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QUALITY ASSURANCE IN THE SURFACE WATER AND LEACHING AND METAL PATHWAYS PROGRAM OF THE REGIONAL COPPER-NICKEL STUDY

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Minnesota Environmental Quality Board
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I. INTRODUCTION

Conclusions about the environmental quality of the Copper-Nickel Study Region are only as good as the data on which they are based. Interpretation of this data must be done within the content of known accuracy and preci~~s~~sion limits. To determine these limits for water quality parameters, ~~on~~ extensive quality assurance (QA) program was undertaken. an

The analysis of a sample involves several steps. The sample is collected according to a standard procedure. There is often a certain amount of processing done in the field prior to shipment. The sample is shipped to the analytical laboratory where it is unpacked and stored prior to the actual analysis. Sample contamination may occur at any of these points. Even slight contamination is potentially serious when actual concentrations are at or near detectable limits. Therefore, quality control measures must be taken at each of these steps. Internal laboratory quality control procedures are not discussed here but may be found in the Operations Manual. This report details both routine field quality control procedures and a number of special experiments designed to aid in the determination of accuracy and precision. Both the surface water quality program and the leaching and metal pathways program are discussed.

Besides data validation, the QA program also should have the effect of increasing the quality of the data. Procedures of the sort outlined in this report allow correction of contamination problems at an early stage. They also promote awareness in field personnel of the importance of quality control, and as a result lessen contamination due to careless handling.

As a part of this effort, the taking of accurate and complete field notes was stressed, and any event or situation which might affect the quality of the data was recorded.

II. Methods and Procedures

The following definitions are used throughout the report. Accuracy is defined as the degree to which the data reflect the actual concentrations in the natural sample. Pression refers to the reproduceability of results.

Several laboratories were involved with the project. Surface water quality samples were analyzed by the United States Geological Survey (USGS) and the Minnesota Department of Health (MDH). Samples for the leaching program were analyzed by the State Health Department and Dr. Steven Eisenreich of the University of Minnesota. Complexing capacity measurements were made by Dr. Thomas Bydalek of the University of Minnesota - Duluth. Analysis of sediment data was performed by the laboratory of the Minerals Division of the Department of Natural Resources (DNR). The values of several parameters, notably pH and conductivity, were not determined by any analytical laboratory but by fiels personnel. In addition, certain QA projects involved other laboratories connected either directly or indirectly with copper-nickel mining in Minnesota.

The quality control procedures performed by the Copper-Nickel Study staff were numerous and are outlined below. On a routine basis, quality assurance procedures included:

1). Calibration of field instruments.
2). Collection and analysis of duplicate (or in the case of sediment, triplicate) samples.
3). Submission of samples containing only distilled water (blanks) by the leaching program.

Special experiments included:

1). The submission of identical samples to USGS and MDH.

2). A joint sampling and analysis program of the Regional Copper-Nickel Study and Amax, Inc.

3). A "round robin" program involving the submission of identical samples to sic different laboratories.

4). Studies of the effect of temperature and storage time on field pH readings.

5). A study to determine the extent of contamination due to field acidification.

6). A study to determine the extent of contamination due to improperly cleanes Kemmerer bottles.

7). A comparison of complexing capacity values resulting from two different methods of analysis.

III. Results

A. Field procedures

1. Surface Water

pH and conductivity and dissolved oxygen meters were calibrated on a routine schedule. pH meters were calibrated daily with atleast two standard buffer solutions. Detailed calibration procedures can be found in the Operations Manual.

On a monthly basis, conductivity meters and cells were calibrated for a temperature correction factor and also against a solution of potassium chloride with known conductivity. Detailed calibration procedures may be found in appendix A. Comparisons were also made with conductivity meters routinely used by the U.S. Forest Service.

The dissolved oxygen meter was calibrated at least weekly using either the Winkler method or air calibration method as described in Appendix A.

Field thermoneters were checked in the laboratory against a certified American Society for Testing and Materials extreme precision grade therometer.

All meters were maintained as per their respective instructions. Batteries were checked routinly and replaced when neede. Table 1 contains a list of manufacturers stated accuracies for all field parameters.

Procedures for maintaining sample equipment, collecting samples and preparing samples for analysis followed those outlined in Standard Methods (1971). More detail can be found in the operations manual.

2. Leaching and Metal Pathways

Field procedures for the leaching and metal pathways study closely resembled the surface water study. pH meters were calibrated daily using standard buffer solutions of pH 4.0, 7.0, and 10.0. Conductance meters were calibrated at least every two weeks using a standard potassium chloride solution. The dissolved oxygen meter was calibrated weekly using the Winkler method. Preparation of samples again followed Standard Methods (1971). A detailed description of sampling procedures can be found in the operations Manual.

3. Groundwater

Groundwater samples were collected and analyzed by the United States Geological Survey (USGS). A summary of this project may be found in Siegel and Ericson (1978). Sampling and QA procedures followed Brown et al. (1970).

B. Duplicate Samples

1. Surface Water

A major component of the surface water quality assurance program was analyses of duplicate samples by both the U.S. Geological Survey (USGS) and the Minnesota Health Department (MDH). Duplicates were taken routinely as part of the surface water monitoring program and cover the spatial and temporal range of copper-nickel water sampling.

Duplicates were taken every ten to fifteen samples. For lakes, this implies two duplicate samples every time the lakes were sampled and for streams approximately tw per month. Table 2 (attached) contains listing of duplicate sampling sites and dates. Most duplicate samples were analyzed for both primary and secondary parameters (see Operations Manual).

Thirteen duplicate samples were analyzed by USGS between March and August, 1976. Four of these did not include primary metals.

A duplicate sample consists of two sets of bottles for the desired parameters. They are filled, one set after the other, from different kemmerer fills. The correct sampling time is recorded for one set and a time three hours later for the second set. These bottles are then sent to the analytical laboratory in the same shipment.

Statistical analysis proceded along three lines of inquiry. The first was to determine the varibility of each parameter as a means of assessing precision. Secondly, analysis was performed on the duplicate as a group in order to ascertain patterns between parameters. This type of multivariate analysis sought to answer questions such as "does ;ack of precision in one metal imply that other metals in the same sample are also imprecise?" Finally, the question of the relative performance of the Minnesota Health Department and USGS laboratories was addressed.

An initial problem was the frequent occurance of values below detection limits. For several parameters, most if not all readings fall into this category. No analysis was done in these cases. For parameters which fell below the detection limit less frequently a conservative convention was followed throughout the analysis. These readings were considered to be either at the detection limit or zero, depending on which maximized the difference between it and its corresponding duplicate value. For example, the pair (<.5, 1.0) would be considered as (o, 1.0) while the pair (<.5, <5) would be considered as (0, .5).

An additional problem was posed by the levels of precision of the two laboratories. Foe example, USGS reports aluminum readings to the nearest 10μg/l. A reported value, then of 30 μg/l represents an actual observed value between 25 μg/l and 35 μg/l. The Health Department, on the other hand, reports aluminum to the nearest 1 μg/l. A reading of 30 μg/l from the Health Department might actually represent values between 29.5 μg and 30.5 μg/l. Each reported value, therefore, may be considered as representing upper and lower bounds for the true value.

As was done with values below detection limits, a convention was adopted with regards to reporting precision that maximizes differences. In a duplicate pair, the larger observation was increased to its upper bond, while the smaller observation was decreased to its lower bound. For example, if for a given duplicate USGS reported aluminum concentrations of 30 and 40 μg/l, this pair would be considered to be 25 and 45 μg/l. Similarly, if the Health Department recorded concentrations of 30 and 34 μg/l, the pair would be adjusted to read 29.5 and 34.5 μg/l.

The net effect of these conventions is to make all estimate of precision reported below as conservative as possible. The true precision of each parameter is probably better than presented here; it is certainly no worse.

A final decision involved criteria for omitting certain points from the data. It was decided that if a reading was such that it would not be included in regional characterization analysis, the duplicate for that paramtere at that time would not be considered. There was no hard and fast rule used here; a rough guide is that if a reading was an order of magnitude or more above other readings at that site, it was dropped. Table 3 contains a list of these observations.

Two statistics were used to summarize the precision of the data. The first is an upper confidence bound on percentiles of the differences. Computation of this statistic enables us to make statements of the form "with 90% confidence we can say that X% of our observations have a precision greater than or equal to this computed value." Here, the differences between duplicates is considered to be a measure of precision.

An alternative way of expressing this figure is to say "if duplicates were taken of all samples, x% of them would show differences less than or equal to this figure."

As the differences for most parameters do not seem to follow a normal distribution, these confidence limits had to be computed by non-parametric means. The method used here, based on the binomial distribution, is described in detail in Conover (1971). The figures reported here not only reflect the magnitude of the observation but also the sample size. The fewer duplicates taken, the more conservative the estimate of precision. Upper confidence bounds were placed on the 50th, 75th, and 90th percentiles for each parameter. The results are summarized in Table 5.

As a second estimate of precision, the coefficient of vatiation was computed for each parameter. This statistic enables us to express the precision of each parameter as a percentage and then rank parameters according to relative precision. To compute this statistic, first calculate the differences observed in the n duplicate samples $(X_1 - X_2)$. . . . . $(X_1 - X_2)_n$ and use these to calculate the standard deviation

$$S = \sqrt{\sum_{L=1}^{n} (X_1 - X_2)_i{}^2/2n} \qquad \sqrt{\sum_{i=1}^{n} (X_1 - X_2)^2 / 2n}$$

The coefficient of variation is obtained by dividing this figure by the mean of the observations

$$\overline{X} = \sum_{\overset{L}{i}=1}^{n} (X_1 - X_2)_i/2n$$

Results from this calculation are summarized in tables 5 and 6. A general rule of thumb for interpretation of this figure is that a figure of 20% or under is very precise, data with a coeffieienct of variation between 20 and 50% is probably useful, while a figure of over 50% indicates a significant lack of preci~~s~~sion.

It is entirely possible that the precision of a parameter depends on the true level of that parameter. A laboratory may be able to make a $\overset{m}{\text{n}}$ore precise estimate of a parameter when that substance is present in high amounts than when it is present only in small quantities. Two methods were used to explore this problem. For each parameter, a graph was made of the magnitude of the difference against the average of the two observations. In addition, the correlation coefficient of these two figures was computed.

Temporal variability was explored by plotting the magnitude of the differences over time. This was used to locate time periods where laboratory analysis tended towards being out of control. This was not found to be a problem with any parameter and so this analysis will not be discussed further.

All of the above figures are reported without regard to laboratory if it could be assumed that the precision of the two laboratories is identical. This assumption is tested by the Wilcoxon rank-sum test (Conover, 1971; Snedecor and Cochran, 1967). If this test revealed differences between the populations represented by each laboratory, analysis was done separately for each.

The multivariate portion of the analysis atempted to relate precision of the various parameters to each other. This was done primarily by analysis of correlation matrices. The correlation coefficients of each pair of parameters were computed and put into matrix form. Principal components analysis (Morrison, 1976) was performed in an effort to ascertain any petterns in the correlations.

III. Results

The results show that surface parameters very greatly in their precision. Some are quite precise, others so variable as to pose problems for interpretation. Happily there are many of the former and few of the latter. The parameters for which lack of precision is a problem are : zinc, sulfide, arsenic, lead (USGS readings only) nonfilterable residue, ortho-phasphorus (USGS only), and ammonia. Cadium, turbidity, fluoride (USGS), mercury and total phosphorus (USGS) are marginal. Tables 4 and 5 summarize these results.

Differences between laboratories were few. Precision appears to be identical for most paramteres. Those for which analysis had to be performed separately foreach laboratory were: aluminum, potssium, manganese, lead, ortho-phosphorus, and total phosporus.

It seemed that for a number of parameters, precision was dependant on concentration. Relationships of decreasing precision with increasing concentration were found for aluminum, cadium, copper, lead, zinc, ammonia, total phosphorus, fluoride, mercury, COD, and turbidity. The attached graph for leads (Figure 1) is typical of these paramters. No parameters were found that show precision with increasing concentration. This is not suprising. The higher actual concentration, the more room there is for error.

Multivariate analysis failed to show any meaningful patterns on the correlation matrix. Significant correlations were found between a number of parameters but the lack of patterns and consistancy in these results leads to conclusion that the parameters behave independently of each other.

Lack of precision can result from any number of factors. At low levels such as those observed in this study two important ones are detection limits and the interval at which values are reported. These factors become less important as concentrations get high. Certainly the impre~~s~~cision observed in arsenic, sulfide, fluoride and calcium is largely a function of these two factors rather than inability of laboratories to reporduce results. Imprecision in phosphorus to a large extent results from concentrations that are small relative to the scale on which they are reported.

It is clear that for most parameters precision is adequate for purposes of regional characterization and impact analysis. It should be mentioned, however, that this says nothing about accuracy. Duplicate analysis is not a suitable tool for assessing this quality which is necessary to full determine the value of the data.

2. Leaching and Metal Pathways

Duplicate samples were also taken on a routine basis by the leaching and metal pathways team. One duplicate sample was collected for every day of sampling. The location each say was chosen at random. One sample was sent to the analytical laboratory (Eisenreich or MDH) with the proper identification while the second was identified as being from a non-existant station. In this fashion, the laboratories were not aware which samples were duplicates.

A list of duplicate samples is found in table 7.

Statistical analysis was identical to that outlined for the surface water program with one exception. Due to the wide range of values observed, differences between values were expressed as a percentage of the mean value of the duplicates. The statement being made, then, is: if duplicates were taken on all samples, 50% of them would show differences of less than X% of the observed value. Coefficient of variation is computed the same way as for surface water. Because of the large differences in water quality observed between the United States Steel bulk sample pit and the sites on Unnamed Creek and Bob Bay, the U.S. Steel duplicates were considered seperatly.

Results for all samples except U.S. Steel arepresented in tables 8 and 9. No significant differences were detected in precision between Eisenreich and MDH, so no distinction was made in the computation of results. In general, it appears that precision was greater in the leaching program than for surface water quality. This is very likely due to the greater concentrations of most parameters found at the leaching stations. An error of 5 ug/ℓ is not very significant when concentrations are well over 100 ug/ℓ, but may be very significant when concentratins are near detectable limits. For the leaching program, no parameters with a reliable sample size exhibited a coefficient of variation greater than 20%. By all indications, then, precision in the leaching program is quite good.

Water quality in the U.S. Steel pit differed dramatically from all other sampling locations. Among the most notable characteristics were a low pH, very high concentrations of copper nad nickel, and negligible concentrations of nutrients and organic substances. Estimates of precision for all important parameters from this site indicate excellent precision (Tables 10, 11). No parameters with an adequate sample size had a coefficient of variance over 20%, and indeed only three (chloride, magnesium and sulfate) were over 10%. From the estimates of actual imprecision (upper confidence limits for percentiles) it appears that we would not expect any sample to vary more t-an a few percent upon repeated analysis.

C. Distilled Water Blanks

In an effort ot estimate sample contamination, samples containing deionized water ("blanks") were submitted for analysis by the leaching team. One blank sample was sent ot coincide with each day's sampling. These samples were "masked" with the name of a non-existant sampling station.

Table 12 summarizes the results of this program. Most parameters were not found in detectable amounts most of the time, and when contamination did occur, it was rarely substantial. Some contamination was found, however, primarally in non-metalic parameters such as silica, chloride and organic and inorganic carbon. Contamination was also found in dissolved copper, when 60% of the samples were reported to have concentrations above detectable limits.

Statistical analysis was also performed to determine if relationships exuted between parameters and particularly to see if contamination in any one parameter seemed to imply contamination in others. This was done by categorizing the result for each parameter as "above detection limit" or"below detection limit"and then establishing a 2x2 table for each pair of parameters. Table 13 illustrates one of these tables. A test for independence was t-en performed using Fisher's exact test (Dixon and Massey, 1969). Very few relationships were found. Only two (total calcium - total copper and total iron-dissolved iron) were found with significance levels less than 2=0.05, while three others had significance levels between 0.10 and 0.05 (table 14). It appears, then, that contamination of more than one parameter did not occur on any systematic basis.

D. Lake Sediments

As little temporal variability is expected is lake sediments, samples were not taken at any location at more than one time. Rather, three samples were taken at thesame location at the time ofsampling. Variability between these measurements represents the best available estimates of precision for hte lake sediment analysis, although there is probably some small actual variation between samples. Analysis was performed by the Hibbing laboratory of the Minerals Division of the Department of Natural Resources.

Coefficients of variation were computed to ten major parameters at nine randomly selected sites. These figures are presented in table 15. It appears that variability is fairly low for most parameters, although lead may be an exception. It also seems that variability for certain metals (Co, Ni, Fe) may be greater for surface samples than for those from deeper in the sediment. This may relate to the higher concentrations for these metals found at the top of the sediments.

III. Special Projects

A. Comparison of USGS and MDH

Surface water quality data for the Copper-Nickel Study has been obtained from analysis of samples by the U.S. Geological Survey (USGS) and the Minnesota Department of Health (MDH). The USGS laboratory performed analyses until approximately September 1, 1976, while analyses after this date were performed by MDH.

At the time of the changeover, a number of samples were split and sent to both laboratoies. Duplicate samples of this nature were taken from eight lake stations between August 16 and August 30, 1976, and from ten stream stations between September 8 and September 23 of the same year. Fourteen of these duplicates were only analyzed for primary metals (cadmium, cobalt, copper, lead, nickel, zinc), one only for nonmetallic parameters, and three for all parameters. While this sample size is adequate for assessing differences in primary metal analysis, it is inadequate for detection of real interlaboratory differences in the other parameters.

Statistical analysis of these duplicate samples was designed to determine the differences between laboratories. Ideally, the differences (USGS reading-MDH-reading) should be close to zero with as many positive differences (USGS higher than MDH) as negative differences (MDH higher than USGS). There are standard statistical tests for this sort of hypothesis. If the differences are normally distributed, the paired t-test can be used. The quantity is computed and compared

$$t = \frac{\bar{D}}{S_{\bar{D}}}$$

where $\bar{D}$ = average difference

$S_{\bar{D}}$ = standard deviation of the differences

to a table of student's t-distribution with (n-1) degrees of freedom (n = number of pairs). If, however, the differences are not normally distributed, the hypothesis that the median difference is zero can be tested by nonparametric means. This test is known as Wilcoxon's signed rank test (Snedecor and Cochran, 1967). Most of the metal differences proved to have nonnormal distributions, lead being the notable exception. Because of the small sample size, differences for parameters other than the primary metals were assumed to follow a normal distribution. It must be emphasized that the sample size for these parameters is too small to make definitive statements; the tests only suggest possible trends.

Further analysis can be done graphically. Ideally, a plot of Health Department readings against USGS readings would have all points lying along the line y=x. More practically, all points should be located near this line and randomly located above or below it. Systematic departures from this pattern can shed some light on the differences between laboratories.

A problem with this data is that metal levels are often at or near detection limits. This obviously presents problems for analysis, especially when detection limits for each laboratory are not identical. For analytical purposes, the following conventions were adopted: if both laboratories reported values below detection limits for a given sample, that sample was not considered, if both readings were below the higher detection limit. In the case where one laboratory reported a value below the detection limit and the other a value above, the value below the detection limit was considered to be zero, thus assuming the maximum possible difference between laboratories. In summary, given the following three readings;

In the case of differing detection limits, the [illegible] was not considered if ...

	USGS	MPH
1)	<.1	<.1
2)	.3	<.5
3)	<.5	.7

observations 1 and 2 would not be included in the following analysis, while the USGS reading on observation 3 would be considered to be zero and the point included.

The results of the analysis indicate that there was no difference between laboratories for most parameters. The results from this sampling program are quite consistent with the results from the routine duplicate sampling program. For almost all parameters, we may work as if the readings were all from the same source. A parameter-by-parameter analysis follows.

Cadmium

The Wilcoxon rank-sum test indicates significant differences between the laboratories (p=.05). Analysis was complicated by a large number of values below detection limits but the result is consistent even if all these are deleted. The attached graph (figure 2) indicates that on most splits, MDH obtained higher readings than did USGS.

Cobalt

Formal analysis of cobalt data could not be performed due to Health Department's relatively high detection limit (0.5 μg/l.). Only two out of 17 MDH observations were above this level. However, in 12 of the cases where MDH reported <0.5 USGS reported values greater than this amount. This strongly suggests that USGS and Health Department cobalt readings are not strictly comparable; USGS readings are higher.

Copper

Both the Wilcoxon test and the scatter plot (figure 3) indicate that there is no difference between the copper readings obtained by both laboratories.

Lead

The t-test for lead duplicates indicates that the mean difference is indeed zero and the scatter plot (figure 4) shows no significant deviation from the hypothesis that both laboratories report identical values.

Nickel

The Wilcoxon test for differences between samples yields marginally significant results for nickel. This, however, is greatly influenced by the large readings obtained by Bob Bay. At this site, USGS reported a value of 110 μg/l while the Health Department reported 82 μg/l. When this point is deleted, results become somewhat confusing. The scatter plot (Figure 5) seems to indicate that USGS has a tendency to produce higher readings than MDH at extreme ends of the scale while they tend to be closer together in the middle of the observed range.

Zinc

There appears to be no interlaboratory differences in zinc readings. The scatter plot (Figure 6) does indicate a tendency for readings to be further apart at low concentrations, but neither laboratory is consistently higher or lower than the other.

Other Parameters

A table (Table 16) of other parameters including approximate p values for the hypothesis of no difference between laboratories for which split samples were taken is attached. The p value may be interpreted as the probability that the statement "there is a significant difference between the laboratories" would be in error. Values less than .05 are generally interpreted as indicating a real difference, while values between .10 and .05 are looked on with some suspicision. It must again be emphasized that the sample size is small enough that these test must be regarded as suggesting possible trends, not as providing difinitive results. It appears that MDH may obtain higher readings on identical samples for nonfilterable residue, ammonia (NH_4), potassium, and possibly sodium. USGS may obtain higher readings for fluorides and nitrites + nitrotes (NO_2 + NO_3).

AMAX - COPPER-NICKEL JOINT METALS SAMPLINGS

The joint sampling program of AMAX, Inc. and the Regional Copper-Nickel Study consisted of dissolved metals samples taken in May and June, 1976 from the upper Dunka River (Copper-Nickel Monitoring Station D-2), and February, 1977 samples for both total and dissolved metals taken from the upper Dunka River and the upper Partridge River (P-5). Four samples were taken simultaneously at each sampling time. Two of the four samples were taken by a team from the Copper-Nickel Surface Water Project; the other two by a Barr Engineering, Inc. team for AMAX. One of the Copper-Nickel samples was given to AMAX for analysis while one of the AMAX was given to Copper-Nickel. Acidification and filtration were performed befor samples were exchanged. In May and June, 1976 Copper-Nickel samples were analyzed by the U.S. Geological Survey Laboratories and in February, 1977 by the Minnesota State Health Department. AMAX samples were analyzed by SERCO laboratory.

Analysis of the results of this program shows little difference resulting from collection procedures but some significant differences due to analytic procedures. This is particularly pronounced in dissolved metals, and is one reason why sampling for dissolved metals was discontinued by the surface water program. Differences were somewhat less in February, 1977 than in May and June 1976. This may be due to the change in laboratories by Copper-Nickel.

Statistical analysis was performed using standard analysis of variance techniques.
The model employed for the 1976 sample was:
$Y = \mu + Ai + Cj + Dk + ACij + ADik + CDjk + Eijkl$

mall letters are subscripts

when Y = concentration of parameter
Ai = Analytical laboratory effect (USGS or SERCO)
Cj = Collection effect (AMAX or Cu-Ni)
Dk = date effect (May or June)
The model employed for the 1977 sample was:
$Y = \mu + Ai + Cj + Sk + ACij + ASik + CSjk + Eijk$
when Y = concentration of parameter
Ai = Analytical laboratory effect (MDH or SERCO)
Cj = Collection effect (AMAX or Cu-Ni)
Sk = Site effect (P-5 or D-2)

Copper

Results for the 1976 samples for dissolved copper showed significant differences due to both collection and analysis. Analysis of variance indicates that samples collected by Copper-Nickel gave higher readings than those collected by AMAX ($p <.025$). Additionally, samples analyzed for AMAX produced significantly lower results ($p < .025$) than did those analyzed by Copper-Nickel. In particular, it should be noted that the samples both collected and analyzed by Copper-Nickel were an order of magnitude higher than any of the others (see Table 17).

The February sampled showed no difference due to collection procedure but again showed significantly higher results from Cu-Ni analysis as opposed to AMAX ($p < .005$).

Analysis of total copper in February is complicates by the differences between the two sites. It appears, however, that the Cu-Ni results are again significantly higher than AMAX readings ($p < .005$).

Lead

The results for dissolved lead in May and June are very similar to those observed for dissolved copper. AMAX collection produced lower readings than did CU-Ni collection ($p < .05$) and Cu-Ni analysis produced higher results than did AMAX analysis ($p < .05$). In particular, the samples both collected and analyzed by Copper-Nickel produced much higher results than any other combination.

The situation for dissolved lead in February is much different. No significant differences were observed for either collection or analysis. The results for total lead are difficult to interpret but it appears that readings from AMAX analyzed samples were significantly lower ($p < .05$) than those resulting from Copper-Nickel analysis. No difference was noted between collection procedures.

Nickel

No significant differences due either collection or analysis were noted for dissolved nickel in May and June ($p > .10$). This is also the case for the February split sample ($p > .75$).

The February total nickel sample is distinguished by one very high reading (30 μg/l) obtained on an AMAX collected Copper-Nickel analyzed sample from P-5. This observation runs counter to the trends suggested by the rest of the data and is probably best considered as an anomaly, an infrequent occurance not indicative of a general trend. If this reading is deleted, it appears that AMAX analysis produced slightly higher results than Copper-Nickel analysis ($p < .005$). No difference was noted between collection procedures when this sample is omitted.

Zinc

The major feature of the May and June sample for dissolved zinc is the high variability of the observations. Although the observed values for May alone range from 4 μg/l to 22 μg/l and for June from 6 μg/l to 18 μg/l these differences do not appear to be at all systematic. Any differences in collection or analysis are obscured by the high random variability of the readings. The February dissolved zinc samples do not appear to be quite a variable as those taken the previous year but again variability was high enough that no significant differences were observed.

The results for total zonc in February are quite confusing. It appears that Copper-Nickel analysis produced significantly higher results on the Dunka River samples while AMAX analysis gave higher readings on the Partridge River water. This may be a random occurance reflecting no more than a high degree of experimental error or it may indeed reflect some systematic occurence it is impossible to say.

Cadmium

No significant differences due to analysis were observed in the May-June dissolved cadmium sample. However, it does appear that copper-Nickel collection resulted in higher readings than did AMAX collection ($p < .01$). The opposite appears to be true in February, where AMAX collection produced significantly higher results than Copper-Nickel ($p < ,05$). Again, no differences due to analysis were noted. No significant differences of any sort were noted in the total cadmium sample.

Discussion

It is interesting to compare these results to those obtained by the interlaboratory Round Robin program (III C) which includes both SERCO laboratory and the State Department of Health. The second round involved a joint sampling for total metals by AMAX and Copper-Nickel. Consistant with the total metals results obtained from the February 1977 sample reported above, no differences were found between the samples collected by either team.

The Round Robin results seem to indicate a tendency for the State Health Department to produce higher readings for the total copper than SERCO; this is consistent with the February results. The first round of the Round Robin saw higher readings from the State Health Department for the total lead as opposed to SERCO as was the case in the February joint sample but the second round produced no significant difference.

No significant differences were observed in the Round Robin for nickel; the joint sample seems to indicate higher SERCO readings. Zinc results in both the joint sample were inconclusive, whi;e the round robin results indicated higher SERCO readings.

Round 2 of the Round Robin showed significantly higher total cadmium readings from SERCO; the February joint sample and round 1 and 3 revealed no such difference.

Pertaining to dissolved metals it is worth noting that descripancies due to both collection and analysis were much greater in the May-June joint sample than in February. A number of explanations (including random chance) are possible but the most likely would appear to be the change in analytical laboratories by Copper-Nickel fromUSGS to the State Health Department. It is apparent, though that problems exist with dissolved metals determinations and caution should be exercised in applying any results from these readings.

For a discussion of the accuracy of these two laboratories see the discussion of the fourth Round Robin (Section III. C.).

C. Interlaboratory Round Robin

On four occasions, water samples were obtained and distributed to six laboratories. These labortories were: Minnesota Department of Health (MDH), SERCO, Inc., The Environmental Research laboratory of the U.S. Environmental Protection Agency (ERL), Erie Mining Company, Dr. Steven Eisenreich of the University of Minnesota, and Mr. Donald Siegal. Analysis was done for seven parameters: total copper, total nickel, total zinc, total cadmium, total lead, sulfate, and alkalinity.

The first three rounds consisted of natural water samples taken from the study region. Samples were taken for round one from Unnamed Creek (BB-1) by the surface water quality team on March 29, 1977. An additional set of samples was collected simultaneously by Erie Mining personnel. Water for the second round was obtained from the Upper Dunka River (D-2) on May 11, 1977, and was jointly sampled by field workers from the Copper-Nickel Study and AMAX, Inc. Round three consisted of samples from Filson Creek (F-1) and Stony River (SR-2) taken by the Copper-Nickel staff on July 25, 1977. The fourth round consisted of a sample from a Twin Cities area lake which was spiked with standard additions obtained from the U.S. Environmental Protection Agency.

Results were compared using standard analysis of variance. Analysis was complicated by the fact that not all labortories completed each round for all parameters. As result, comparisons were made for each round separately. The models used were

$$Y = \mu + Li + Cj + Eij$$

for rounds 1 and 2, and

$$Y = \mu + Li + Sj + Eij$$

for round 3, where

Y = observed concentration
Li = difference due to laboratory
Cj = difference due to collection team
Sj = difference due to location of sample.

Round 4 will be considered separately. A parameter-by-parameter of the first three rounds follows. All raw data may be found in tables 18-21 and are graphed in Figures 7-12. In no ease in rounds 1 and 2 were significant differences found due to the collection team; this factor will not be considered further.

Copper: Highly significant differences between laboratories were found in rounds 1 and 2 ($p<.005$). In round 1 this appears to be due to MDH, which recorded a significantly higher ($p < .005$) level than did the rest of the laboratories. In round 2, Erie Mining obtained significantly lower results than the other four laboratories ($p <.005$). The readings obtained by ERL and MDH appear to be identical ($p \geq 0.25$) while SERCO lies between these two and Erie ($p < 0.01$). No differences were found in round 3. Figure 7 contains a graph of all results.

Nickel: Water from the first round samples contained an unusually high amount of nickel. SERCO appeared to obtain a value significantly lower than the other four laboratories ($p < 0.005$). Then also appeared to be a difference between the remaining four with ERL and Erie obtaining higher recordings than MDH and Eisenreich.

Due to a high detection limit (5 μg/l), Erie Mining results were not considered in round 2, non for the SR-2 sample in round 3. Aside from this, no significant differences were found in either of these rounds.

Zinc: No significant differences were found in round 1. However, in both round 2 and round 3 SERCO reported significantly higher results than the other laboratories involved. Again, Erie Mining was eliminated from round 2 because of a high detection limit (10 μg/l).

Cadmium: Significant differences were found in round 2 only, although Erie Mining was eliminated from rounds 1 and 2 because at a high detection limit. In round 2, SERCO reported significantly higher results did ERL and MDH ($p < 0.005$).

Lead: Results for lead were quite confusing. In round 1, each laboratory appeared to be significantly different from every other, with the largest difference being due to high readings obtained by MDH ($p < 0.005$). Erie Mining was eliminated from round 3 because at a high detection limit (1 μg/l) leaving results in round 2 and 3 only from MDH and SERCO. No significant differences were found between them.

Sulfate: In the first round, five laboratories reported results that were not significantly different from any other. In the second round each of the four laboratories involved reported results significantly different from each of the others. The greatest difference was between SERCO and the next lowest lab, Siegal ($p < 0.005$). Siegal appeared to be significantly lower than MDH ($p < 0.025$) while MDH in turn was significantly lower than Erie ($p < 0.025$).

Alkalinity: In both rounds 1 and 2 Erie Mining obtained significantly higher results than MDH, SERCO, or Siegal. No difference was found in round 3, although Erie appeared to obtain much higher results than the other three on the F-1 sample.

Summary: Few consistent differences were found between laboratories in the first three rounds for most parameters. It does, however, appear that Erie Mining obtained systematically higher results for alkalinity than did other laboratories and that SERCO reported higher results than other laboratories for Zinc.

Round 4

Results from round 4 were submitted only by MDH and SERCO. A total of four samples were analyzed by each laboratory, two relicates each at natural water spiked with two different standard additions. Analysis of variance was again used for statistical analysis, with the model being:

$$Y = \mu + Li + Sj + Sij + Eijk,$$

where Y = reported concentration
μ = overall mean
L_i = differences due to laboratories ($i = 1,2$)
S_j = differences due to different spikes ($j = 1,2$)
LS_{ij} = laboratory x spike interaction

Results are graphed in Figure 13.

Copper: SERCO obtained significantly lower ($p = .01$) results than the standards on the first spike (lower metal concentrations) and significantly higher ($p < .005$) results than the standard on the second spike (higher metal concentrations). MDH obtained significantly higher results from the first spike ($p = .05$), but there was no signigicant difference between SHD MDH and the standards on the second spike.

Nickel: SERCO obtained results on both spikes that were slightly lower than but significantly different ($p = .05$) from standards. No difference was found between the standards and the MDH results.

Zinc: Again, SERCO reported results significantly lower than the standards on both samples ($p < .005$), while no significant difference was found between the standards MDH.

Cadmium: No difference was found between MDH and the standards, SERCO was again significantly lower than the standards ($p = .05$).

Lead: Both SERCO and MDH reported significantly lower results than standards ($p < .005$). These differences were more pronounced on the second spike (higher concentrations) than on the first, and in both cases SERCO reported significantly lower results ($p = .05$) than MDH.

D. pH Study

1. Surface Water

With the exceptions of the cummer months, pH readings were taken by field personnel at the Kawishiwi field laboratory and not in the field. In an attempt to study the effects of time and temperature on the pH of a water sample two one liter samples were collected in the field. The pH was recorded in the field and the samples returned to the laboratory. One sample was allowed to warm up to room temperature, the other was refrigerated at about 3°c.

The pH at collection time was 7.0 and the water temperature 1.5°. pH was taken periodically for five days. At the end of that time, the pH in the unchilled bottle had risen to 7.6 and the temperature to 19°. The pH in the chilled bottle rose to 7.1 during the same period. The pH meter was recalibrated before each set of measurements was taken

The attached graphs (Figures 14, 15) show the relationships between pH, temperature and time. It is clear that the refrigerated sample was affected to a much lesser extent than the unchilled sample. It is also clear that given enough time, an unchilled sample can be drastically affected. Fortunately, pH determinations were made within a few hours of the collection of the sample. The field laboratory determinations, then, are probably quite close to the actual field values.

2. Leaching and Metal Pathways

pH is particularly important in predicting heavy metal behavior. In some instances, small shifts in pH can have drastic effects on metal speciation. Whenever possible, readings were taken insitu. However, there are times when this is not practical (i.e. during heavy rains, extreme cold, equipment breakdown, etc.). In these cases, samples must be transported to the meter. During these periods, it is desirable to predict the maximum potential shift; and to set a maximum holding time for a sample without having shifts in pH. For the leaching program, the maximum shift acceptable is 0.1 pH unit or a 1.3 percent variation from the insitu reading. In order to evaluate the maximum holding time, data were collected at the EM-1 site. EM-1 was chosen because it is an "average" site in the Unnamed Creek drainage and represents the outflow of the watershed. To delineate the time involved for the shift, pH readings were taken five separate samples with time intervals from 0 to 26 hours (Table 22). The results show that the time of >.1 shift is between 5.6 and 26 hours. Therefore, it will be assumed that the maximum holding time is six hours for the Unnamed Creek drainage. This is also within the recommended time given by the U.S. EPA in the <u>Manual of Methods for Chemical Analysis of Water and Wastes</u>, 1974.

Mention is made that EM-1 represents an "average"; water quality will vary somewhat from one tributary to another. To define this variation, both insitu pH readings and lab readings were taken. These are compiled in Table 23. There is insufficient data to show any shifts occurint (g) in <6 (less than) hours.

US Steel bulk sample site pH stability was also tested. The mean percent variation for 45 minutes was 1.9 percent and mean unit variation of 1.1. This type of shift is not within acceptable tolerance limits. Therefore, all pH readings were taken insitu at this site.

E. Field Acidification Study

Three total and three dissolved metals bottles were filled with deionized distilled water and acidicified with 10% v/v ultropure (a) nitric acid. One of each type of bottle was kept in the Minnesota Department of Health laboratory. The other two bottles of each type, one of which was sealed and marked not to be opened, were sent to field personnel. The remaining set of bottles had accompanying preservative vials which were to be added to the sample bottles. The four bottles were then returned to the laboratory in the usual manner.

The purpose of this study was to determine what effect field acidification and transport of samples had on metal analyses. If there was no effect, it would be expected that all three bottles showed nearly identical low readings. The results are listed in table 24.

Little change was noted in most metals. However, lead and zinc content appears to be higher in transported samples than in samples left in the laboratory. Overall, it appeats that fiels acidification was not a major contributor sample contamination.

F. Kemmerer Study

The Kemmerer bottles used in sampling were checked as a possible source of trace metal contamination. After normal cleaning, distilled deionized water was left in a kemmerer bottle for 15½ hours. This water was acidified along with a blank of distilled water. Both were sent to the Minnesota Department of Health for primary metal analysis.

The results (Table 25) show significant quantities of all metals except cobalt. Therefore, the experiment was repeated. One sample again followed normal cleaning of the bottle, a second was taken after "soaking" the bottle in a lake for a few minute. A series of withdrawls were made fron each kemmerer starting 15 minutes after filling.

Substantial contanination was wvident in the insoaked kemmerer within fifteen minutes (Table 26). However, the lake soaked kemmerer bottle showed little, if any, contamination of the water. It appears, then, that contamination of samples in the kemmerer bottle can be caused by faulty rinsing.

Complexing Capacity

Complexing capacity measurements were performed by Dr. Thomas Bydalek of the University of Minnesota - Duluth. Most analysis was performed using a method developed by Dr. Bydalek refered to as the titration metho~~s~~d. Two qualtiy assurance procedures were performed. The first was a comparison of the titration method to the standard methed orinally developed by Chav et al. (1974). Secondly, duplicates were analyzed throughout the course of the complexing project.

Eighteen samples were split and analyzed by Dr. Bydalek using both methods. Statistical analysis of the results indicates no difference in the readings obtained by the two methods ~~(see table ——— for details);~~ it can be safely stated that use of the two methods did not affect the results.

Duplicate analysis was performed on seven lake samples analyzed by the titration method. These duplicates revealed a coefficient of variation of 11.71% at a mean complexing capacity of 2.54. The mean difference between duplicates was 0.38 with standard deviation 0.18. If duplicate analysis were performed on all samples, it can be stated with 90% confidence that half of the duplicates would be less than 0.41 apart, and 75% of them would be less than .60 apart. It appears that complexing capacity movements are quite precise.

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Appendix A. Calibration of Meters

Conductivity Meter Calibration:

Conductivity measurements are expressed at 25°C; therefore, readings at temperatures below 25°have to be converted. The correction factor is obtained by measuring the conductance of a chilled stream sample at each degree centigrade as it warms slowly to 25°C, then by dividing conductance values of each temp into the conductance value obtained at 25°C you obtain a correction factor which applies to other stream samples which might be measured at below 25°C in the field. Monthly, two liters of water (usually SH-1 water) is collected; one is frozen, one is refrigerated. A large beaker with thermometer and conductivity probe suspended in it is placed on a hot plate stirrer. The beaker is filled with sample water and ice chips from the frozen sample are added to chill the solution to as near to zero as possible. Heat and stirrer are turned on and just as the last of the ice melts into soultion, conductivity measurements are begun and taken at each degree to 25°C. This was done monthly and these correction factors apply only to the bridge and probe set used. Chart A shows a completed temp correction curve. After several months; therefore, this calibration is now done approximately every three months.

Also, monthly the probe and bridge is checked against a known conductance solution. Potassium chloride solutions are mixed up as outlined in Standard Methods (13th Ed. p 325) in 0.001M (147 μmho/cm) or 0.001M (1413 μmho/cm) concentrations. When a conductance standard solution is mixed up, a number of other conductance meters (USFS watershed and Cu-Ni leaching) are also tested. If the platinum black has flaked off the conductance probe, it is replatinized with a #3139 Yellow Spring platinizing instrument using YSI platinizing solution (Platinum chloride 3% dissolved in 0.025% lead acetate solution).

Calibration of Dissolved Oxygen Meter:

The YSI 57 Dissolved oxygen meter was used only for lake sampling and was calibrated just prior to a sampling series by one of the following methods.

Winkler Titration: A small kemmerer type sampler is used to fill two 300 ml BOD bottles from a natural water source (SH-1). They are fixed immediately at the site. The kemmerer is then filled and stopped and hurried back to lab where BOD bottles are titrated as soon as possible. After a value from the titration is obtained the D.O. meter probe and stirrer is immersed into the kemmerer and the meter is adjusted to that value with the calibration control.

Saturated Water: A volume of water (1000ml) is aerated about ½ hour with a aerating pump. The probe with stirrer is immersed. The temperature is taken and a PPM oxygen value is obtained from Table 1 for air saturated fresh water for that temp. This value is further corrected for effects of atmospheric pressure by obtaining a correction factor off Table 2 for the corresponding atmos. pressure of the day. Table 1 value is multiplied by table 2 value and the D.O. meter is adjusted to this corrected value using the calibrate knob.

Air calibration: The probe is placed in a moist air environment. This is done by wrapping the probe in a damp cloth so that cloth isn't touching the membrane Wait 10 minutes for temperature stabilization, read temp temperature and look up correction factors from table 1 and Table 2 and adjust the calibrate knob till until the meter reads the correct calibration value.

List of Tables

Table 1. Accuracy limits for field parameters

Parameter	Analytical Methods	Manufacturers Stated Accuracy
Dissolved oxygen	Polarographic submersible probe	± 1% or[a] ±0.1 ppm
Temperature	Double thermistors in submersible probe	± 0.1°C
pH	pH meter with combined electrode	± 0.1[b] pH unit
Specific conductance	Wheatstone bridge	± 1%
Secchi disk	20 cm diameter, black and white	± 0.12 m[c]

[a] Which ever is larger
[b] At full scale
[c] Estimated based on experience

TABLE 2 Surface Water Sampling Program

Duplicate Sample Dates and Locations

Location	Date	Laboratory	Parameters*
K-1	3/17/76	USGS	1
SR-1	3/25/76	USGS	1
BI-1	4/12/76	USGS	1
E-2	4/29/76	USGS	1
SR-3	5/13/76	USGS	1
K-6	5/19/76	USGS	1
K-5	6/ 3/76	USGS	3
SL-3	6/23/76	USGS	3
LA-2	6/30/76	USGS	3
LBH-3	7/ 1/76	USGS	3
I-1	7/19/76	USGS	1
SL-1	7/22/76	USGS	1
LGO-1	8/16/76	MDH	2
LBH-2	8/17/76	MDH	2
LBH-3	8/19/76	MDH	1
LCY-1	8/23/76	MDH	2
P-2	8/24/76	USGS	1
LWF-1	8/24/76	MDH	2
LWI-1	8/25/76	MDH	4
LSB-1	8/30/76	MDH	2
LA-1	8/31/76	MDH	2
P-1	9/23/76	MDH	1
SL-2	10/25/76	MDH	1
SR-2	11/ 4/76	MDH	1
K-7	11/17/76	MDH	1
SR-3	1/13/77	MDH	1
P-3	1/14/77	MDH	1
LBH-2	2/22/77	MDH	1
LBH-3	2/24/77	MDH	1
BB-1	3/28/77	MDH	1

*Parameter Code

1 All parameters
2 Primary metals (cadmium, cobalt, copper, lead, nickel, zinc, iron, aluminum)
3 All parameters except primary metals
4 Primary parameters only

Table 3 Surface Water Quality
Points Deleted from Duplicate Analysis

Site	Date	Parameter	Value	Lab
K-6	5/19/76	Cadmium	0.37	USGS
LBH-3	2/24/77	Copper	10.0	MDH
LBH-2	2/22/77	Total Phosphorus	308.0	MDH
SR-1	3/25/76	T.O.C.	0.5	USGS
SR-3	5/13/76	C.O.D.	830	USGS
SR-2	8/24/76	C.O.D.	830	USGS

Table 4

Surface Water Quality
Detection Limits and Sensitivity

Parameter	Lab	Detection Limit	Reported at Intervals of
I. Metals (All concentrations in μg/l)			
Aluminum	USGS	10	10
	MDH	0.5	1 (<100) 10 (>100)
Arsenic	USGS	1	1
	MDH	0.3	.1
Cadmium		0.01	.01
Calcium	USGS	100	100
	MDH	200	200
Chromium		0.1	100
Cobalt	USGS	0.3	0.1
	MDH	0.5	0.1
Copper		0.1	0.1
Iron		20	10 (<1000) 100 (>1000)
Lead		0.1	0.1
Magnesium	USGS	100	100
	MDH	30	10
Maganese	USGS	1.0	10
	MDH	0.4	1
Mercury	MDH	0.10	0.01
Nickel	USGS	1.0	1.0
	MDH	0.5	1.0
Potassium	USGS	100	100
	MDH	10	10
Silver	USGS	0.05	0.01
	MDH	0.02	0.01
Sodium	USGS	100	100
	MDH	15	100
Zinc	USGS	1	0.1
	MDH	0.1	0.1
II. Nutrients (All concentrations in mg/l)			
Ammonia	USGS	0.01	0.01
	MDH	0.05	0.01
Nitrite		0.01	0.01
Nitrate + Nitrite		0.01	0.01
Total Organic Nitrogen	USGS	n.a.	0.01
Kjeldhal Nitrogen	USGS	0.1	0.01
	MDH	0.5	
Total Nitrogen		n.a.	0.01 (<1) 0.1 (>1)
Ortho-Phosphorus	USGS	0.01	0.01
	MDH	0.001	0.001
Total Phosphorus	USGS	0.01	0.01
	MDH	0.001	0.001

Table 4 cont.

	Parameter	Lab	Detection Limit	Reported at Intervals of
III.	General Parameters (All Concentrations in mg/l)			
	Alkalinity		10	1.
	Chloride		0.5	0.1
	Color		1 pt-co unit	10. pt-co uni
	Fluoride	USGS	0.1	0.1
		MDH	0.01	0.01
	Hardness	MDH	n.a.	1.0
	Oil and Grease	USGS	1.0	1.0
		MDH	1.0	1.0
	Nonfilterable residue	USGS	1.0	1.0
		MDH	0.5	0.1
	Silica		1	0.1
	Sulfate		1	0.1
	Sulfide	MDH	0.01	0.01
	Turbidity		1 unit	0.1 JTU
IV.	Demand (All Concentrations in mg/l)			
	C.O.D.			1
	T.O.C.		1.0	1.0

n.a. = not applicable

Table 5

Surface Water Quality
Upper 90% Confidence Limits for Percentiles and Coefficient of Variation

Parameter	Sample Size	Upper Bound on Percentiles			C.V.(%)
		50%	75%	90%	
I. Metals (All concentrations in µg/l)					
Aluminum (USGS)	11	20	50	*	12.4
Aluminum (MDH)	13	9	20	*	12.0
Arsenic	12	0.2	0.3	*	84.0
Calcium	22	800	2000	17,100	28.0
Cadmium	24	0.02	0.03	0.11	56.9
Chromium	10	0.2	0.3	*	35.3
Copper	26	0.3	0.6	1.2	26.2
Iron	26	60	90	160	9.4
Lead (USGS)	9	2.4	3.9	*	81.0
Lead (MDH)	17	0.2	0.3	0.8	36.4
Magnesium	22	300	580	2,000	7.2
Manganese (USGS)	13	20	50	*	26.3
Manganese (MDH)	10	17	24	*	10.8
Mercury (MDH)	5	0.09	0.32	*	53.3
Nickel	26	1.0	2.0	25	42.4
Potassium (USGS)	13	0.2	0.3	*	15.9
Potassium (MDH)	9	0.04	0.06	*	2.1
Sodium	26	100	500	1,500	10.5
Zinc	26	0.8	3.8	7.2	88.7
II. Nutrients (All conecntratons in µmg/l)					
Ammonia	23	0.03	0.20	0.20	61.2
Nitrate + Nitrite	23	0.03	0.05	0.07	28.2
Kjeldhal Nitrogen	20	0.07	0.15	0.37	21.7
Total Nitrogen	19	0.10	0.19	0.48	17.2
Total Organic Nitrogen (USGS)	7	0.8	0.14	*	8.4
Ortho-phosphorus (USGS)	13	10	20	*	67.2
Ortho-phosphorus (MDH)	9	2	5	*	44.1
Total phosphorus (USGS)	13	20	20	*	53.1
Total phosphorus (MDH)	9	6	10	*	44.1
III. General Parameters (All concentrations in µmg/l)					
Alkalinity	23	2.	4	7	6.0
Chloride	23	0.3	0.6	1.1	12.1
Bicarbonate(USGS)	13	2	8	*	8.4

Table 5 cont.

Upper 90% Confidence Limits for Percentiles and Coefficient of Variation

Parameter	Sample Size	Upper Bound on Percentiles			C.V%
		50%	75%	90%	
III General Parameters cont.					
Color (pt-co units)	23	10	30	65	18.1
Fluoride (USGS)	13	0.3	0.8	*	55.6
Fluoride (MDH)	10	0.1	0.1	*	27.1
Hardness (MDH)	9	2.0	8.0	11.1	3.7
Non Filterable Residue	21	1.7	3.1	*	80.7
Silica (USGS)	13	0.2	0.3	*	2.2
Silica (MDH)	10	1.0	3.0	3.0	7.7
Sulfate	24	1.1	1.7	*	10.1
Sulfide(USGS)	11	0.6	4.4	8.3	87.4
Turbidity	23	0.3	0.9		55.6
IV. Demand (All concentrations in µg/l)					
C.O.D.	14	6	42	*	31.7
T.O.C.	10	1	2	*	27.1

*insufficient sample size

Table 6

Surface Water Quality

Parameters ranked by coefficient of variation

Parameter	Coefficient of Variation (%)	at Mean Value
Zinc	88.7	4.97
Sulfide (USGS)	87.4	1.16
Arsenic	84.0	0.80
Lead (USGS)	81.0	0.84
Nonfilterable residue	80.7	2.85
Ortho-phosphorus(USGS)	67.2	14.5
Ammonia	61.2	0.06
Cadmium	56.9	0.04
Turbidity	56.6	2.50
Fluoride(USGS)	55.6	0.25
Mercury (MDH)	53.3	0.18
Total Phosphorus (USGS)	53.1	24.4
Ortho-Phosphorus (MDH)	44.1	4.39
Nickel	42.4	3.44
Lead(Health)	36.4	0.51
Chromium (USGS)	35.2	0.38
C.O.D.	31.7	32.1
Nitrate + Nitrite	28.2	0.09
Calcium	28.0	9.8
Fluoride (MDH)	27.1	0.04
T.O.C.	27.1	14.68
Manganese (USGS)	26.3	49.5
Copper	26.2	1.87
Total Phosphorus (MDH)	22.1	14.8
Kjeldahl Nitrogen	21.7	0.55
Color	18.1	87.9
Total Nitrogen	17.2	0.65
Potassium (USGS)	15.9	0.82
Aluminum (USGS)	12.4	135.9
Chloride	12.1	3.29
Aluminum (MDH)	12.0	94.7
Manganese (MDH)	10.8	76.9
Sodium	10.5	2876
Sulfate	10.1	14.48
Iron	9.4	604.4
Bicarbonate (USGS)	8.4	33.1
Total Organic NItrogen	8.4	0.64
Silica (MDH)	7.7	11.17
Magnesium	7.2	5.8
Alkalinity	6.0	37.5
Hardness (MDH)	3.7	61.8
Silica (USGS)	2.2	6.67
Potassium (MDH)	2.1	1.09

Table 7 Leaching and Metal Pathways Program
Duplicate Sample Dates and Locations

Location	Date	Laboratory
EM-1	9/8/76	Eisenreich (1)
EM-1	10/25/76	Eisenreich
EM-1	12/ 1/76	(3)
EM-1	12/ 7/76	MDH (2)
EM-1	1/31/77	MDH
EM-1	4/ 8/77	Eisenreich
EM-1	4/11/77	Eisenreich
EM-1	5/ 5/77	Eisenreich
EM-1	5/13/77	(3)
EM-2	8/12/76	Eisenreich
EM-2	5/ 5/76	(3)
EM-3	12/10/76	Eisenreich
EM-3	3/18/77	(3)
EM-3	5/13/77	Eisenreich
EM-4	7/ 1/76	Eisenreich
EM-4	4/11/77	Eisenreich
EM-5	5/13/77	Eisenreich
EM-6	5/ 5/77	(3)
EM-6	6/28/77	Eisenreich
EM-8	5/ 5/77	Eisenreich
EM-8	7/27/77	Eisenreich
EM-8	8/ 1/77	(3)
Em-9	7/15/77	Eisenreich
Seep-1	9/ 8/76	(3)
Seep-1	9/21/76	Eisenreich
Seep-1	10/ 5/77	Eisenreich
Seep-3	8/26/76	Eisenreich
Seep-3	4/12/77	Eisenreich
Seep-3	5/23/77	Eisenreich
Seep-3	6/ 6/77	Eisenreich
Seep-3	8/24/77	(3)
BB-2	1/31/77	MDH
BB-5	1/31/77	MDH
BB-7 (surface)	1/31/77	MDH
BB-7 (bottom)	1/31/77	MDH
BB-7 (surface)	5/ 5/77	MDH
BB-7 (bottom)	5/ 5/77	MDH
BB-7 (surface)	7/ 2/77	MDH
BB-7 (surface)	8/17/77	MDH
BB-7 (bottom)	8/17/77	MDH
ML-1	2/ 8/77	(2)
ML-1	3/22/77	Eisenreich
3-7W	6/13/77	MDH
W23	10/18/76	MDH
U.S. Steel	7/29/76	Eisenreich
U.S. Steel	9/ 1/76	Eisenreich
U.S. Steel	10/25/76	Eisenreich
U.S. Steel	11/18/76	Eisenreich

Table 7 cont.

Location	Date	Laboratory
U.S. Steel	1/ 3/77	Eisenreich
U.S. Steel	2/ 7/77	Eisenreich
U.S. Steel	3/11/77	Eisenreich
U.S. Steel	3/18/77	Eisenreich
U.S. Steel	3/22/77	Eisenreich
U.S. Steel	3/28/77	Eisenreich
U.S. Steel	4/11/77	Eisenreich
U.S. Steel	4/22/77	Eisenreich
U.S. Steel	4/25/77	Eisenreich
U.S. Steel	5/ 2/77	Eisenreich
U.S. Steel	5/ 9/77	Eisenreich
U.S. Steel	5/16/77	Eisenreich
U.S. Steel	5/23/77	Eisenreich
U.S. Steel	5/31/77	Eisenreich
U.S. Steel	6/ 6/77	Eisenreich
U.S. Steel	6/13/77	Eisenreich
U.S. Steel	6/20/77	Eisenreich

(1) Eisenreich = Dr. Steven Eisenreich, Univeristy of Minnesota
(2) MDH = Minnesota Department of Health
(3) Field parameters only

Table 8. Leaching and metal pathways duplicates
Upper 90% confidence limits for percentiles
and coeffieient of variations

	Parameter	Sample Size	Upper Bound on Percentiles(%)			C.V.(%)
			50%	78%	90%	
I.	Metals					
	Total Copper	27	22.2%	35.3%	153.4%	32.2
	Dissolved Copper	14	25.0	66.7	*	11.3
	Total Nickel	27	13.5	40.0	100.0	6.7
	Dissolved Nickel	13	5.6	7.2	*	2.4
	Total Zinc	13	78.7	121.2	*	7.7
	Dissolved Zinc	3	*	*	*	10.4
	Total Iron	28	12.5	18.2	61.7	18.5
	Dissolved Iron	13	26.7	84.2	*	11.8
	Total Cobalt	10	4.8	17.5	*	3.5
	Total Magnesium	18	2.3	4.1	15.4	1.5
	Total Calcium	17	3.8	9.6	32.1	22.2
	Total Manganese	19	11.1	28.6	64.7	9.8
II.	Nutrients					
	Dissolved Organic Carbon	14	5.4	20.7	*	7.7
	Dissolved Inorganic Carbon	13	6.6	12.0	*	8.6
	Nitrite and Nitrate	4	*	*	*	46.2
	Nitrite	2	*	*	*	40.0
	Total Phosphorus	2	*	*	*	96.3
III.	General Parameters					
	pH	33	1.0	1.7	2.3	1.0
	Alkalinity	26	1.7	2.9	3.3	1.3
	Specific Conductance	32	1.4	2.8	18.2	7.5
	Dissolved Oxygen	10	1.7	6.5	*	2.2
	Silica	11	5.6	6.7	*	5.2
	Chloride	26	8.7	21.1	194.0	6.6
	Sulfate	24	27.0	58.6	68.4	34.1
	Color	5	*	*	*	8.5

*Inadequate sample size for accurate determination

Table 9. Leaching and metal pathways parameters ranked by coefficient of variation

Parameter	Coefficient of Variation (%)	At Mean Value(mg/1)
Total Phosphorus	96.3(*)	0.067
$NO_2 + NO_3$	46.2(*)	0.116
NO_2	40.0(*)	0.013
Sulfate	34.1	320.28
Total Copper	32.2	40.02
Total Calcium	22.2	62.14
Total Iron	18.5	687.69
Dissolved Iron	11.8	879.32
Dissolved Copper	11.3	53.14
Dissolved Zinc	10.4(*)	40.34
Total Manganese	9.8	501.98
Dissolved Inorganic Carbon	8.6	23.35
Color	8.5(*)	83.0
Total Zinc	7.7	40.29
Dissolved Organic Carbon	7.7	19.41
Specific Conductance	7.5	1114.13
Total Nickel	6.7	1573.77
Chloride	6.6	27.06
Silica	5.2	11.42
Total Cobalt	3.5	36.01
Dissolved Oxygen	2.2	8.07
Total Magnesium	1.5	53.34
Alkalinity	1.3	90.76
pH	1.0	7.50

*Inadequate sample size for accurate determination

Table 10. Duplicates from U.S. Steel Bulk Sample Pit upper 90% confidence limits for percentiles and coefficient of variation

Parameter	Sample Size	Upper Bound On Percentiles (%) 50%	75%	90%	C.V. (%)
I. Metals					
Total Copper	17	1.52	2.35	8.51	1.57
Dissolved Copper	18	2.53	3.81	9.29	1.94
Total Nickel	19	1.50	2.14	6.78	1.16
Dissolved Nickel	15	0.39	1.15	6.03	0.66
Total Zinc	3	*	*	*	0.38
Total Iron	18	11.38	16.67	170.73	6.34
Dissolved Iron	16	6.90	49.10	93.33	1.40
Total Cobalt	5	*	*	*	2.72
Total Magnesium	13	1.27	22.77	*	15.95
Total Calcium	15	1.50	4.96	9.73	2.38
Total Manganese	12	0.75	1.69	*	0.80
Dissolved Calcium	2	*	*	*	0.41
Dissolved Magnesium	2	*	*	*	1.03
Total Cadmium	4	*	*	*	7.57
Total Sodium	4	*	*	*	56.21
II. General Parameters					
pH	12	0.21	1.54	*	0.52
Alkalinity	6	7.75	*	*	9.82
Specific Conductence	7	0.00	2.99		0.94
Dissolved Oxygen	2	*	*	*	1.64
Chloride	14	10.00	14.12	*	16.41
Sulfate	15	6.06	12.74	87.07	12.17
Dissolved Oxygen Carbon	11	32.26	127.27	*	55.42
Dissolved Inorganic Carbon	4	*	*	*	52.84
Color	12	0.64	1.96	*	1.00

* Inadequate sample size for accurate determination.

Table 11. Water samples from U.S. Steel Bulk Sample Pit parameters ranked by coefficient of variation

Parameter	Coefficient of Variation(%)	At Mean Value (mg/l)
Total Sodium	56.2*	377.5
Dissolved Organic Carbon	55.4*	3.6
Dissolved Inorganic Carbon	52.8*	1.8
Chloride	16.4	2.1
Total Magnesium	16.0	49.3
Sulfate	12.2	337.6
Alkalinity	9.8	3.6
Total Cadmium	7.8	4.6
Total Iron	6.3	368.8
Total Cobalt	2.7*	995.6
Total Calcium	2.4	46.3
Dissolved Copper	1.9	11,364.4
Dissolved Oxygen	1.6*	9.1
Total Copper	1.6	11,806.5
Dissolved Iron	1.4	242.7
Total Nickel	1.2	19,455.3
Dissolved Magnesium	1.0*	48.0
Color	1.0	5.8
Specific Conductance	0.9	767.5
Total Manganese	0.8	5.6
Dissolved Nickel	0.7	18,577.7
pH	0.5	5.2
Dissolved Calcium	0.4*	50.2
Total Zinc	0.4*	6,176.0

*Inadequate sample size for accurate determination

Table 12. Summary of Analysis of Distilled Water Blanks.

Parameter	Percentage of Samples below detectable limits	Maximum observed value	Sample size
Dissolved Manganese	100	0.0 µg/l	13
Total Manganese	93	2.0 µg/l	15
Total Nickel	91	3.4 µg/l	23
Total Magnesium	90	0.2 mg/l	10
Dissolved Nickel	86	5.0 µg/l	14
Total Calcium	76	1.2 mg/l	17
Sulfate	76	6.1 mg/l	17
Total Iron	74	31 µg/l	23
Total Copper	71	1.0 µg/l	21
Total Zinc	71	0.8 µg/l	7
Dissolved Iron	68	13 µg/l	19
Dissolved Inorganic Carbon	57	4.1 mg/l	14
Dissolved Zinc	57	3.0 µg/l	7
Silica	50	5.3 mg/l	4
Dissolved Organic Carbon	50	1.8 mg/l	16
Chloride	46	2.2 mg/l	24
Dissolved Copper	40	1.4 µg/l	15
Total Phosphorus	33	0.13 mg/l	3
Alkalinity	30	3.8 mg/l	23
Total Sodium	20	0.17 mg.1	5

	Minimum	Maximum	Median
pH	4.2	6.5	5.7
Specific Conductance	0	55	2.0

Table 13. Example of a 2 x 2' contingency table for distilled water blanks

	Total Calcium	
	Below Detection Limit	Above detection Limit
Below Detection Limit	9	3
Above Detection Limit	1	1

Fisher's Exact Test: $p = 0.51$ (not significant)

Table 14. Parameter pairs with statistically significant relationships in distilled water blanks.

Parameters	Fisher's Exact Test Level
Chloride-Dissolved Copper	0.09*
Total Calcium - Total Copper	0.01
Dissolved Copper - Dissolved Iron	0.09
Total Nickel - Dissolved Nickel	0.08
Total Iron - Dissolved Iron	0.02

* Inverse relationship - contamination of one seemed to imply non-contamination of other.

Table 15. Lake Sediment Analysis

Coefficients of Variation (%) at selected locations.

Surface Samples

Parameter	LCW2-S	LSB1-S	LTF1-S
	Location		
Co	21.9	12.2	12.1
Cu	3.3	12.5	1.2
Ni	10.3	12.2	4.4
Pb	10.3	13.2	19.3
Zn	3.2	8.2	12.3
Fe	16.4	26.7	9.5
Mn	5.5	19.5	8.3
LOI (1)	5.0	10.5	0.7
Water (2)	0.3	81.2	0.5
% C (3)	4.4	2.5	6.7

Mid-depth Samples

Parameter	Location		
	LBB6-M	LBH3-M	LWI2-M
Co	33.1	4.4	4.5
Cu	5.8	2.2	8.2
Ni	14.9	4.0	5.9
Pb	70.9	13.9	26.7
Zn	22.4	0.9	7.8
Fe	13.1	5.0	7.5
Mn	10.1	3.5	14.5
LOI (1)	4.6	0.9	1.4
Water (2)	1.9	0.0	2.3
% C (3)	-	5.9	10.5

(cont'd)

Table 15 cont'd

Bottom Samples

Parameter	Location		
	LWI4-B	LCY1-B	LST1-B
Co.	8.5	7.2	12.6
Cu	3.6	2.9	3.0
Ni	7.7	6.5	7.1
Pb	21.1	70.5	28.4
Zn	2.8	11.5	2.6
Fe	5.6	7.9	2.7
Mn	6.5	4.9	1.5
LOI (1)	5.2	1.5	7.2
Water (2)	0.3	1.2	2.7
% C (3)	11.9	17.3	17.3

(1) LOI: Loss on ignition (%)

(2) Water: Water Content (%)

(3) % C: Percent Compaction

Table 16. Comparison of split samples: USGS and MDH.

Parameter	P Value	Sample Size	Result
Alkalinity	>.75	4	USGS = MDH
Calcium	.25	3	USGS = MDH
Chloride	.60	4	USGS = MDH
Color	.40	4	USGS = MDH
Fluoride	.04	4	USGS > MDH
Hardness	.20	4	USGS = MDH
Iron	.14	4	USGS = MDH
Magnesium	.20	3	USGS = MDH
Manganese	.45	4	USGS = MDH
NH_4	.04	4	USGS < MDH
NO_2	>.75	4	USGS = MDH
$NO_2 + NO_3$	.05	4	USGS > MDH
Nonfilterable Residues	.02	4	USGS < MDH
Total Phosphorus	.40	4	USGS = MDH
Ortho-Phosphorus	>.75	4	USGS = MDH
Potassium	.05	3	USGS < MDH
Silica	.25	4	USGS = MDH
Sodium	.07	3	USGS < MDH ?
Sulfate	.40	4	USGS = MDH
Turbidity	.25	4	USGS = MDH

Table 17
AMAX - CuNi JOINT SAMPLES
May - June 1976
Upper Dunka River (D-2)

	AMAX Collected SERCO Analysis	AMAX Collected USGS Analysis	Cu-Ni Collected Serco Analysis	Cu-Ni Collected USGS Analysis
Dissolved Copper (μg/l)				
May	1.4	3.7	2.5	43.0
June	1.3	1.8	5.2	30.0
Dissolved Lead (μg/l)				
May	0.2	0.9	0.5	5.6
June	0.4	0.4	1.2	3.6
Dissolved Nickel (μg/l)				
May	<1.0	4.0	1.0	2.0
June	1.0	2.0	1.0	3.0
Dissolved Zinc (μg/l)				
May	12.0	22.0	4.0	13.0
June	7.0	6.0	13.0	18.0
Dissolved Cadmium (μg/l)				
May	0.12	0.36	0.08	0.15
June	3.50	2.30	0.10	0.18

Ta 17 cont'd

AMAX-COPPER-NICKEL JOINT SAMPLES
UPPER DUNKA RIVER (D-2) AND UPPER PARTRIDGE RIVER (P-5)
February, 1977

	AMAX Collected SERCO Analysis	AMAX Collected MDH Analysis	Cu-Ni Collected SERCO Analysis	Cu-Ni Collected MDH Analysis
Dissolved Copper (g/1)				
P-5	0.6	5.5	0.7	5.1
D-2	1.4	5.0	1.3	5.9
Dissolved Nickel				
P-5	2	<1	2	4
D-2	6	7	6	<1
Dissolved Zinc				
P-5	9.0	16.0	10.0	15.0
D-2	11.0	14.0	11.0	5.2
Dissolved Lead				
P-5	<.2	<.2	0.2	0.2
D-2	0.4	1.4	0.2	0.2
Dissolved Cadmium				
P-5	0.06	0.16	0.14	0.16
D-2	0.24	0.41	0.12	0.11
Total Copper				
P-5	1.4	1.9	6.1	8.2
D-2	3.9	5.8	3.7	6.6

Table 17 cont'd

AMAX - COPPER-NICKEL JOINT SAMPLE
UPPER DUNKA RIVER (D-2) AND UPPER PARTRIDGE RIVER (P-5)
February, 1977

	AMAX Collected SERCO Analysis	AMAX Collected MDH Analysis	CuNi Collected SERCO Analysis	CuNi Collected MDH Analysis
Total Nickel				
P-5	2	30	2	<1
D-2	8	7	8	7
Total Zinc				
P-5	22.0	9.2	21.0	8.9
D-2	9.0	21.0	11.0	25.0
Total Lead				
P-5	1.0	0.8	0.9	0.8
D-2	0.3	1.4	0.4	1.8
Total Cadmium				
P-5	0.34	0.14	0.32	0.20
D-2	0.20	0.52	0.30	0.36

Table 18. Results-first round robin.

LABORATORY	SAMPLE*	Cu ug/l	Ni ug/l	Zn ug/l	Cd ug/l	Pb ug/l	SO_4 mg/l	Alk mg/l
Environmental Research Lab-Duluth	BB-1A	3.49±.10	57.8±4.0	2.19±.03	0.021±.002	0.30±.05	-	-
	BB-1B	3.79±.12	60.4±4.4	1.42±.03	0.014±.002	0.23±.08	-	-
Erie Mining Company	BB-1A	4	61	<2	<.4	<1	62	84
	BB-1B	3	60	<1	<.4	<1	54	86
State Health Department	BB-1A	7.9	49	1.6	0.015	1.5	54	71
	BB-1B	8.8	56	1.6	0.015	1.6	55	71
Serco	BB-1A	2.5	34	<2	0.04	<0.2	54	70
	BB-1B	2.5	34	2	0.06	<0.2	54	71
Eisenreich	BB-1A	2.4	51.2	-	-	-	51.0	-
	BB-1B	2.4	55.2	-	-	-	53.4	-
Siegal	BB-1A	-	-	-	-	-	58.8	67
	BB-1B	-	-	-	-	-	54.5	62

*BB-1A = Copper-Nickel collection.
BB-1B = Erie Mining collection.

Table 19. Results-second round robin.

LABORATORY	SAMPLE*	Cu ug/l	Ni ug/l	Zn ug/l	Cd ug/l	Pb ug/l	SO_4 mg/l	Alk mg/l
Environmental Research Lab-Duluth	D-2A	1.62±.07	1.44±.13	1.63±.02	0.014±.004	--	--	--
	D-2B	1.72±.12	1.08±.16	1.68±.08	0.018±.001	--	--	--
Erie Mining Company	D-2A	1	<5	<10	<0.3	--	33	24
	D-2B	1	<5	<10	<0.3	--	33	16
State Health Department	D-2A	1.8	<1	1.4	0.016	0.18	30	12
	D-2B	1.7	<1	2.0	0.014	0.25	27	11
Serco	D-2A	1.4	1	4	0.06	<0.2	14	10
	D-2B	1.4	1	7	0.06	<0.2	12	6
Eisenreich	D-2A	1.3	<1.5	-	-	-	51.0	-
	D-2B	1.5	<1.5	-	-	-	53.4	-
Siegal	D-2A	-	-	-	-	-	25.6	12.0
	D-2B	-	-	-	-	-	25.6	12.0

D-2A = Copper-Nickel Collection

D-2B = AMAX Collection

Table 20. Results-third round robin.

LABORATORY	SAMPLE*	Cu ug/l	Ni ug/l	Zn ug/l	Cd ug/l	Pb ug/l	SO_4 mg/l	Alk mg/l
Erie Mining Company	F-1	8	30	3	0.1	<1	<5	46
	SR-2	1	<3	3	0.1	<1	<5	36
State Health Department	F-1	8.4	7	2.7	0.03	0.07	<1.0	9
	SR-2	1.4	1	2.4	<0.01	0.26	8.0	19
Serco	F-1	6.4	8	4	0.06	0.4	<1	13
	SR-2	0.9	2	4	0.10	<0.2	9	37
Eisenreich	F-1	7.2	4.0	-	-	-	-	-
	SR-2	0.8	1.5	-	-	-	-	-
Siegal	F-1	-	-	-	-	-	1.7	11
	SR-2	-	-	-	-	-	2.5	21

Table 21.

Results - Fourth Round Robin

	LAB	Cu (μg/ℓ)	Ni (μg/ℓ)	Zn (μg/ℓ)	Cd (μg/ℓ)	Pb (μg/ℓ)
Addition 1	SERCO	3.0,4.0	7.0,3.0	9.0,8.0	1.54,1.54	2.3,2.4
	State Health Department	6.0,6.0	4.0,4.0	17.7,17.7	2.48,2.28	2.7,3.0
	Standard	5.0	4.0	17.0	2.0	4.0
Addition 2	SERCO	15.0,15.0	6.0,6.0	24.0,25.0	3.76,3.96	5.1,4.8
	State Health Department	10.0,9.0	6.0,8.0	27.7,30.7	6.08,4.58	5.5,5.9
	Standard	9.0	8.0	28.0	5.0	9.0

Table 22. Leaching and metal pathways
EM 1-pH-Stability Test, 8/10/76 - 8/11/76
(all samples taken at 1045)

Time	Time Interval-Hours	pH		Units Diff. from Insitu	% Variation from Insitu
1045	0	7.55	Insitu	0	
1046	.02	7.55			
1115	0.5	7.58		.03	.40
1300	2.2	7.50	Separate Bottles	-.05	-.66
1515	4.5	7.60		.05	.66
1620	5.6	7.60		.05	.66

5.6 hour maximum total variation from insitu = .05 units
Maximum percent variation =0.66 percent

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1300	26.	7.40		-.15	-2.0
1300	26.	7.60	Same Bottle	.05	.66
1303	26.	7.61		.06	.79
1304	26.	7.68		.13	1.7

Table 23. Leaching and metal pathways
pH stability

Site	Date	Time	Hours	pH	Units Difference from Insitu	% Variation from Insitu
Em-1	8/12/76	1600	---	7.55	---	---
	8/12/76	1645	.08	7.50	.05	.66
	8/26/76	1500	---	7.36	---	---
	8/27/76	0900	18	7.95	.59	.25
	9/8/76	2030	--- ---	EM-7 7.90 EM-1 7.90	doubles --- .10	--- 1.3
	9/9/76	0945	13 "	EM-7 7.90 EM-1 7.80	doubles --- .10	--- 1.3
	9/16/76	1215	---	7.85	---	---
	9/17/76	0830	21	7.98	.13	1.6
Em-3	8/26/76	Insitu 1135	---	7.82	---	---
	8/27/76	0910	16.7	8.09	.27	3.3
	9/8/76	Insitu 1245	---	8.30	---	---
		1455	2.2	8.19	-.11	1.4
Em-4	7/15/76	Insitu 0855	---	6.40	---	---
		1600	7	6.62	.22	3.3
	8/9/76	Insitu 1120	---	7.80	---	---
		1400	2.7	7.55	-.25	3.2
	8/26/76	Insitu 1135	---	7.41	---	---
	8/27/76	0915	21	7.42	.01	1.3
Em-5	7/2/76	0915	---	7.35	---	---
	7/3/76	1440	31	7.40	.05	.60
	8/26/76	Insitu 0920	---	7.80	---	---
	8/27/76	0920	24	7.98	.18	2.2
	9/8/76	Insitu 0830	---	8.10	---	---
		1420	6	8.20	.10	1.2
	10/5/76	Insitu 0940	---	7.70	---	---

Table 24. Results of field acidification study.
(All concentrations in ug/l)

PARAMETER	SAMPLE KEPT IN LAB	TRANSPORTED, NOT OPENED	TRANSPORTED, PRESERVATIVE ADDED
Copper, total	<0.2	<0.2	<0.2
Cadmium, total	0.007	<0.01	<0.01
Nickel, total	<1	<1	<1
Zinc, total	<0.03	<0.03	0.07
Lead, total	0.097	0.12	0.078
Iron, total	40	<20	20
Cobalt, total	<0.43	<0.5	<0.5
Manganese, total	<2	<2	<2
Aluminum, total	0.78	0.90	<0.6
Copper, dissolved	<0.2	0.3	<0.2
Cadmium, dissolved	<0.004	<0.010	0.011
Nickel, dissolved	<1	<1	<1
Zinc, dissolved	<0.03	0.13	0.23
Lead, dissolved	0.059	0.16	0.30
Iron, dissolved	<20	<20	<20
Cobalt, dissolved	<0.43	<0.5	<0.5

Table 25. Results of initial Kemmerer Bottle Contamination Study

	Cu	Ni	Cd	Zn	Pb	Co	Fe
Kemmerer Bottle	1.7	2	0.09	5.4	0.23	<0.3	<40
Distilled H_2O blank	<0.1	<1	<0.01	<0.1	<0.1	<0.3	<40

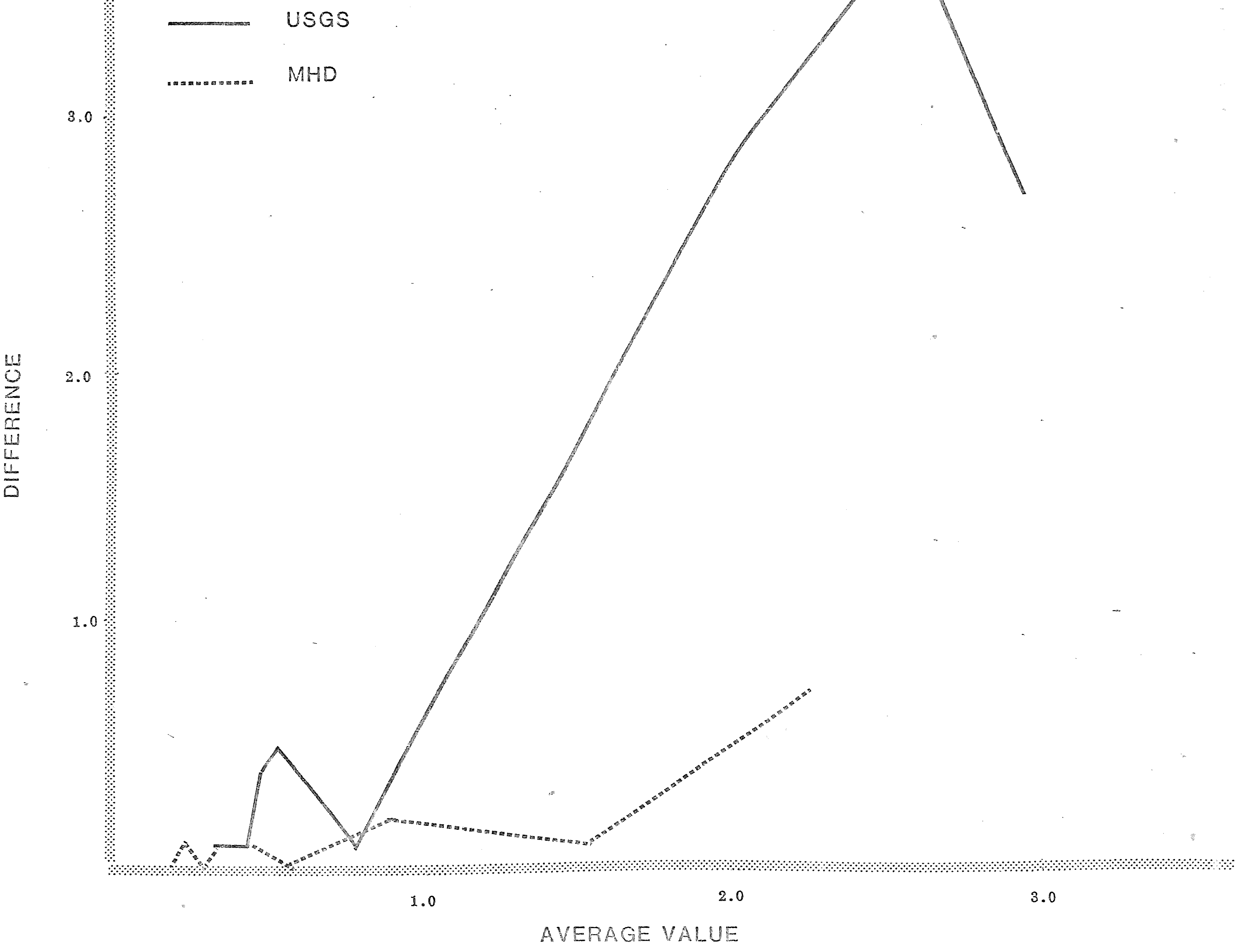
Table 26. Acid-cleaned Kemmerer Bottle vs "soaked" Kemmerer Bottle

Acid cleaned Kemmerer	Cu	Ni	Cd	Zn	Pb
15 minutes	1.9	<1	0.019	2.7	0.28
30 minutes	3.0	<1	0.027	6.6	0.49
1 hour	2.4	<1	0.023	5.8	0.25
2 hours	2.1	<1	0.012	3.3	0.28
12 hours	2.3	<1	0.011	4.3	0.17
"soaked" Kemmerer					
15 minutes	<0.25	<1	<0.01	0.25	0.20
30 minutes	0.3	<1	<0.01	0.27	0.23
1 hour	0.3	<1	<0.01	0.24	0.10
2 hours	0.3	<1	<0.01	0.32	0.22
12 hours	0.3	<1	<0.01	0.35	0.10
Blank	<0.25	<1	0.01	0.05	0.14

LIST OF FIGURES

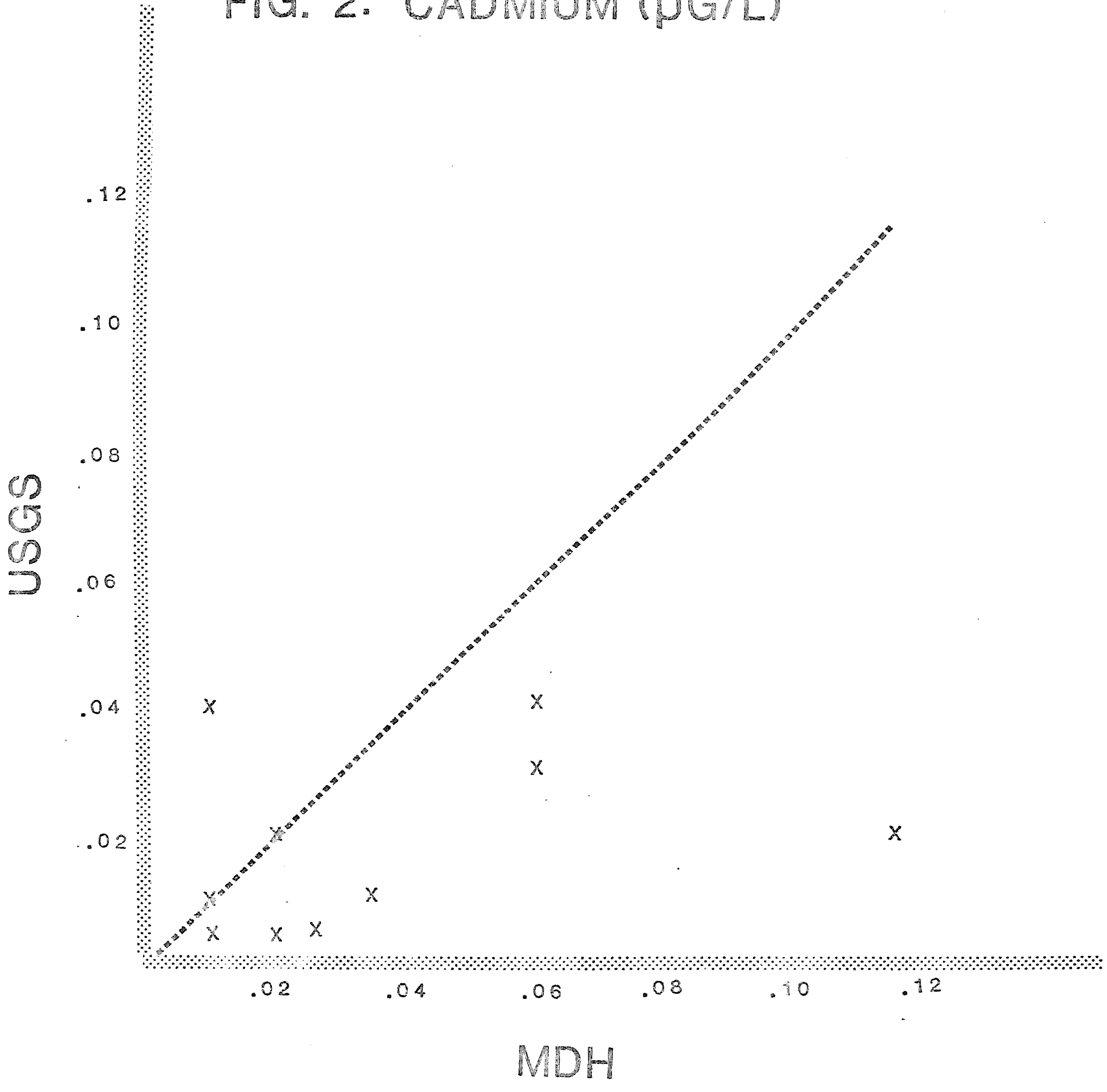
FIGURE 1

LEAD DUPLICATES -- SURFACE WATER



USGS-MDH SPLIT SAMPLES

FIG. 2: CADMIUM (µG/L)



USGS-MDH SPLIT SAMPLES

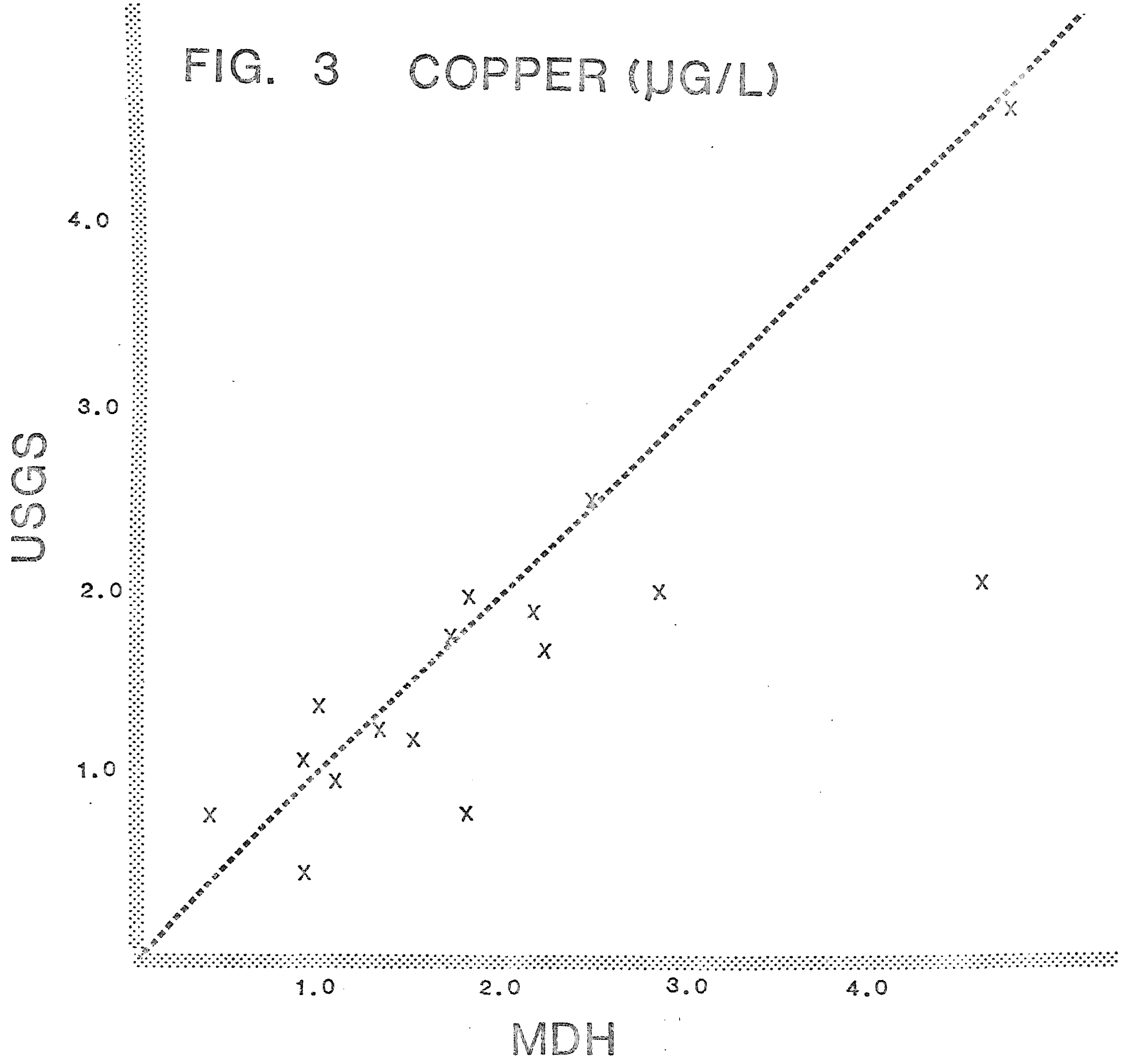


FIG. 3 COPPER (µG/L)

FIG 4:

USGS-MDH SPLIT SAMPLES

LEAD (µG/L)

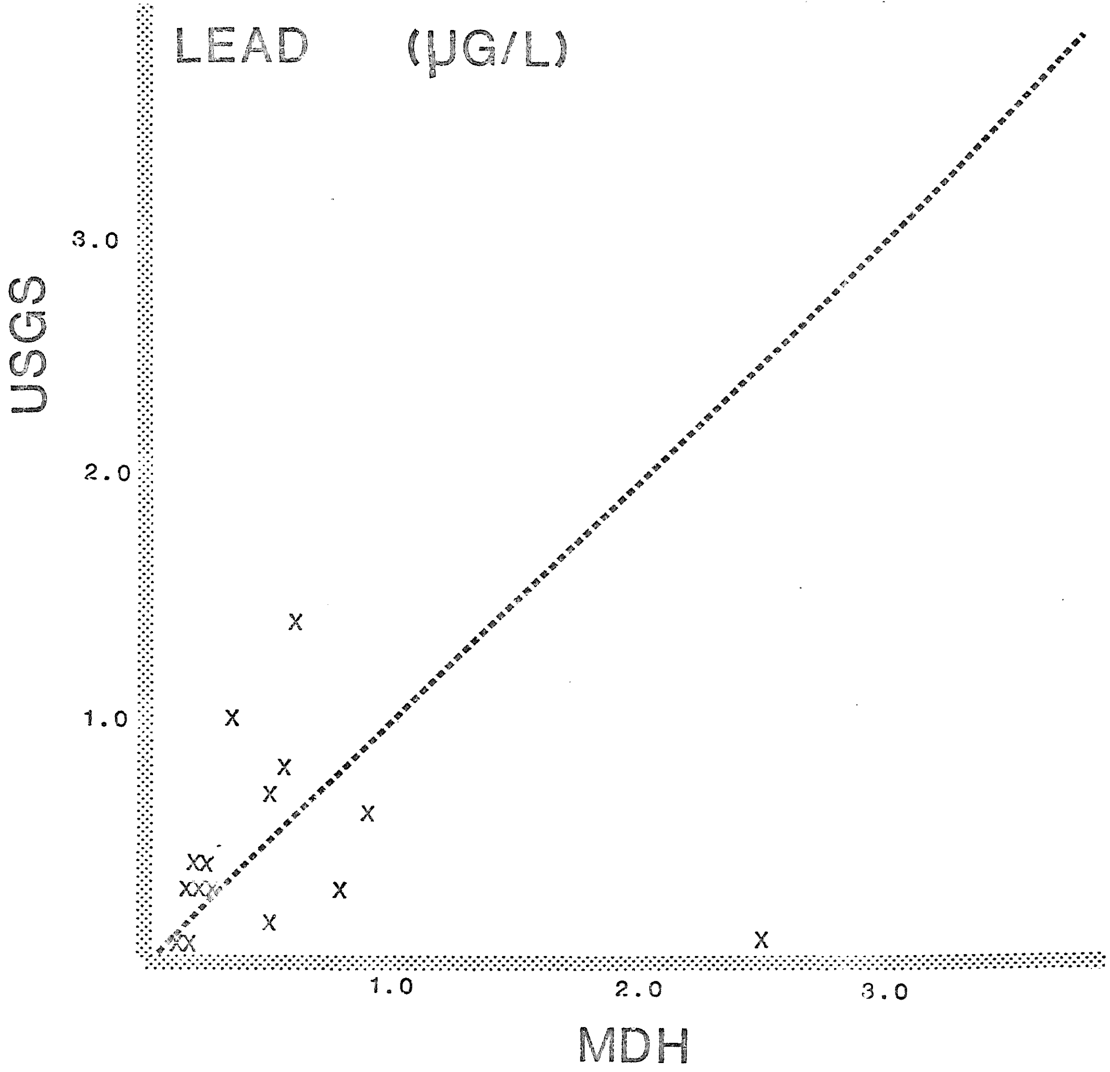


FIG. 5:

USGS-MDH SPLIT SAMPLES
NICKEL (µG/L)

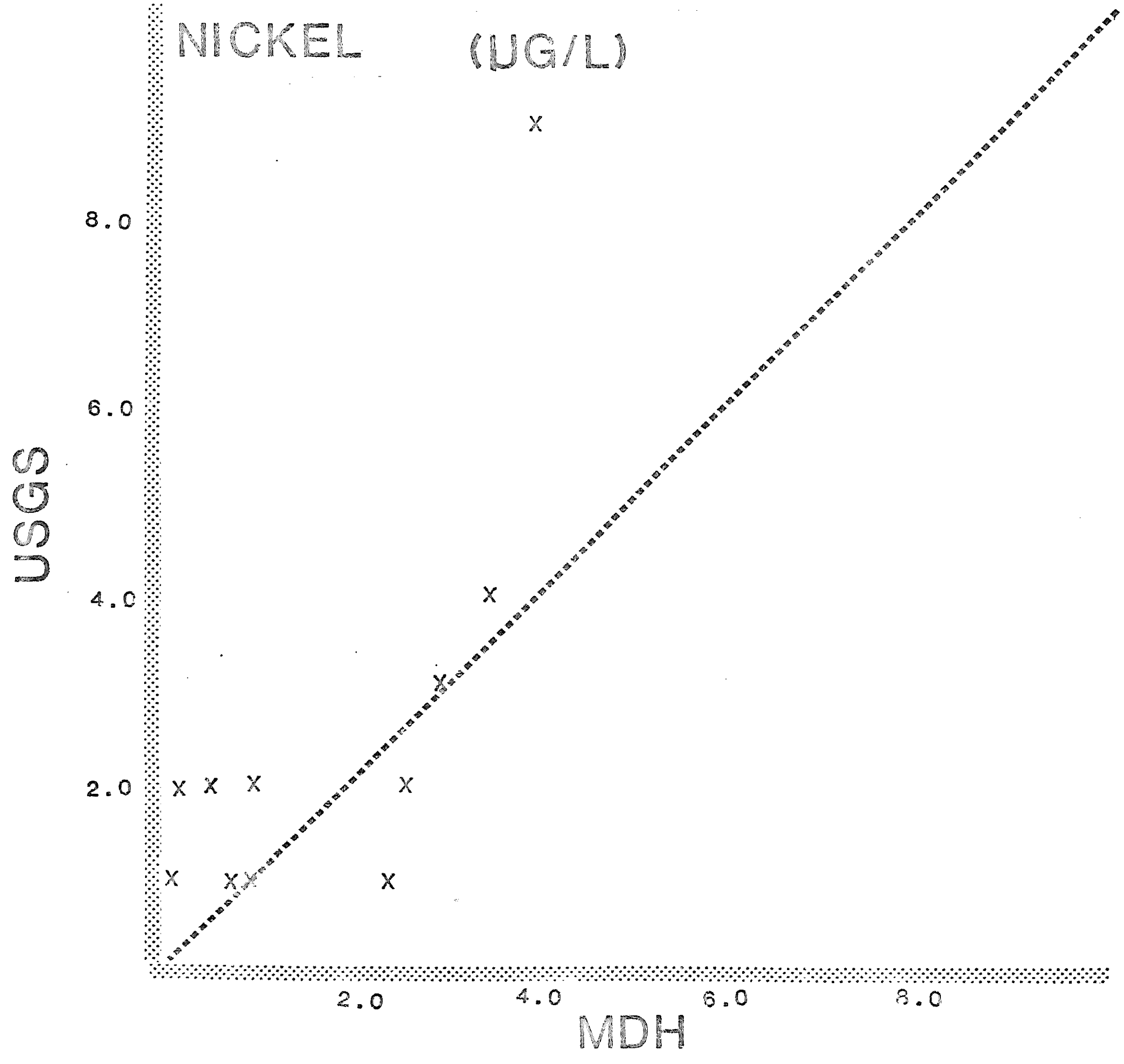


FIG. 6:

USGS-MDH SPLIT SAMPLES

ZINC (µG/L)

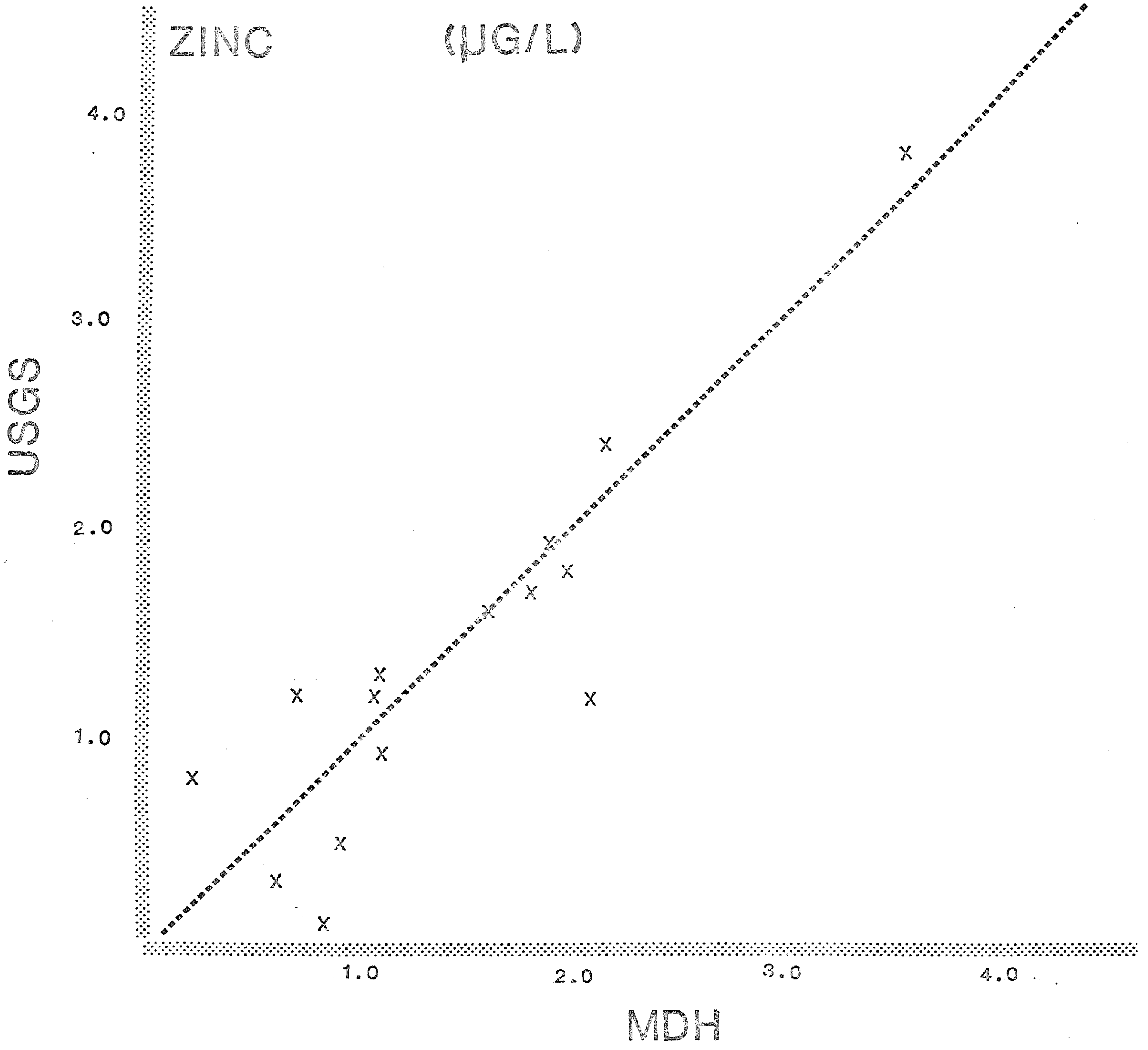
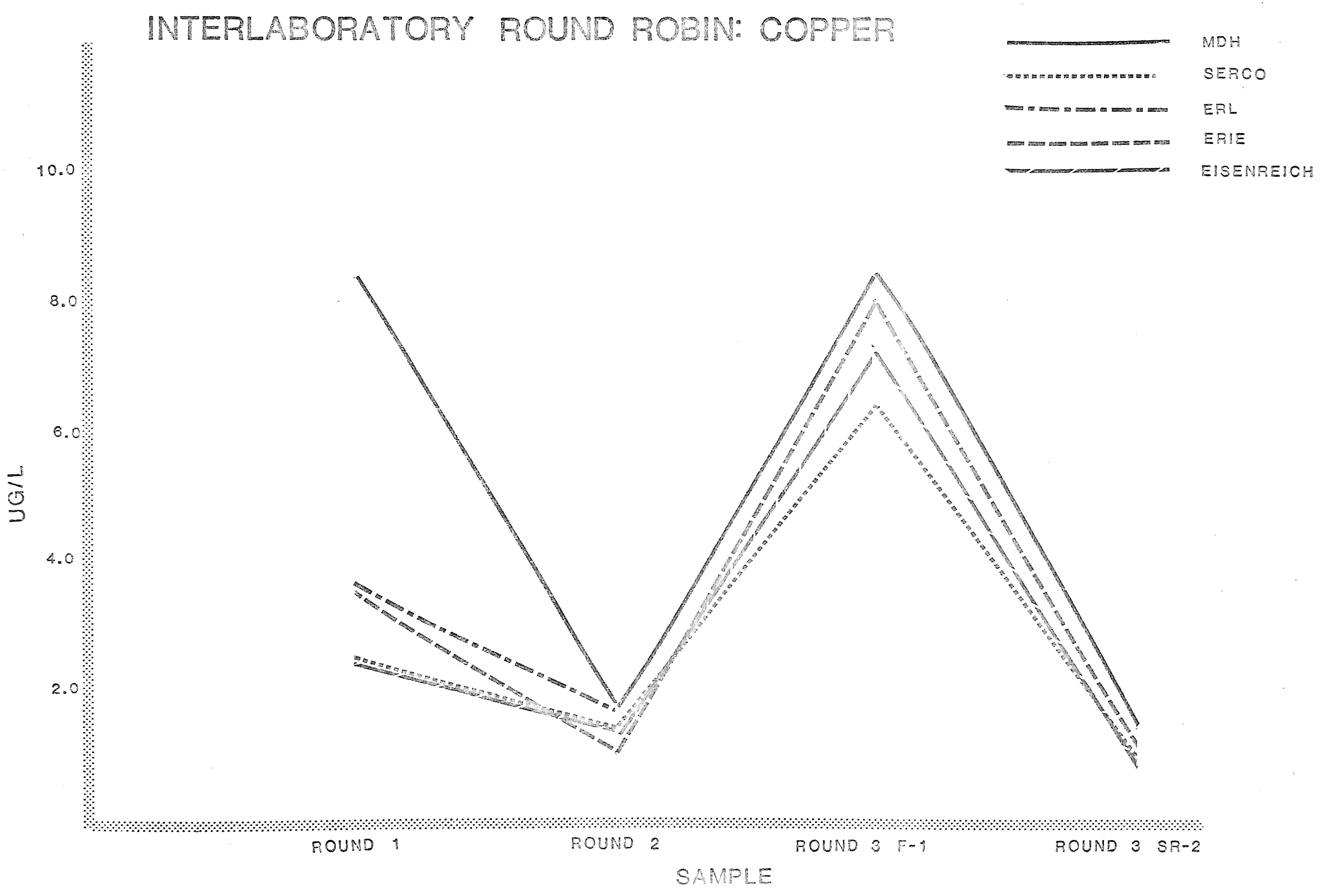
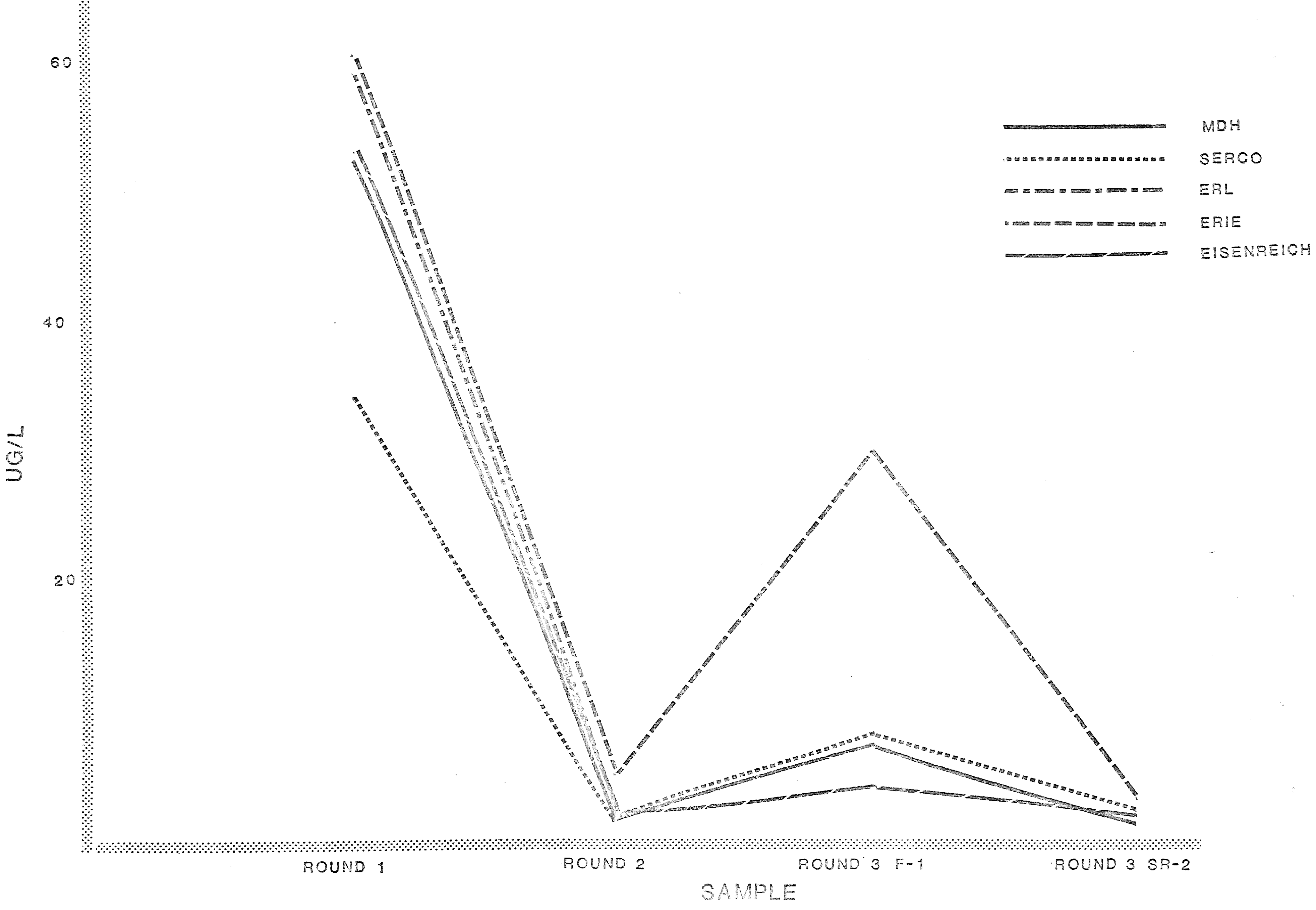


FIGURE 7



INTERLABORATORY ROUND ROBIN: COPPER

FIGURE 8



INTERLABORATORY ROUND ROBIN: NICKEL

FIGURE 9

INTERLABORATORY ROUND ROBIN: ZINC

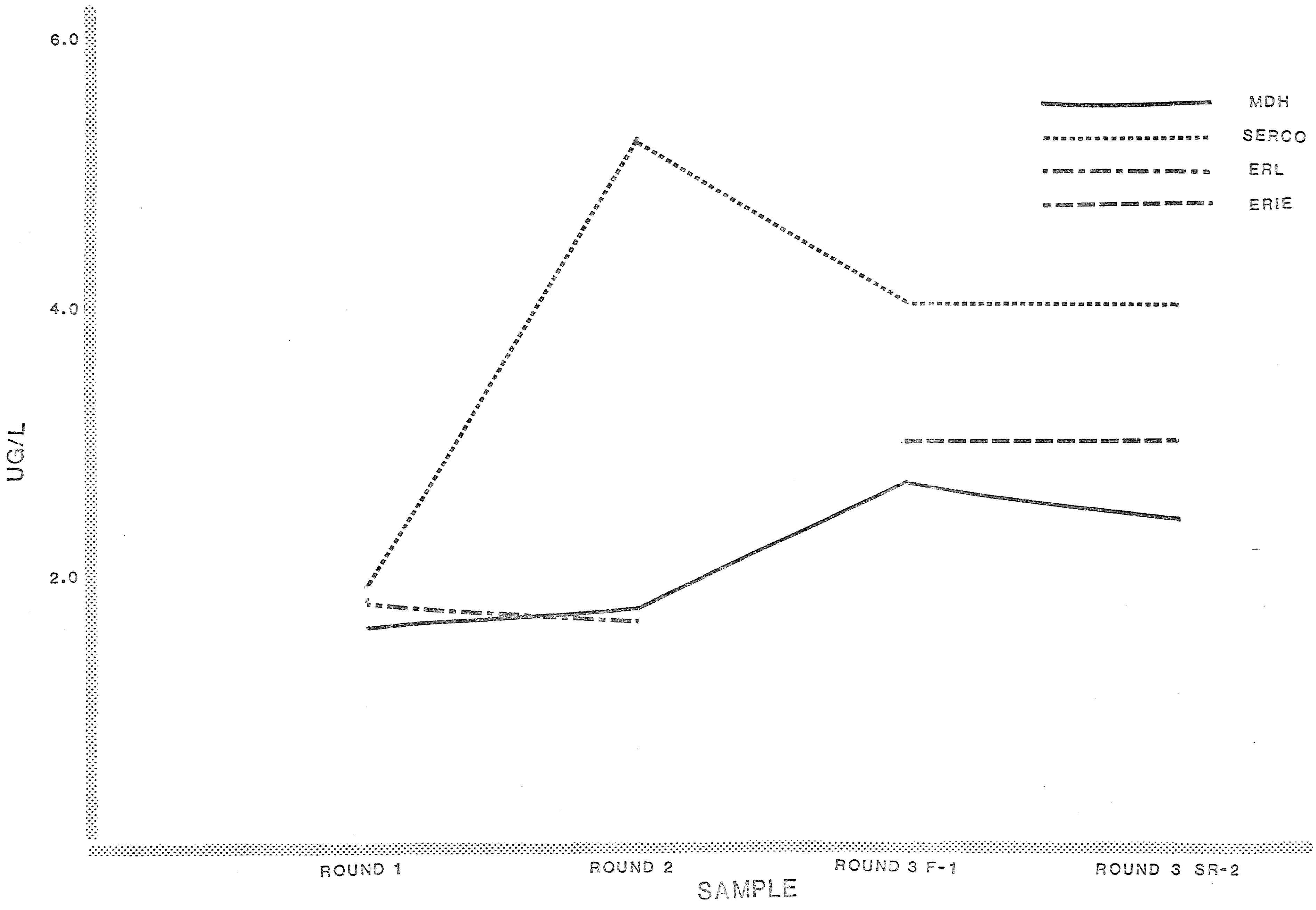


FIGURE 10

INTERLABORATORY ROUND ROBIN: CADMIUM

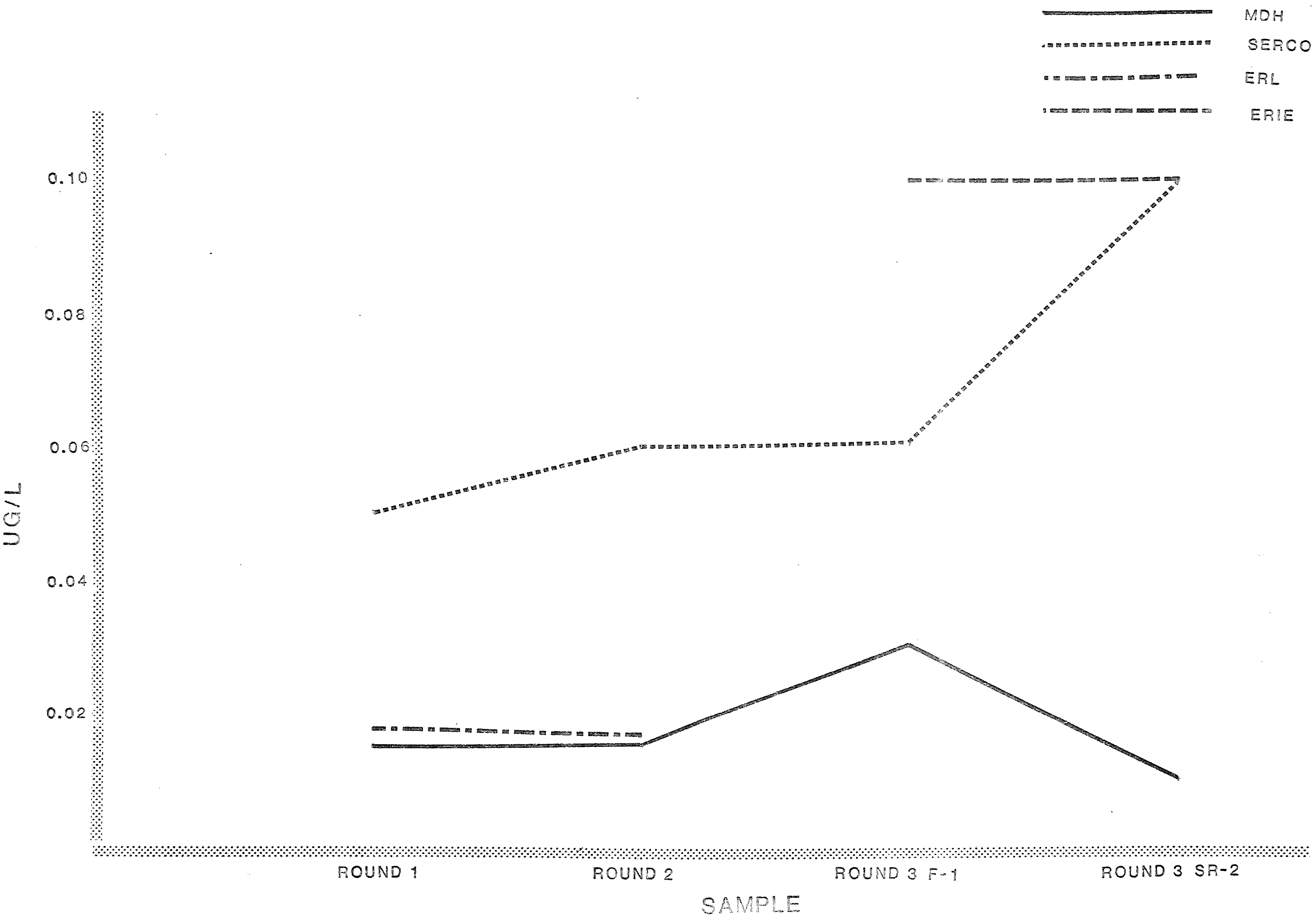
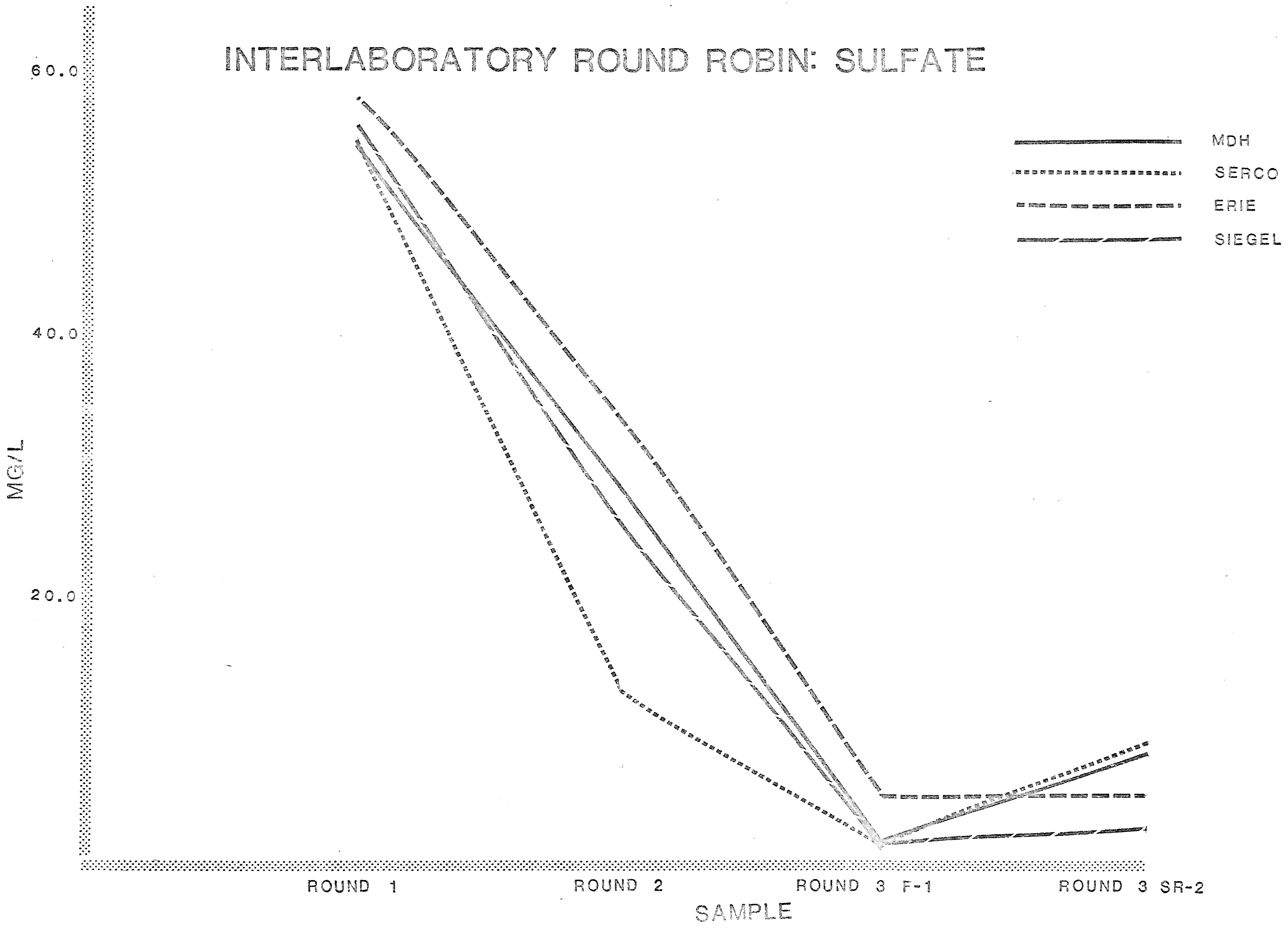


FIGURE 11



INTERLABORATORY ROUND ROBIN: SULFATE

FIGURE 12

INTERLABORATORY ROUND ROBIN: ALKALINITY

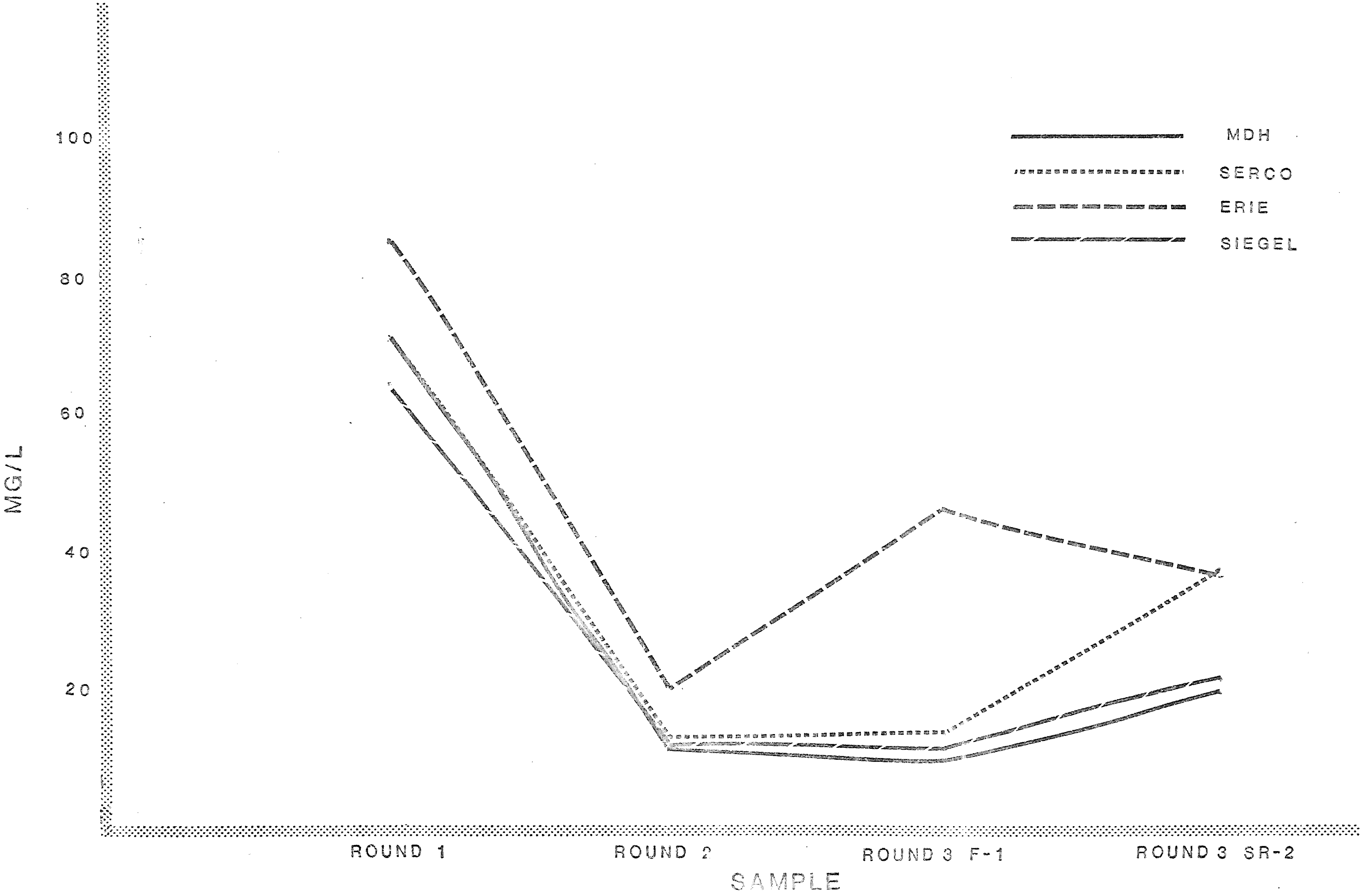


FIGURE 13
INTERLABORATORY ROUND ROBIN: ROUND 4

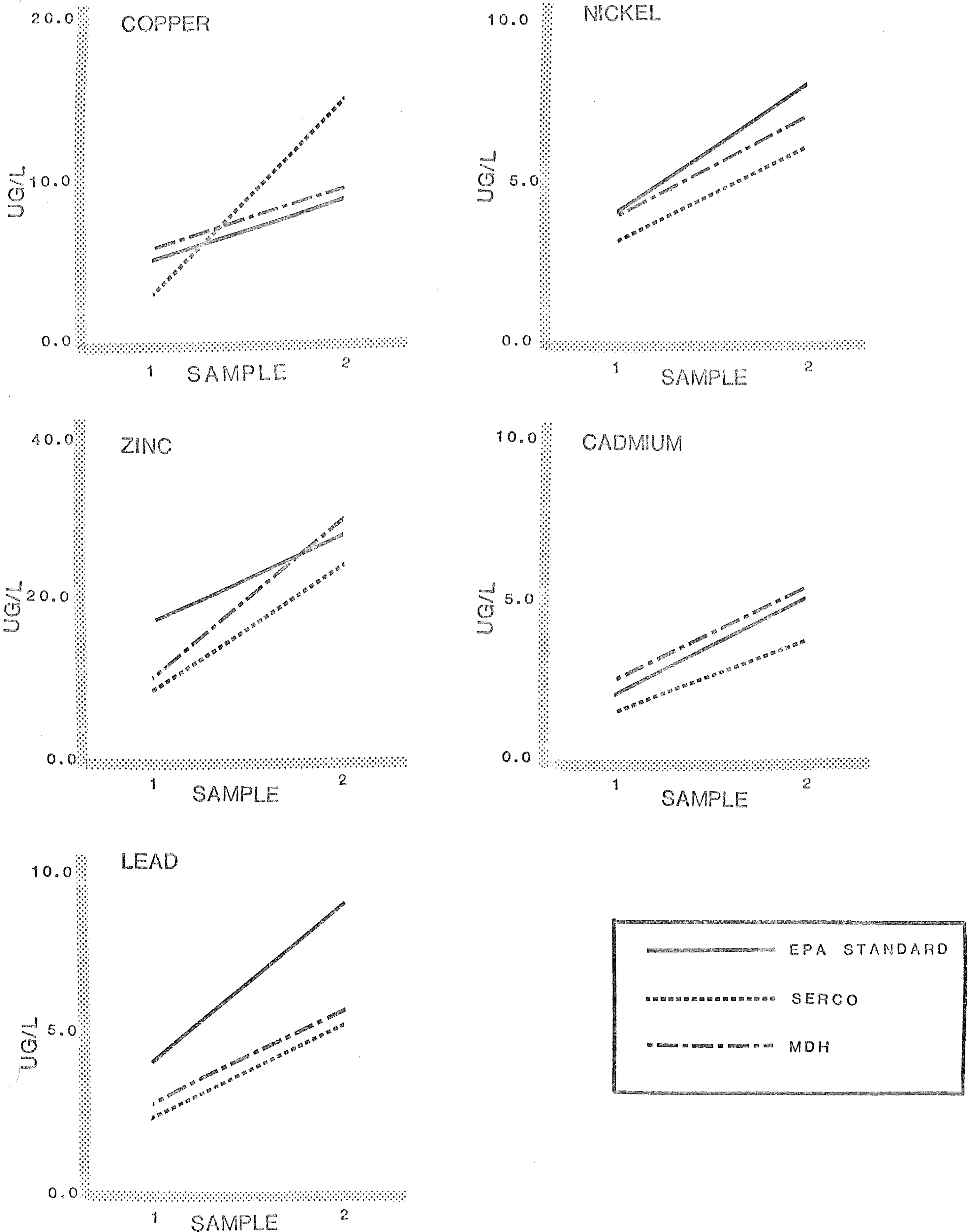


FIGURE 14
PH VS SAMPLE TEMPERATURE

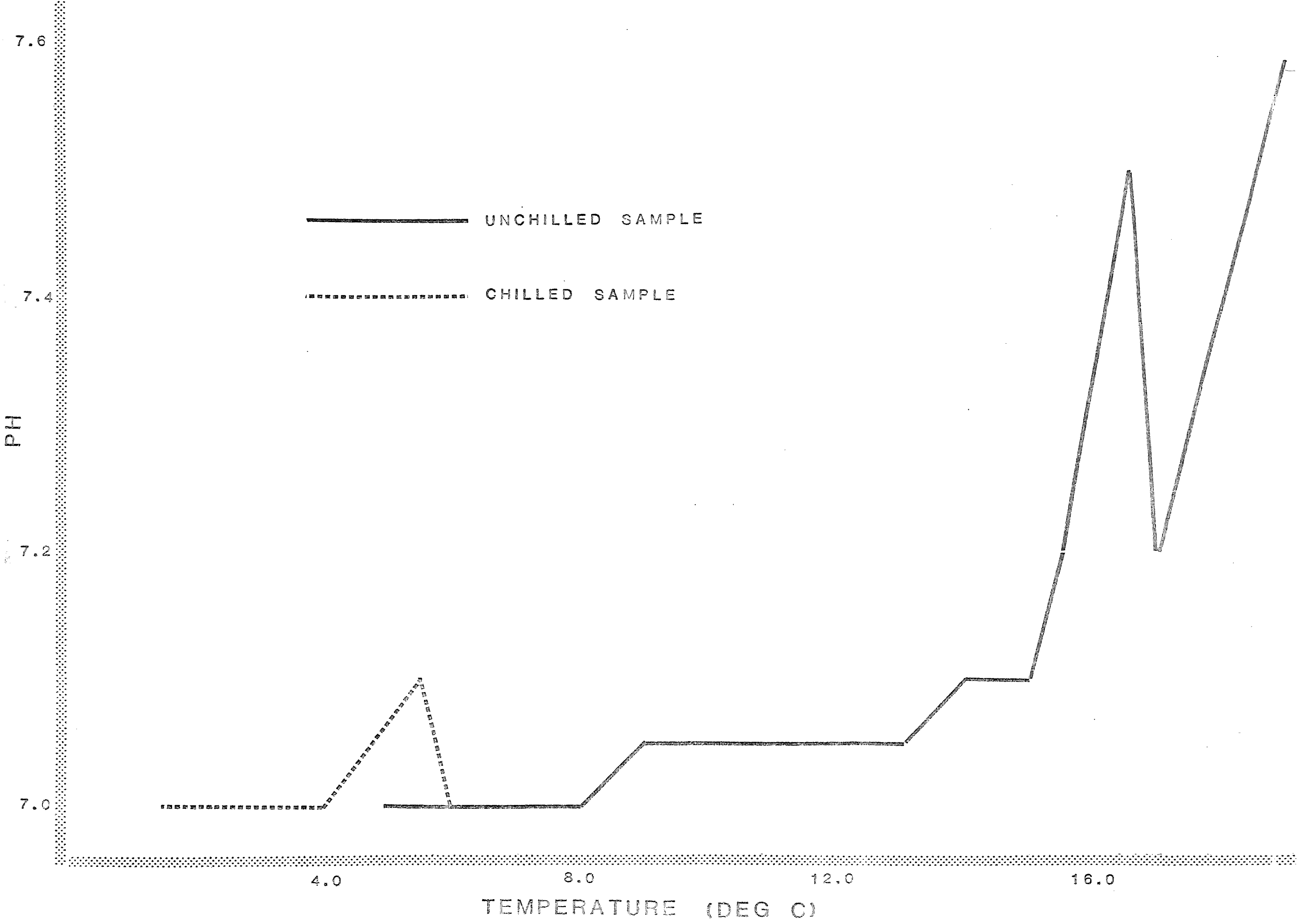


FIGURE 15
PH VS SAMPLE HOLDING TIME