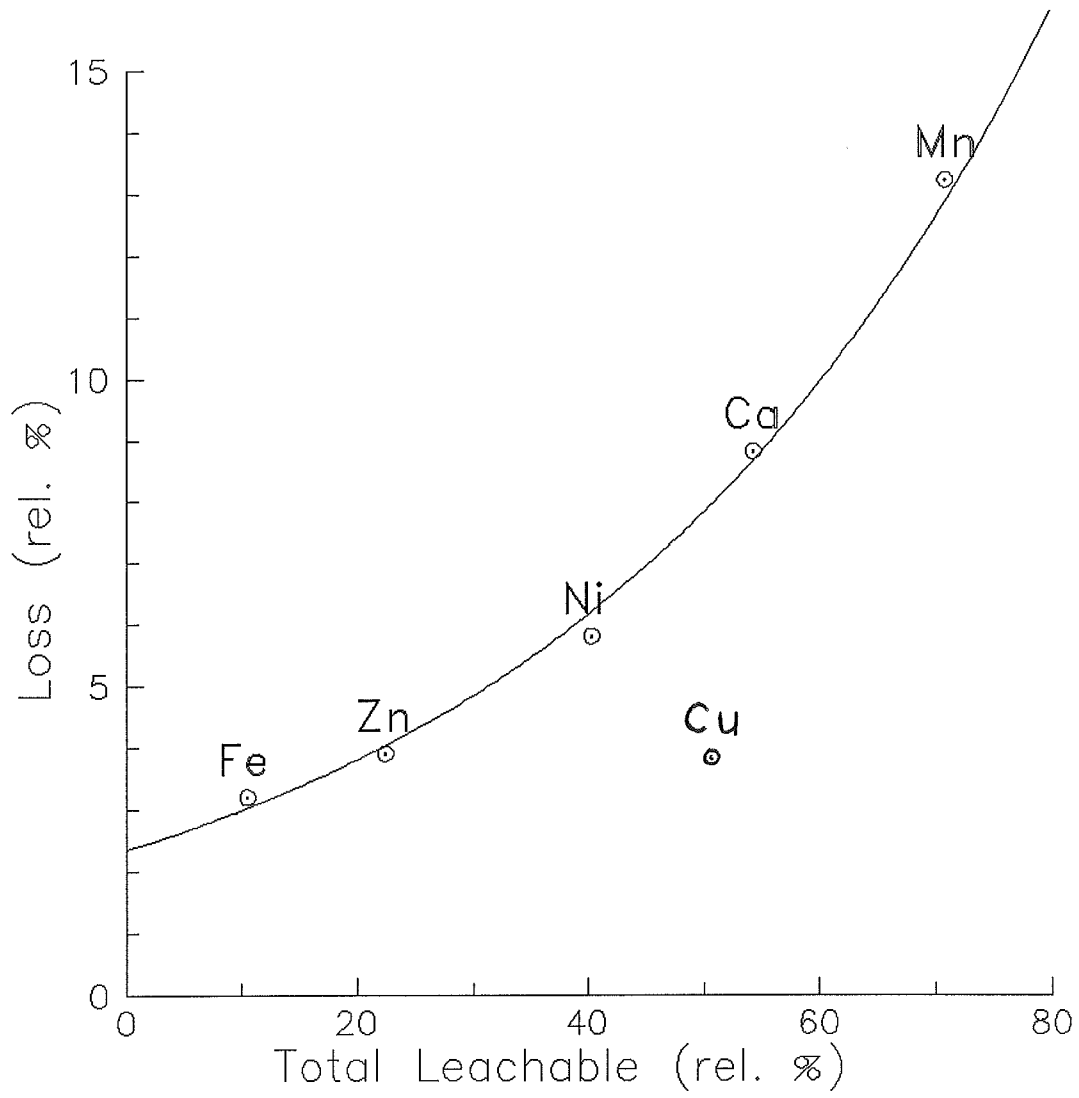


Figure 2. Relative % loss of a metal versus the relative % total leachable metal.

replicate subsamples. For all comparisons (table 4), the precision expressed as the standard error for the estimate for Y given X, "SEE", is much less than the standard deviation for the mean concentration except for the NiWAsq versus NiWA results (NiWAsq = 2.6 ± 2.1 and SEE = ± 2.1). All of these NiWAsq concentrations are low and most of the concentrations are at or below the detection limit which is 2.1 ppm.

Metals which are more labile (ie. Mn and Ca, which have the highest relative % in a leachable form) appear to have a greater loss during the sequential leaching procedure than do other metals which are bound to a less reactive fraction of the sediment (ie. Fe in clays). This observation is demonstrated in figure 2. The relative percentage loss of a metal increases exponentially as the relative percentage of 'total leachable' (summation of results for leaches 1, 2, and 3) metal increases. The series of decreasing relative reactivity appears to be Mn > Ca > Ni > Zn > Fe. The position of Cu is uncertain. The more reactive metals which show the greatest losses are probably associated with carbonates, oxyhydroxides and the very fine grained fraction of the sediment. These fractions may be subject to preferential loss during the decanting of the weak acid leach and the subsequent deionized water washes.

The mean mass of each metal loss can also be expressed as a percentage of the mean mass of the unaccountable sediment residue loss. First we must compute the mean residue mass and by difference determine the residue loss. The mean residue loss was 127 mg. Then we assumed that the oxides and carbonates being leached could be approximated as Fe_2O_3 , $MnCO_3$, $CaCO_3$, ZnO , CuO and NiO . The total leached mass for these metals could then be computed. The sediment samples also received the sea salts which were a constituent of the pore water. To compute this mass we assumed a total dissolved salt content of 35 mg/g and we then use the variation in water content (%water) to compute:

$$\text{sea salts (mg)} = 35 * \%water / (100 - \%water).$$

An average of 25 % of the pore water had been removed by centrifugation at the time of subsampling, and the approximations for weight of sea salts are similarly reduced by 25 % from 32.4 mg to 24.3 mg. The mean leach loss for the Fe, Mn, Ca, Zn, Cu and Ni compounds was 25.8 mg. Thus the mean for the total accountable loss was the 50.1 mg. Then the mean unaccountable residue loss by difference was 76.9 mg.

Individual metal losses (which were computed as the difference between the means for total concentrations and the means for the sum of the leaches) were expressed as a percentage of the unaccountable residue loss (Table 5) which were then compared to the total metal concentrations for the sediment (from Table 1). These comparisons indicated that the lost sediment fraction was enriched in Mn and Ca by 89 and 15 %, respectively. The comparisons for Fe, Zn, Cu and Ni all indicated reduced concentrations by 58, 40, 39 and 32 %, respectively. The lost sediment was probably a fine grained carbonate and/or Mn oxide.

Table 5. Individual metal losses are computed as the difference between the total analyses and the leach procedure summations. Relative metal losses are expressed as a percentage of the average sediment unaccountable loss (76.9 mg). Mean total metal concentrations are from Table 1.

Metal	Loss mg/g	Relative Loss %	Total %
Fe	1.76	2.3	5.5
Mn	0.28	0.36	0.19
Ca	0.91	1.18	1.03
Zn	0.0060	0.0078	0.0129
Cu	0.0034	0.0044	0.0072
Ni	0.0032	0.0042	0.0062

There were 7 points (3 leaches and 4 deionized water washes) in the procedure where loss could have occurred and a 1 % loss of sediment at each point would account for the total loss of 76.9

mg of leach residue. The 3 points in the procedure where the sediment losses most probably occurred were:

1. At the end of the first elutriation (the weak acid leach). Although, the elutriate appeared to be clear at the end of the 24 h settling period, it may have contained some very fine clay size material.
2. At the end of the third leach (heated hydroxylamine) an elutriate suspension is produced which clears slowly during a 1 h cooling period prior to decanting. A 1 h settling time may not be sufficient for complete phase separation.
3. During the recovery of the sediment residue after drying, the dry sediment is difficult to quantitatively remove from the test tube, which makes it difficult to obtain an accurate weight for determining the sediment residual mass.

CONCLUSIONS

One of the prime reasons for developing and evaluating a sequential leach technique for application in studies of deep sea sediments was to reduce the need for large numbers of subsamples, which might be required by a batch technique. Our research has demonstrated that batch and sequential leach results provide comparable data, but only one subsample (two if an independent total analysis is included), is required for the sequential method. This technique then has 4 advantages:

- (1) When limited subsample volumes are available, as is often the case in deep sea sediment cores with thin homogeneous lithostratigraphic units only one or two 1 g subsamples need to be taken;
- (2) Data errors due to multiple subsampling are reduced with the sequential leach method;
- (3) Large errors due to unavoidable sample losses are more easily detected in the sequential method due to the internal consistency checks;
- (4) Analytical results obtained with the sequential method are

direct measurements of the labile metal content, whereas the batch technique must determine easily reducible metal content by difference between the weak acid labile metal and the total labile metal.

The overall precision of the leach techniques appears to be generally within 15 % of the amount present. Although this precision might be improved with better reaction vessel design and sample handling techniques, the present results will probably be adequate to detect sedimentological and diagenetic variations in most deep sea sediments.

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