MRI REPORT

ASSESS RESERVE MINING COMPANY'S SURFACE AND GROUNDWATER MONITORING AND QUALITY ASSURANCE PROGRAMS AT MILE POST 7

QUARTERLY REPORT

MRI Project No. 4558-N

April 24, 1979

For

MINNESOTA POLLUTION CONTROL AGENCY
1935 West County Road B2
Roseville, Minnesota 55113

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PREFACE

This report presents the activities of a project sponsored by the Minnesota Pollution Control Agency, "Assess Reserve Mining Company's Surface and Groundwater Monitoring and Quality Assurance Programs at Mile Post 7." The report covers the quarter beginning December 1, 1978, and ending March 31, 1979. The data were collected from documents supplied by the Minnesota Pollution Control Agency and Reserve Mining Company. MRI personnel also made an on-site visit during the week of March 5, 1979. Observations made during that visit are also included. The Technical Project Officer is Mr. Loren Voigt.

Ms. Janine L. Neils is project leader and was assisted by Dr. Lawrence Rust. The work of organizing, analyzing and reporting is performed in the Analytical Chemistry Department of Midwest Research Institute at the North Star Analytical Laboratories.

The cooperation of personnel from MPCA and Reserve Mining Company made this project possible. MRI personnel are grateful for their efforts.

Chemical Sciences Division
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INTRODUCTION

The objective of this program is to provide the State of Minnesota through the Minnesota Pollution Control Agency (MPCA) with consultant services which include ongoing information on and assessment of the surface and groundwater and quality assurance programs of Reserve Mining Company (Reserve) at the Mile Post 7 site. This project is stipulated by Reserve's disposal system permit (Permit No. MNCO 40509).

Midwest Research Institute personnel are charged with the assessment of: 1) the split sample program conducted between Reserve and the Minnesota Department of Health (MDH); 2) Reserve's biological monitoring program; 3) Reserve's intra-laboratory quality assurance program; and 4) Reserve's fiber monitoring program. Recommendations are also made by MRI personnel which will substantially improve the quality of these programs.

Data for these assessments were provided by the MPCA staff and Reserve Mining officials. Observations of actual sampling and analysis practices were accomplished by MRI personnel during the week of March 5, 1979. MRI personnel observed the winter stream sampling activities and the chemical analyses performed during that week. No biological sampling or identification was accomplished during this quarter.

ASSESSMENT OF THE SPLIT SAMPLE PROGRAM BETWEEN RESERVE MINING AND THE MINNESOTA DEPARTMENT OF HEALTH

Three sets of monthly data have previously been compared (February, May, and August 1978). Data for the month of November 1978 has been made available and is compiled in Tables 1 and 2. This data has been analyzed to detect differences between Reserve and MDH test results. The test for differences for each parameter has been completed for each of the four months as well as for composite cumulative data for the first two months, first three months, and all four months. Each test for the quality of means between Reserve and MDH has been conducted at the five percent significance level.

Results of Paired Sample Analysis for Four Sets of Monthly Data

1. There is no significant difference between Reserve and MDH test results for each of the four sets of monthly data or for the two-, three-, and four-month composite test results for the parameters listed in Table 3.

2. Insufficient data exists to use the paired-difference test for five parameters. In most cases, the parameter level is below the lower detection limit for Reserve, MDH, or both. In these cases, the reported value has been indicated as a "less than" value (e.g., <0.2). Even though a formal test for differences cannot be made, each pair of values can be compared for consistency. For example, if Reserve reports a value of 0.05 and MDH reports a value of <0.2, these results are consistent with one another. Conversely, if Reserve reports a value of 2.0 and MDH reports <1.0, the results are inconsistent. A summary of the five parameters is presented in Table 4. The number of consistent and inconsistent pairs is also presented.

3. Twelve parameters exhibit no significant difference between values determined by Reserve and MDH when a t-test is applied to the combined data for all four months. However, significant differeces do exist for

Table 1. Surface Water Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from November 1978

	107		109		110	
	RMC	MHD	RMC	MHD	RMC	MHD
Calcium	14.8	14.4	18.1	19.6	10.0	11.6
Magnesium	4.19	3.9	5.28	4.9	3.12	2.9
Sodium	2.62	2.9	3.17	3.6	2.56	2.9
Potassium	0.51	<0.5	0.40	<0.5	0.22	<0.5
Sulfate	6.3	7.2	7.8	7.6	7.3	8.2
Chloride	1.6	1.4	2.3	3.0	2.1	2.3
Nitrate-N + Nitrite-N	0.24	<0.01	0.12	0.02	0.16	0.08
Ammonia-N	0.059	<0.09	0.047	<0.09	0.048	0.12
O-Phosphorous	0.001	0.006	0.002	0.006	0.001	0.003
Iron µg/l	460	520	460	530	240	240
Manganese µg/l	8	15	15	19	2	3
Copper µg/l	1.3	1.6	0.7	1.8	0.7	1.0
Zinc µg/l	1.2	1.7	<0.5	2.2	<0.5	1.2
Nickel µg/l	3	<1	<2	<1	<2	<1
Cadmium µg/l	<0.2	0.011	--	0.044	<0.2	<0.01
Lead µg/l	<2	0.24	--	0.51	<2	0.28
Cobalt µg/l	2	0.9	--	1.0	1	0.7
Chromium µg/l	<1	0.6	<1	<0.5	<1	<0.5
Mercury µg/l	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Barium µg/l	12	7	17	10	10	<5
Fluoride	<0.5	0.10	<0.5	0.10	<0.5	0.20
TDS	68.9	96	85.1	93	52.6	74
TSS	2.1	4	1.3	2	0.9	<0.5
COD	29	33	27.3	27	30.6	28
Color	50	60	45	50	65	70
pH	7.34	8.0	7.42	7.9	7.33	8.1
Spec. Cond.	106	140	131	140	81	90
Selenium µg/l	<5	<1	<5	2.2	<5	1.8
Silica	8.8	8.7	9.9	9.5	10.2	9.3
Turbidity	3.1	2.0	2.3	3.0	1.0	1.0
Organic-N	0.418	0.48	0.387	0.38	0.393	0.43
TKN	0.477	0.48	0.434	0.38	0.442	0.55
Total PO_4	0.010	0.241	0.009	0.320	0.006	0.173
Silver µg/l	<1	<0.02	<1	<0.02	<1	<0.02
Arsenic µg/l	<5	<0.5	<5	<0.5	<5	<0.5

Table 2. Groundwater Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from November 1978

	M-5		M-5A		M-5B		Well 9		M-10A		M-9A	
	RMC	MHD	RMC	MHD	RMC	MHD	RMC	MHD	RMC	MHD	RMC	MHD
Calcium	10.6	12.4	22	24	34	68	36.7	40	38.8	4.4	36.1	38
Magnesium	0.74	<2	5.28	5.1	12.4	15.3	8.2	7.8	11.33	<2	8.68	8.3
Sodium	24.95	28	12.94	14	10.5	15	3.95	4.1	12.24	25	4.39	4.4
Potassium	0.17	<0.5	0.34	<0.5	4.37	1.6	0.11	<0.5	3.95	8.8	0.17	<0.5
Sulfate	26.1	29	15.4	16	9.8	8.7	8.8	9.4	13.6	10	10.6	10
Chloride	10.9	12	<1	<0.5	<1	0.75	<1	<0.5	<1	0.64	<1	<0.5
Nitrate-N + Nitrite-N	<0.1	0.03	<0.1	0.02	<0.1	0.06	0.2	0.18	0.131	0.29	<0.1	0.10
Ammonia-N	<0.01	<0.09	<0.01	<0.09	0.012	0.13	<0.01	<0.09	0.011	<0.09	<0.01	<0.09
O-Phosphorous	0.002	0.006	0.003	0.006	<0.001	0.003	0.002	0.003	0.002	0.002	0.004	0.004
Iron µg/l	10	<20	6	<20	39	<20	3	<20	5	<20	7	<20
Manganese µg/l	4	5	7	7	610	320	<1	<3	<1	<3	<1	6
Copper µg/l	0.5	0.44	0.5	0.5	30.2	8.9	3.0	3.1	2.6	1.9	23.1	55
Zinc µg/l	<0.5	0.52	<0.5	0.42	40	22	<0.5	1	<0.5	0.24	0.5	1.9
Nickel µg/l	<2	<1	3	<1	16	2	3	<1	3	<1	3	2
Cadmium µg/l	0.4	0.017	0.5	<0.01	0.9	0.57	<0.2	0.015	<0.2	<0.01	0.2	0.023
Lead µg/l	<2	0.12	<2	0.14	<2	0.30	<2	0.45	<2	0.16	2	1.5
Cobalt µg/l	<1	0.6	<1	1.5	2	2.4	<1	1.9	<1	0.7	<1	2.4
Chromium µg/l	<1	<0.5	<1	<0.5	<1	0.5	<1	0.8	2	1.8	<1	0.6
Barium µg/l	15	<5	18	10	52	44	15	<5	19	8	19	11
Fluoride	0.7	0.6	0.5	0.5	<0.5	0.3	<0.5	<0.1	<0.5	0.2	<0.5	0.1
TDS	115.7	120	126.7	120	318.5	280	162.5	150	221	98	162.5	150
COD	3.2	6	1.4	<5	10.1	26	4.5	6	5.4	7	4.5	<5
Color	<5	<5	<5	<5	<5	10	<5	<5	<5	<5	<5	<5
pH	8.84	8.5	8.41	8.4	7.65	7.7	7.98	8.3	8.71	9.9	7.84	8.4
Spec. Cond.	178	180	195	210	490	430	250	240	340	160	250	240
Silica	19.9	19	11.4	12	10.9	13	17.6	17	13.2	12	14.2	14

Table 3. Parameters for Which No Significant Differences Exist in Monthly or Combined Data

Parameter	Number of Paired Samples Available				
	February	May	August	November	Total
Potassium	3	10	1	2	16
Sulfate	9	10	10	9	38
Chloride	7	4	3	4	18
Nitrate-N	3	8	5	4	20
Copper	7	10	10	9	36
Chromium	2	0	6	1	9
Suspended Solids	3	4	4	2	13
Total Dissolved Solids	9	10	10	9	38
Turbidity	3	4	4	3	14
Ammonia-N	0	0	0	2	2
Nickel	0	0	1	2	3
Cobalt	0	0	0	3	3
TKN	0	0	0	3	3

Table 4. Parameters for Which Data is Unsuitable to Test for Difference in Means

Parameter	Number of Paired Values That Are:	
	Consistent	Inconsistent
Mercury	10	0
Silver	14	0
Arsenic	14	0
Selenium	14	0
Cyanide	7	0

one or more of the monthly data sets. These twelve parameters are presented in Table 5 along with a description of the individual monthly differences and composite differences.

In this table the following notation has been used:

R = M: No significant difference between Reserve and MDH;
R > M: Reserve values consistently larger than MDH values;
R < M: Reserve values consistently smaller than MDH values.

4. Six parameters exhibit significant differences between values determined by Reserve and MDH when all four months of data are combined. These parameters are presented in Table 6 in the same format as Table 5.

5. T-test data for November data and cumulative T-test data for February, May, August, and November are summarized in Table 7.

Table 5. Parameters for Which Composite of Four Months of Data Indicate No Differences But With One or More Sets of Monthly Data Indicating Significant Differences

Parameter	Type of Difference For:						
	February	May	February + May	August	February + May + August	November	February + May + August + November
Calcium	R>M	R<M	R=M	R=M	R=M	R=M	R=M
Magnesium	R>M	R=M	R=M	R=M	R=M	R=M	R=M
Sodium	R>M	R=M	R=M	R=M	R=M	R=M	R=M
Silica	R>M	R<M	R=M	R=M	R=M	R=M	R=M
Iron	R=M	R=M	R=M	R<M	R=M	R=M	R=M
Specific Conductivity	R>M	R=M	R=M	R=M	R=M	R=M	R=M
Cadmium	*---	R=M	R=M	---	R=M	R>M	R=M
Barium	R=M	R=M	R=M	---	R=M	R>M	R=M
Manganese	R=M	R<M	R<M	R<M	R<M	R=M	R=M
Zinc	R<M	R=M	R<M	R=M	R<M	R=M	R=M
Lead	---	---	---	R>M	R>M	---	R=M
pH	R>M	R>M	R>M	R=M	R>M	R<M	R=M

*Data for comparative purposes not available.

Table 6. Parameters for Which Composite of Four Months of Data Indicate Significant Differences Between Reserve and MDH

Parameter	Type of Difference For:						
	February	May	February + May	August	February + May + August	November	February + May + August + November
COD	R=M	R=M	R=M	R<M	R<M	R=M	R<M
Color	R=M	R=M	R=M	R<M	R<M	R=M	R<M
Organic-N	---	R=M	R=M	R<M	R<M	R=M	R<M
Soluble Orthophosphorus	R=M	R=M	R=M	R=M	R=M	R<M	R<M
Fluoride	R=M	R=M	R=M	---	R=M	R=M	R>M
Total Phosphorus	R=M	R=M	R=M	R=M	R=M	R<M	R<M

Table 7. T-Test Data from the Split Sample Program Cummulative and November Comparisons

Parameter	November					Combined				
	N	$\bar{D}$	S	T	RMC ≠ or = MDH at Five Percent Significance Level	N	$\bar{D}$	S	T	RMC ≠ or = MDH at Five Percent Significance Level
Potassium	2	-1.04	5.388	-0.273	R=M	16	-0.408	1.865	-0.875	R=M
Sulfate	9	-0.044	1.778	-0.075	R=M	38	-0.358	2.513	-0.878	R=M
Chloride	4	-0.45	0.569	-1.583	R=M	18	-1.496	5.980	-1.062	R=M
Nitrite-N	4	0.010	0.118	0.174	R=M	20	0.010	0.072	0.623	R=M
Copper	9	-1.293	13.501	-0.287	R=M	36	-0.518	6.520	-0.477	R=M
Chromium	1	0.2	---	---	---	9	2.956	5.449	1.627	R=M
Suspended Solids	2	-1.3	0.849	-2.167	R=M	13	-0.546	1.465	-1.344	R=M
Total Dissolved Solids	9	14.72	45.13	0.979	R=M	38	21.61	72.36	1.841	R=M
Turbidity	3	0.133	0.907	0.255	R=M	14	0.321	1.775	0.678	R=M
Ammonia-N	2	-0.095	0.0325	-4.130	R=M	2	-0.095	0.0325	-4.130	R=M
Nickel	2	7.5	9.192	1.154	R=M	3	5.333	7.506	1.231	R=M
Cobalt	3	0.333	0.751	0.769	R=M	3	0.333	0.751	0.769	R=M
TKN	3	-0.019	0.082	-0.401	R=M	3	-0.019	0.082	-0.401	R=M
Calcium	9	-1.256	17.146	-0.220	R=M	38	-0.055	8.873	-0.038	R=M
Magnesium	7	-0.15	1.216	-0.327	R=M	30	0.382	1.714	1.222	R=M
Sodium	9	-2.509	4.142	-1.817	R=M	38	-0.104	2.871	-0.223	R=M
Silica	9	0.178	1.005	0.531	R=M	38	-0.203	1.945	-0.642	R=M
Iron	3	-0.043	0.038	-1.983	R=M	17	-0.071	0.152	-1.939	R=M
Specific Conductivity	9	21.22	64.90	0.981	R=M	38	22.68	72.94	1.917	R=M

Table 7. T-Test Data from the Split Sample Program Cummulative and November Comparisons (Continued)

Parameter	November					Combined				
	N	$\bar{D}$	S	T	RMC ≠ or = MDH at Five Percent Significance Level	N	$\bar{D}$	S	T	RMC ≠ or = MDH at Five Percent Significance Level
Cadmium	3	0.297	0.107	4.804	R≠M	10	0.119	0.230	1.633	R=M
Barium	6	7.833	1.941	9.887	R≠M	11	2.727	8.765	1.032	R=M
Manganese	6	46.17	119.48	0.947	R=M	29	4.828	55.678	0.467	R=M
Zinc	3	5.367	10.950	0.849	R=M	32	-0.742	4.258	-0.986	R=M
Lead	1	0.50	---	---	---	3	1.28	0.683	3.247	R=M
pH	9	-0.409	0.462	-2.658	R≠M	38	0.137	0.527	1.601	R=M
COD	7	-3.271	5.964	-1.451	R=M	24	-2.433	4.400	-2.710	R≠M
Color	3	-6.667	2.887	-4.000	R=M	14	-15.357	16.695	-3.442	R≠M
Organic-N	3	-0.031	0.035	-1.521	R=M	11	-0.061	0.066	-3.048	R≠M
Soluble Orthophosphorus	8	-0.0024	0.0019	-3.494	R≠M	31	-0.0016	0.0038	-2.315	R≠M
Fluoride	2	0.05	0.071	1.000	R=M	9	0.033	0.040	2.481	R≠M
Total Phosphorus	3	-0.236	0.072	-5.674	R≠M	14	-0.066	0.101	-2.425	R≠M

ASSESSMENT OF THE INTRA-LAB QUALITY ASSURANCE PROGRAM

On March 5, 6, and 7, 1979, Ms. Janine Neils of MRI made a site visit to Reserve Mining to observe sampling from ice-covered monitoring sites as well as sample preparation and the performance of analyses accomplished just following sample arrival in the laboratory.

Sampling Procedure

Sampling beneath the ice-cover of surface water sites causes some unique sampling problems. Gaining access to the monitoring sites can be difficult. Holes were drilled through the ice in areas where high water flow was expected. The access holes were cleaned thoroughly to exclude any ice or snow from the sample. All bottles except those for oil and grease and dissolved oxygen were rinsed three times with the sample prior to filling. Samples were taken from below the surface and upstream of any contaminants introduced by sampling personnel. Techniques for the collection of surface water samples under ice practiced by the Reserve Mining personnel were found to be satisfactory. Representative samples were being collected.

Sampling at several groundwater sites was also observed. The sites observed were all free-flowing and except for access difficulties, procedures were similar to those described in the July 1978 report. Care was being taken by the Reserve Mining personnel to not include any contamination in the sample from the Kemmerer sampler. In some cases, the monitoring wells do not contain sufficient water for bottle rinsing. Therefore, bottles used for all groundwater samples are prepared by preliminary washing with nitric acid. The careful cleaning of these bottles by acid washing followed by distilled water rinse will minimize sample contamination where insufficient sample is available for rinsing. This washing procedure, as an alternative to rinsing, is accepted by MRI personnel.

Sampling procedures practiced by Reserve Mining personnel for both groundwaters and surface waters were observed to be acceptable for the collection of contaminant-free samples.

Methods of Analysis

Several chemical analyses as well as sample splitting and preservation techniques were observed. Although all the analyses which were initiated on the first day following collection were not observed by MRI personnel, the analyses which were completed were those for parameters with the shortest holding times. The priority by which the analyses are initiated conforms to EPA suggested guidelines. All analyses which were observed were completed without deviation from EPA approved methods. Upon questioning, it was found that most methods in which deviations were found and stated in the December 1978 report have either since been corrected or the utilized method has been approved by MPCA personnel.

A misunderstanding occurred while MRI personnel were gathering data for the December 1978 report which resulted in a statement in the December 1978 report to the effect that biochemical oxygen demand (BOD) analyses were to be dropped from the RMC monitoring program. Biochemical oxygen demand will remain a required analysis in the Reserve Mining monitoring program. Therefore, an evaluation was made of the current method. Several improvements in the BOD analysis have been made since the July 1978 report. Samples are set-up daily for analysis rather than being batched as before. Analysis within the maximum six-hour time lapse between collection and analysis is maintained as closely as possible. Reserve personnel standardize the dissolved oxygen probe by the Winkler method as well as calibration to atmospheric oxygen. This is a good practice to assure correct calibration of the probe.

Reserve Mining laboratory personnel are calculating total dissolved solids results from specific conductivity using the .65 factor recommended by the Upper Great Lakes Reference Group of the International Joint Commission

for use with surface waters in that geographical region on groundwater samples. Upon questioning the validity of this procedure, MRI personnel were assured that a study had been completed proving that the comparison between the calculated method and the actual filtration and drying of the sample was acceptable. A request was made for this data but it had not been received at the time this report was prepared. It is still the contention of MRI personnel that using the EPA method of filtration and drying groundwater samples would result in more accurate results. Unless Reserve's comparison study shows a statistically stable factor exists for the conversion of specific conductivity results to total dissolved solids concentration, MRI stands by its recommendation to use federally-approved methods.

In general, except for total dissolved solids, the methods used by RMC for the analyses of required parameters correspond to federally-approved or MPCA approved (as agreed upon between MPCA and RMC) methods.

Laboratory Quality Assurance

This is one area where little has been done in reaction to the previous MRI reports. Duplicate sample collection and duplicate analyses have been initiated but nothing has been done statistically or graphically with this data. Results are visually compared with no long-term comparisons. Although collection and analysis of duplicate samples are setps in the right direction, it is still a long way from an effective and meaningful quality assurance program. The types of programs outlined in the text of the July 1978 report including the EPA program attached to that report as Appendix A, should be initiated in the Reserve Mining laboratory as soon as possible.

The U.S. EPA considers an active quality assurance program essential to the optimum operation of an analytical chemical laboratory and the personnel of MRI concur. Until such time that long-term matrix effects and operator variance are ascertained by analysis of spiked sample and spiked laboratory distilled/deionized waters, the accuracy of results achieved by the Reserve

Mining laboratory will be subject to question. Proper documentation including graphic representation is essential to note any long-term trends in analytical data which may be missed when only visual comparison is used.

It is the recommendation of MRI personnel that a quality assurance program similar to the one described in the July 1978 report be initiated during the next reporting period.