

IN: J.W. Gadsby, J.A. Malick, and S.J. Day, eds., Acid Mine Drainage - Designing for Closure, Geological Association of Canada/Mineralogical Association of Canada Conference, Vancouver, British Columbia, May 16-18, 1990

A Case Study of Data Quality in Routine Chemical Analyses of Acid Mine Drainage

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ABSTRACT

This case study of routine data quality in water analyses examined both the precision and accuracy of 16 parameters based on five sets of seven replicates, with portions of each set distributed to three laboratories. Analytical precision was found to be dependent on the experience of the laboratory at high concentrations of metals and to be relatively poor below a concentration of about 0.4 mg/L from all laboratories. For anions other than sulfate, analytical precision was found to be relatively poor at all concentrations due to interferences with the analytical techniques. Accuracy was assessed by statistically testing the hypothesis that all mean concentrations from the laboratories were identical. On average, the means were judged to be identical in 3 of the 5 piezometers on the 99% confidence level. The accuracy of specific metals such as aluminum were significantly poorer than the average. Similar conclusions on accuracy were drawn for many parameters by Rice et al. (1988), suggesting that the results of this study may be used as an indicator of potential accuracy whenever site-specific data are not available. Where the reliability of analytical data is critical, such as in regulatory enforcement and the prediction of environmental impacts, thorough assessments of data quality should be conducted on a site-specific basis.

INTRODUCTION

Acid drainage from mining operations typically has a pH value in the range of 1.5 to 6 and concentrations of dissolved metals and non-metals from trace levels up to thousands of mg/L. In order to properly determine site-specific geochemical factors leading to acid generation and neutralization, and to reliably design water-quality control measures, accurate chemical analyses of the water are essential.

Due to the presence of redox-active species and elevated levels of dissolved metals, acid drainage is often chemically unstable upon sampling. Proper sampling and preservation of water samples in the field will overcome the first hurdle in obtaining quality data on water chemistry (Morin and Cherry, 1988a). The selected analytical laboratories are then responsible for the subsequent tasks that lead to precise and accurate analyses.

Detailed assessments of the quality of chemical analyses are usually undertaken by selecting and notifying laboratories of the assessment and then submitting standardized samples for analysis. This approach yields the optimum data quality that can be provided by a laboratory. A less common approach is to submit a large suite of blind replicate samples to several laboratories in order to determine the "routine" quality of the analyses.

As part of a subsurface study of acid drainage adjacent to an acid-generating tailings impoundment, a detailed assessment of the quality of routine analysis was undertaken. Five sets of seven replicate water samples were collected. The seven samples from each set were distributed to three laboratories.

PROCEDURE AND SAMPLE DISTRIBUTION

Detailed studies of the subsurface migration of acid drainage have been conducted at the Nordic Main Uranium Tailings Impoundment near Elliot Lake, Ontario (Morin et al., 1988a and 1988b; Morin and Cherry, 1988b). These studies have shown that approximately 10^6 liters of acid drainage pass annually through a 3 m² cross-section of the sand aquifer which lies under and laterally downgradient of the impoundment. Concentrations found in the vicinity of the plume ("Seepage Area A") vary over

orders of magnitude (Table 1). In order to determine the quality of the routine analyses of this water, five piezometers with neutralized to moderately severe acid drainage were selected for the collection of replicate samples (Table 2).

TABLE 1--Range of concentrations observed in Seepage Area A, Nordic Main Impoundment, Elliot Lake, Ontario

<u>Parameter</u>	<u>Concentrations¹</u>	<u>Parameter</u>	<u>Concentrations¹</u>
Field pH	3.20-6.81 pH units	Cl	170-5.5
Lab pH	2.4-6.9 pH units	F	33-<0.1
Field Eh	+114- +444 mV	NO ₃	18-<0.4
Field temp	10.5+1.5°C	NH ₃	55.9-0.33
Field cond	1150-380 uS/cm	PO ₄	<0.04
		V	<1
Fe	5930-8	Se	<1
Ca	860-40	DOC	22-8.0
Mg	702-12		
Na	152-1.2	Ra-223	83-6
Mn	56-0.91	Ra-226	213-1
Al	206-<0.02	Pb-210	110-0.1
Cu	0.44-<0.001	Th-227	600-6
Co	5.9-0.01	Th-228	9.7-<0.5
Zn	0.50-0.004	Th-230	48-<0.5
Pb	0.9-<0.003	Th-232	11-<0.5
Ni	6.0-0.015	Total Th	96-11 ug/L
Cr	0.14-<0.01	Ac-227	319-16
Cd	<0.05	U-234	204.5-14.9
		U-238	166.5-3.8
As	0.011-<0.001	U234/U238	1.2 - 3.4
SO ₄	14420-111	Total U	8500-0.4 ug/L
Field alk	290-1 (as HCO ₃)		
DIC	86.4-21.6 (as C)	O-18 ²	-11.9 to -10.2‰
SiO ₂	77.0-<1	H-2 ²	-84 to -69‰
		C-13 ³	-20.8 to -19.2‰

¹ Concentrations of metals and anions in mg/L and concentrations of radionuclides in pCi/L, unless otherwise noted

² ¹⁸O and ²H values are relative to SMOW standard

³ ¹³C values are relative to PDB standard

TABLE 2--Five piezometers selected for replicate sampling, including 1984 water quality

(mg/L)	P I E Z O M E T E R				
Parameter	M1-7	M2-2	M14-2	M24-5	M25-7
pH	4.60	6.25	7.06	5.34	4.40
Fe	4950	2320	60.3	3220	1950
Ca	420	545	277	421	324
Mg	306	313	72.0	245	148
Na	10.7	38.0	35.3	22.3	6.9
K	89.7	119	3.63	100	39.7
Mn	19.7	15.0	4.00	14.3	9.2
Al	81.3	0.05	0.05	4.37	76.3
Cu	0.023	0.063	0.003	0.008	0.006
Co	3.03	1.00	0.017	1.9	1.37
Zn	0.227	0.056	0.002	0.094	0.048
Pb	0.29	0.173	0.005	0.15	0.10
Ni	1.8	0.34	0.022	1.13	1.13
SO ₄	10970	6460	548	7420	4810
SiO ₂	7.33	5.33	8.00	2.00	5.33
Cl	11.2	60.3	73.6	33.6	9.43
NH ₃	35.4	51.5	2.05	41.1	17.6
TDS	>3000	>3000	<3000	>3000	>3000

From each piezometer in Table 2, 14 liters of groundwater were removed with a peristaltic pump, passing directly through a 0.45 um filter and into a large, covered plastic bucket. As the bucket filled, it was gently agitated to promote homogenization and concentrated HCL was added (30 mL of HCl/ 1 L of water) to lower the pH below 2 and thus preserve the sample. Prior to each sampling of a piezometer, the bucket was rinsed with distilled water, rinsed with diluted HCL (pH 1), rinsed again with distilled water, and shaken dry. After the collection of 14 liters, the bucket was gently agitated to homogenize the sample, although no significant difference was noted in alkalinity from the beginning to the end of pumping (Morin, 1985). The 14 liters were then decanted in sequential 500 mL portions into seven polyethylene containers holding 2 liters each. Each container was marked to appear as an integral part of the sampling program. This procedure was repeated for all five piezometers, yielding five sets of seven replicate samples. Separate, unacidified 100-mL samples were collected for analysis of chloride only.

There were three laboratories selected for this study. Laboratory 1 was owned and operated by a local mining company and had analyzed acid drainage for many years. Laboratory 2 was a commercial establishment which had no experience in analyzing acid drainage. Federal personnel operated Laboratory 3 and had several years of

experience in analyzing acid drainage. From each set of seven replicate samples, three samples were forwarded to Laboratory 1, two samples to Laboratory 2, and two samples to Laboratory 3. A letter, reproduced in Table 3, accompanied the samples, following the recommendations of Keith et al. (1983). The laboratories were free to select the techniques for analyses and all reported internal procedures for calibration with standards after every 5 samples.

TABLE 3--Letter accompanying water samples

The accompanying large bottles contain water samples acidified with HCL to a pH of about 1.5. Please analyze for the following. The samples in the small bottles are unacidified and are for Cl analysis only. [The numbers in brackets are approximate concentrations in ppm.]

Ca, Mg, K, Na [400,20,80,200]
Fe, Mn, Co, Cu, Zn, Ni, Pb [3000, 20, 2, 0.04, 0.1,
1.0, 0.2]
SiO₂ [20]
SO₄ [9000]
Cl [10]
NH₃ [20]
NO₃ [2]
Total uranium [0.003 to 1]
Total thorium (x-ray method preferably) [0.04]
Radium-226 [3 to 150 pCi/L]

Please enclose with the results of analyses a brief description of the method used to analyze each species (one or two sentences only), the frequency of calibration for each method, and the precision for each method.

Send results and details on methods to:

Kevin Morin
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RESULTS AND DISCUSSION

For the parameters listed in Table 2, excluding pH and TDS, there were 560 analyses (16 parameters x 35 samples), which are listed in Morin (1985) and are summarized here. This summary will first address analytical precision for metals and anions and then assess analytical accuracy.

Based on the preferences of the laboratories, metal

analyses were performed by atomic absorption by Laboratories 1 and 2, whereas Laboratory 3 used direct current plasma equipment. Analytical precision was determined for each metal from each piezometer on the basis of the replicate analyses by each laboratory. The precision is expressed as the standard deviation divided by the mean, yielding a Coefficient of Variation (CV).

The most experienced laboratory, Laboratory 1, generated acceptably precise data at higher concentrations, but relatively imprecise data begin to appear below a concentration of approximately 0.4 mg/L (Figure 1). This trend of decreasing precision with decreasing concentration is commonly expected; however, the distinct change in precision below 0.3 mg/L is notable and exceeds the 10-20% error reported by the laboratory below 0.2 ppm. In any case, Figure 1 reveals the practical, routine limit at which trace metals can be reliably determined in neutralized to moderately severe acid drainage at this site by atomic absorption analyses. No significant difference was detected in the analytical precision from the more dilute groundwater (TDS <3000 mg/L, Piezometer 14-2) relative to the more concentrated groundwater (other piezometers), suggesting that the variation in the water matrix over this range has no significant effect on analytical precision.

Inexperienced Laboratory 2 generated data of relatively poor precision across the range of metal concentration. Three re-analyses were requested (arrowed lines, Figure 1) to demonstrate that precision could be improved when errors were obvious in the replicate analyses.

Laboratory 3 did not analyze for the lower-concentration metals so that its analytical precision at trace levels could not be determined. However, like Laboratory 1, distinctly poorer precision generally appears below 0.4 mg/L. One very poor result was obtained for lead with a CV of 137% at a mean concentration of 1.43 mg/L in Piezometer M1-7. The other laboratories reported corresponding mean lead concentrations of 0.036 and 0.21 mg/L for this piezometer with CV's of 12.4% and 28.3%, respectively.

For anions, overall precision from all laboratories was generally poor (Figure 2). The data points in Figure 2 above a mean concentration of 100 mg/L represent sulfate analyses, which were performed by the gravimetric (BaSO_4) method, the turbidimetric method, and with Dionex equipment for Laboratories 1, 2, and 3, respectively. For sulfate, experienced Laboratories 1 and 3 produced greater precision than Laboratory 2. Laboratory 1 improved its precision further for sulfate analyses upon

re-analysis of a sample (Figure 2).

The data points at lower concentrations in Figure 2 represent analyses for SiO_2 , Cl, and NH_3 . The imprecision at these lower concentrations reflected the interferences that acid-drainage water can produce with ion-specific electrodes, gravimetric methods, spectrophotometers, and Dionex columns (Morin, 1985).

The assessment of accuracy in this study is difficult because the concentrations of the metals and anions in the samples were not known accurately. Consequently, the degree of accuracy was determined by statistical tests under the hypothesis that the mean concentrations from the laboratories were identical. The tests were made for each analytical parameter from each piezometer, for a total of 80 tests (Morin, 1985). The summary of this assessment (Table 4) shows that the hypothesis can be rejected for many of the parameters from several of the piezometers. On average, analyses for only 3 out of 5 piezometers were taken as accurate on the 99% confidence level, which is not surprising in light of the poor precision of the data especially from Laboratory 2. However, it is important to understand that these findings provide no indication on whether any one of the laboratories might in fact have generated accurate results. For the purposes of the Nordic Main study, the results from Laboratory 1 were assumed to be most accurate for consistency: this laboratory had performed analyses for several years and only analytical data from this laboratory were used for geochemical interpretations.

Rice et al. (1988) reported the results of a data-quality assessment for the Uranium Mill Tailings Remedial Action (UMTRA) Project in the U.S.A using a standardized water sample. Concentrations of most parameters in the sample were known to within 1.2%. Eight laboratories analyzed replicates and an evaluation of accuracy among the laboratories revealed many similarities to the results of Table 4. For example, none of the 8 laboratories (0%) provided an aluminum analysis within 50% of the known concentration (0.126 mg/L) and the reported concentrations ranges over nearly 2 orders of magnitude. On the other hand, all 8 laboratories (100%) determined zinc concentration within 50% of the known value. Additionally, silica analyses were found to be much poorer than sulfate analyses. On average, 67% of all analyses were found to be within the acceptable range of accuracy, similar to the average of Table 4. Consequently, the accuracies expressed in Table 4 and in Rice et al. may be suggestive of analytical accuracies that may be expected in lieu of site-specific data.

TABLE 4--Summary of ANOVA and Student-t Tests: number of piezometers in which hypothesis can be accepted

 HYPOTHESIS: Mean Concentrations from the Laboratories Are Identical

<u>Parameter</u>	Number of piezometers in which hypothesis can be accepted (from a total of 5; 4 for cobalt)	
	<u>95%¹</u>	<u>99%¹</u>
Fe	5	5
Ca	3	3
Mg	3	3
Na	4	4
K	2	3
Mn	0	0
Al	0	1
Cu	4	5
Co	2	2
Zn	4	4
Pb	1	3
Ni	3	5
SO ₄	2	3
SiO ₂	1	1
Cl	3	4
NH ₃	0	2
AVERAGE	2.3	3.0

¹ Confidence Levels

CONCLUSION

This assessment of data quality in routine analyses of acid drainage has addressed both precision and accuracy of analytical data. Analytical precision was found to be dependent on the experience of the laboratory at high concentrations of metals and to be relatively poor below a concentration of about 0.4 mg/L from all laboratories. For anions other than sulfate, analytical precision was found to be relatively poor at all concentrations due to interferences with the analytical techniques. Accuracy was assessed by statistically testing the hypothesis that all mean concentrations from the laboratories were identical. For the 16 selected parameters, the means were judged to be identical on average in 3 of the 5 piezometers on the 99% confidence level. Similar conclusions on accuracy were drawn for many parameters by Rice et al. (1988).

The general lesson taken from this study is that acid drainage presents a complex chemical matrix for

analysis. The resulting analytical difficulties suggest that strict interpretations of one analysis of a sample may be unreliable. Where the reliability of analytical data is critical, such as in regulatory enforcement and the prediction of environmental impacts, thorough assessments of data quality should be conducted on a site-specific basis.

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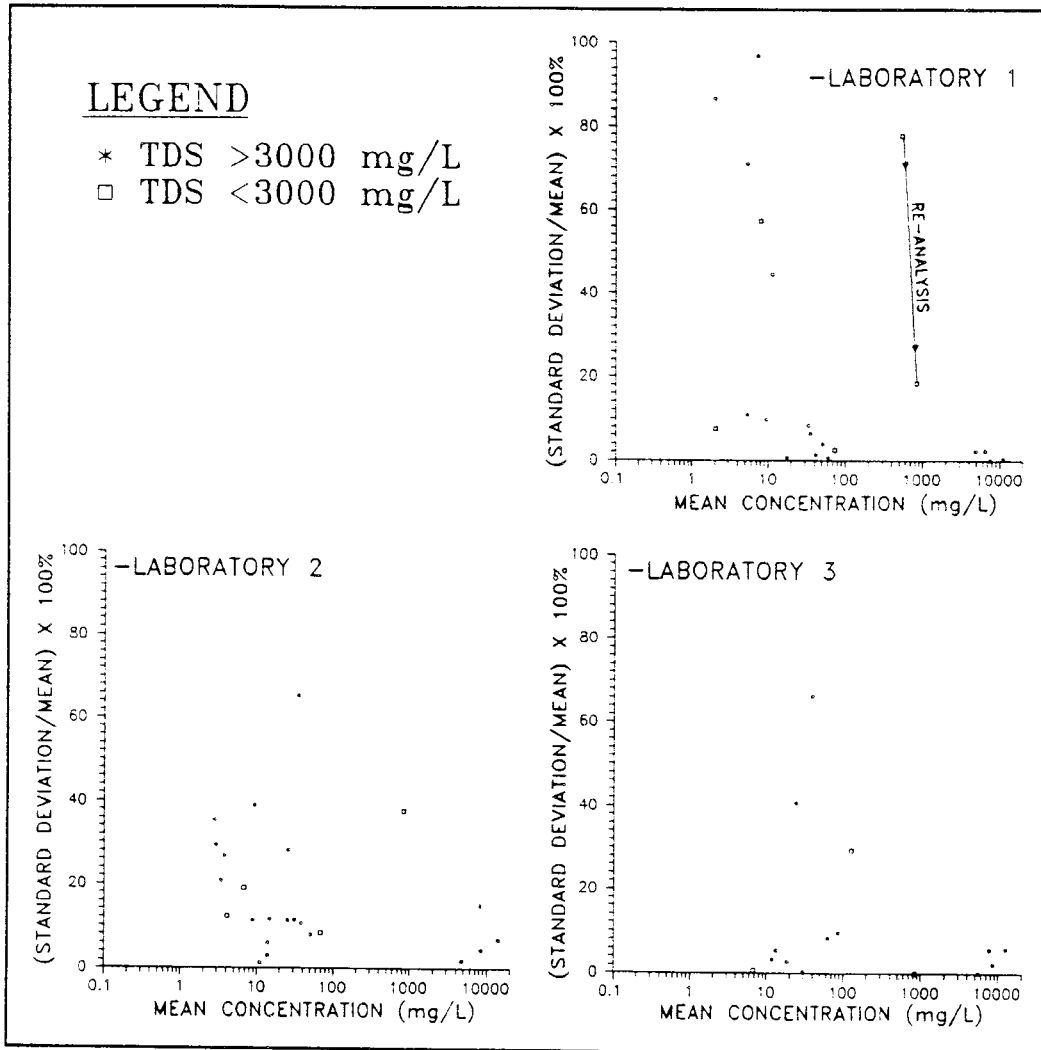


FIGURE 2. Relationship of Coefficient of Variation to mean concentration for anion analyses by the laboratories.

LEGEND

- * TDS >3000 mg/L
- TDS <3000 mg/L

ARROWED LINES CONNECT
RE-ANALYSES OF SELECTED
PARAMETERS

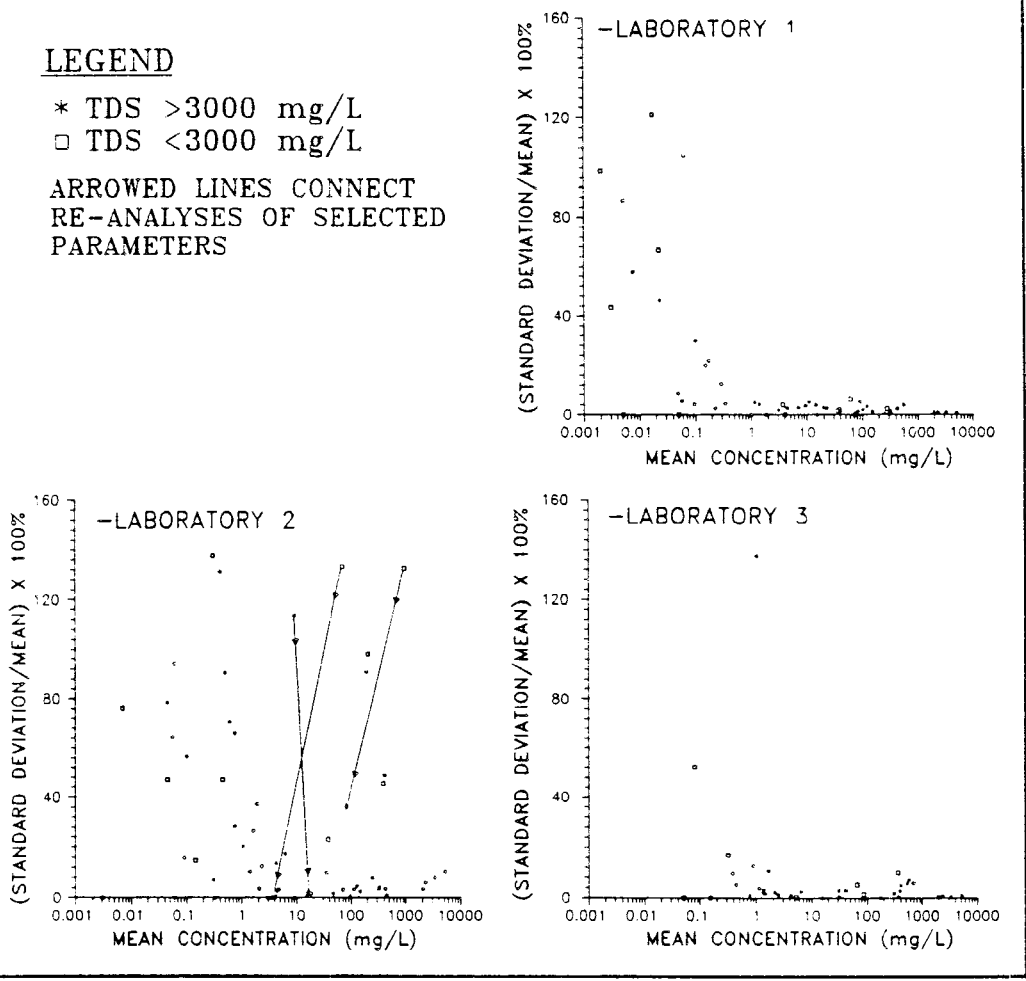


FIGURE 1. Relationship of Coefficient of Variation to mean concentration for metal analyses by the laboratories.