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MRI REPORT

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

Q U A R T E R L Y R E P O R T

MRI Project No. 4558-A

August 31, 1979

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For

MINNESOTA POLLUTION CONTROL AGENCY
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Attention: Loren Voigt

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(2A) ASSESS RESERVE MINING COMPANY'S SURFACE AND GROUNDWATER MONITORING AND QUALITY ASSURANCE PROGRAMS AT MILE POST 7

(2B) QUARTERLY REPORT

MRI Project No. 4558-A

(2C) MRI, North Star Division

(3) August 31, 1979

(4) 24p.

(5) (Consultants' reports)

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

Attention: Loren Voigt

environment - water
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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 April 1, 1979, and ending July 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 July 2, 1979. Observations made during that visit are also included. The Technical Project Officer is Mr. Loren Voigt.

Ms. Janine L. Neils is project leader. The work of organizing, analyzing and reporting is performed at the North Star Laboratories of Midwest Research Institute (MRI) by the Chemical Sciences Division.

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

The project staff also gratefully acknowledges the assistance of Mrs. Jean Williams, Dr. Lawrence Rust, and Dr. Edwin Cook of the University of Minnesota, who acted as consultants on this report.

Chemical Sciences Division
MIDWEST RESEARCH INSTITUTE

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Approved:

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QUARTERLY REPORT

April 1, 1979, through July 31, 1979

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

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 program 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 July 2, 1979. Biological periphyton sampling was observed and chemical procedures were witnessed within the laboratory.

This report contains summaries of a) results of paired sample analysis for six sets of monthly data; b) biological monitoring; c) intra-lab quality assurance program.

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

Results of Paired Sample Analysis for Six Sets of Monthly Data

Four sets of monthly data have previously been compared (February, May, August, and November 1978). Data for the months of February and May 1979 have been made available and have been analyzed to detect differences between Reserve and MDH test results. These data are listed in Tables 1 through 4. The test for differences for each parameter has been complted for data obtained in each of the six months as well as for composite cumulative data through each of the six months. All statistical analyses were conducted at the five percent significance level.

Summary of Results

1. There is no significant difference between Reserve and MDH test results for the six sets of monthly data or for any cumulative test results for the parameters listed in Table 5.

2. Insufficient data exists to use the paired-difference test for the five parameters listed in Table 6. 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 said to be 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 6. To date, all data pairs for these parameters have been consistent.

Table 1. Surface Water Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from February 1979

	Station 101		Station 102		Station 103	
	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	12.9	13.2	14.1	12.8	17.5	17.6
Magnesium	4.29	4.4	4.56	4.4	5.0	4.6
Sodium	3.09	2.7	3.40	2.9	3.14	2.8
Potassium	0.22	<0.5	0.16	<0.5	0.28	<0.5
Sulfate	7.7	6.0	8.8	5.0	7.7	5.0
Chloride	<1.0	0.9	1.0	1.3	<1.0	1.1
Nitrate-N	0.50	0.30	0.38	0.34	0.33	0.16
Silica	15.5	13	14.7	13	16.3	14
Organic-N	0.364	0.27	0.309	0.22	0.344	0.27
Sol. $O\text{-}PO_4$	0.004	0.009	0.003	<0.001	0.005	0.004
Total PO_4	0.012	0.017	0.011	0.015	0.021	0.029
Iron µg/l	965	690	866	740	1580	1500
Manganese µg/l	7	7	25	27	268	440
Copper µg/l	1.0	0.7	0.8	1.0	<0.5	0.8
Zinc µg/l	1.6	1.3	2.4	2.7	3.0	3.0
Nickel µg/l	<2	<1	<2	<1	<2	<1
Cadmium µg/l	<0.2	0.046	<0.2	0.021	<0.2	0.064
Lead µg/l	<2	0.23	<2	0.28	<2	0.69
Cobalt µg/l	<1	<0.5	<1	<0.5	<1	0.6
Chromium µg/l	<1	<0.5	<1	<0.5	<1	0.6
Silver µg/l	<1	0.03	<1	<0.02	<1	0.02
Arsenic µg/l	<5	<0.5	<5	<0.5	<5	0.6
Selenium µg/l	<5	<1	<5	<1	<5	<1
Barium µg/l	17	5	20	5	12	6
Fluoride	<0.5	0.3	<0.5	0.16	<0.5	0.21
TSS	0.7	1.2	0.9	2.8	2.0	4.8
COD	25.3	31	23.2	24	25.2	27
Color	50	100	45	110	45	60
pH	7.53	7.9	7.49	7.8	7.09	7.0
TDS	68.3	95	72.1	93	84.5	100
Turbidity	1.3	10	1.4	10	2.6	11
Ammonia-N	0.064	0.28	0.040	0.18	0.182	0.27
Spec. Cond.	105	100	111	110	130	120
Mercury	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1

Table 2. Groundwater Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from February 1979

	Well M-7		Well M-7A		Well M-7B		Well M-11		Well M-11A		Well M-3	
	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	18.9	18.0	29.1	26.1	38.5	32.1	24.1	21.3	33.7	31.3	100.3	132.3
Magnesium	6.61	6.1	12.3	12.6	10.18	8.5	13.1	12.6	8.52	8.0	0.19	<2
Sodium	16.23	16	7.93	7.4	8.16	8.6	5.73	5.2	5.15	4.6	19.42	19
Potassium	0.34	<0.5	1.14	1.3	1.99	2.3	<0.05	<0.5	0.22	<0.5	1.57	1.0
Sulfate	4.9	5.0	10.5	11	11.3	11	9.4	8.8	9.9	9.9	9.4	7.0
Chloride	<1.0	<0.5	<1.0	0.6	<1.0	1.2	<1.0	0.6	<1.0	0.6	1.3	2.3
Nitrate-N	<0.1	0.02	<0.1	<0.4	1.4	1.1	0.14	0.13	1.14	0.11	0.22	0.08
Silica	12.4	11	11	11	13.8	12	14.6	13	19.9	19	10.8	7.4
Sol. O-PO_4	0.004	<0.001	0.002	0.024	0.001	<0.001	0.002	<0.001	0.002	<0.001	<0.001	<0.001
Iron µg/l	6	100	4	220	4	170	4	190	4	210	5	380
Manganese µg/l	<1	<3	5	6	<1	<3	<1	<3	3	<3	<1	5
Copper µg/l	6.1	2.1	1.0	1.1	1.8	1.9	2.6	3.1	4.5	7.6	5.7	6.1
Zinc µg/l	11.1	2.6	4.0	8.3	<0.5	0.6	5.2	5.8	1.2	3.4	0.9	0.27
Nickel µg/l	2	<1	<2	<1	<2	<1	3	<1	4	1.4	<2	<1
Cadmium µg/l	<0.2	0.03	<0.2	0.066	<0.2	0.015	<0.2	0.077	<0.2	0.051	<0.2	0.023
Lead µg/l	<2	0.74	<2	0.42	<2	0.48	<2	0.53	<2	1.0	9	11
Cobalt µg/l	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	0.7
Chromium µg/l	1	<0.5	<1	0.8	3	2.4	1	0.9	2	1.1	4	3.8
Barium µg/l	12	<5	16	14	18	10	<10	<5	13	5	170	150
Fluoride	<0.5	0.26	<0.5	0.28	<0.5	0.25	<0.5	<0.1	<0.5	<0.1	<0.5	<0.1
COD	2.2	10	1.5	7	3.1	10	3.8	10	2.8	9	3.7	12
Color	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
pH	8.29	7.7	8.3	7.8	8.19	7.8	8.28	7.9	7.65	7.7	12.06	12.0
TDS	126.1	120	169	150	195	170	156	140	162.5	160	747.5	440
Ammonia-N	<0.01	<0.09	<0.01	<0.09	<0.01	<0.09	<0.01	<0.09	<0.01	<0.09	0.030	0.15
Spec. Cond.	194	190	260	240	300	260	240	230	250	240	1150	2500

Table 3. Surface Water Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from May 1979

	Station 104		Station 105		Station 106	
	RMC	MHD	RMC	MHD	RMC	MHD
Calcium	6.9	6.4	5.4	5.2	5.6	5.2
Magnesium	2.29	<2	1.64	<2	1.68	<2
Sodium	1.11	1.5	0.84	1.2	0.93	1.2
Potassium	0.57	<0.5	0.35	<0.5	0.42	<0.5
Sulfate	13.1	10	11.5	8.9	11.2	8.9
Chloride	<1	1.0	<1	0.76	<1	1.1
Nitrate-N	0.20	0.04	<0.10	0.17	0.30	0.14
Silica	7.2	7.4	8.2	7.9	7.8	7.9
Organic-N	0.446	0.32	0.544	0.35	0.543	0.44
Sol. O-PO_4	0.003	0.014	0.003	0.010	0.003	0.013
Total PO_4	0.030	0.058	0.024	0.057	0.025	0.075
Iron µg/l	763	650	558	430	726	460
Manganese µg/l	6	10	2	12	4	14
Copper µg/l	1.9	2.2	1.4	2.0	1.5	2.1
Zinc µg/l	2.0	2.0	1.3	17	1.4	2.0
Nickel µg/l	<2	<1	<2	<1	--	<1
Cadmium µg/l	<0.2	0.022	<0.2	0.014	<0.2	0.021
Lead µg/l	<2	0.21	<2	0.14	<2	0.18
Cobalt µg/l	<1	<0.5	<1	<0.5	<1	<0.5
Chromium µg/l	<1	2.7	<1	1.0	<1	0.8
Silver µg/l	<1	<0.02	<1	<0.02	<1	<0.02
Arsenic µg/l	<5	1.2	<5	0.8	<5	0.9
Selenium µg/l	<5	<1	<5	1.3	<5	<1
Barium µg/l	<10	8	<10	6	<10	6
Fluoride	<0.5	<0.1	<0.5	<0.1	<0.5	<0.1
TSS	5.5	3.6	5.8	3.6	7.9	4.0
COD	28.4	32	31.6	32	31.6	36
Color	65	90	70	90	70	90
pH	7.02	7.5	7.06	7.3	7.11	7.4
TDS	35.1	55	27.9	53	28.6	55
Turbidity	9.3	8.7	3.3	2.2	3.9	3.5
Ammonia-N	0.060	0.08	0.066	0.10	0.063	0.09
Spec. Cond.	54	55	43	45	44	45
Mercury	<0.2	0.11	<0.2	<0.1	<0.2	<0.1
TKN	0.506	0.40	0.610	0.45	0.605	0.53

Table 4. Groundwater Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from May 1979

	Well M-5		Well M-5A		Well M-9		Well M-9A		Well M-10		Well M-10A	
	RMC	MDH	RMD	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	11.1	11.6	23.2	132	37.8	36.5	32.8	32.9	7.3	9.6	3.1	<4
Magnesium	0.84	<2	5.2	6.8	12.17	8.0	12.0	8.0	13.04	13.1	8.41	<2
Sodium	25	29	13.02	13	4.32	4.1	4.15	4.2	18.62	20	28.2	31
Potassium	0.30	<0.5	0.43	<0.5	0.26	<0.5	0.57	<0.5	11.67	11	12.71	11
Sulfate	26.3	29	15.5	16	9.5	7.9	12	10	18.5	14	12.3	8.6
Chloride	10.2	11	<1	0.72	<1	0.56	<1	0.47	<1	0.65	1.3	2.0
Nitrate-N	0.11	<0.01	<0.1	<0.01	0.19	0.16	<0.1	0.05	<0.1	0.02	0.65	0.57
Silica	18.6	19	10.7	11	16.8	17	--	13	11.9	11	16.4	16
Sol. $O\text{-}PO_4$	0.001	0.002	0.004	0.005	0.003	0.008	<0.001	0.003	0.003	0.003	0.002	0.011
Iron µg/l	3	<20	2	<20	2	<20	2	<20	2	<20	7	<20
Manganese µg/l	3	3	8	9	<1	<3	<1	<3	2	8	<1	<3
Copper µg/l	<0.5	<0.2	<0.5	0.3	<0.5	0.6	3.8	3.9	5.2	4.6	5.3	5.2
Zinc µg/l	0.8	0.24	0.9	0.4	1.1	0.22	3.9	3.1	9.9	4.7	10.4	7.3
Nickel µg/l	<2	<1	<2	<1	<2	<1	<2	<1	<2	<1	<2	<1
Cadmium µg/l	<0.2	<0.01	<0.2	0.011	<0.2	<0.01	<0.2	0.058	<0.2	0.15	<0.2	0.19
Lead µg/l	<2	<0.1	<2	<0.1	<2	<0.1	<2	<0.2	2	1.6	2	0.86
Cobalt µg/l	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5	<1	<0.5
Chromium µg/l	<1	<0.5	<1	<0.5	1	0.6	<1	<0.5	<1	<0.5	2	3
Barium µg/l	<10	6	<10	11	<10	5	<10	10	109	90	16	12
Fluoride	0.6	0.58	0.5	0.47	<0.5	<0.1	<0.5	0.12	<0.5	<0.1	<0.5	0.41
COD	4.2	<5	3.9	<5	16	<5	15.2	<5	18.2	<5	15.1	8
Color	--	5	<5	5	<5	5	--	5	--	5	<5	5
pH	9.05	8.5	8.52	8.4	8.08	8.1	8.26	8.3	9.98	9.6	11.34	9.9
TDS	122.8	120	112.4	120	169	150	162.5	140	175.5	130	195	120
Ammonia-N	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02	0.092	0.17	0.084	0.33
Spec. Cond.	189	190	173	205	260	250	250	235	270	245	300	205

Table 5. Parameters for Which No Significant Differences Exist in Monthly or Combined Data

Parameter	Number of Paired Samples Available: February 1978	May 1978	August 1978	November 1978	February 1979	May 1979	Total
Potassium	3	10	1	2	3	2	21
Copper	7	10	10	9	8	6	50
Chromium	2	0	6	1	4	2	15
Suspended Solids	3	4	4	2	3	3	19
Nickel	0	0	1	2	1	0	4
Cobalt	0	0	0	3	0	0	3

Table 6. Parameters for Which Data is Unsuitable to Test for Difference in Means

Parameter	Number of Paired Values that Are: Consistent	Inconsistent
Mercury	16	0
Silver	20	0
Arsenic	20	0
Selenium	20	0
Cyanide	7	0

3. Fifteen parameters exhibit no significant difference between Reserve and MDH when all six months of data are combined. However, significant differences do exist for one or more of the monthly data sets. The data for fifteen parameters is presented in Table 7 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 $\neq$ M: Significant difference exists between Reserve and MDH.

4. Ten parameters exhibit significant differences between samples analyzed by Reserve and MDH when all six months of data are combined. These parameters are presented in Table 8 in the same format as Table 7.

5. The results of a statistical analysis, using t-test criteria, for the data obtained in February and May 1979 are summarized in Tables 9 and 10 respectively.

Table 7. Parameters for Which Composite of Six Months of Data Indicate No Differences But With One or More Sets of Monthly Data Indicating Significant Differences

Parameter	Type of Difference For:										
	February 1978	May 1978	Cumulative	August 1978	Cumulative	November 1978	Cumulative	February 1979	Cumulative	May 1979	Cumulative
Calcium	R≠M	R≠M	R=M	R=M	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	R=M	R=M	R=M	R=M
Sodium	R≠M	R=M	R=M	R=M	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	R≠M	R=M	R=M	R=M
Iron	R=M	R=M	R=M	R≠M	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	---	R=M	---	R=M
Manganese	R=M	R≠M	R≠M	R≠M	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	R=M	R=M	R=M	R=M
Lead	---	---	---	R≠M	R≠M	---	R=M	---	R=M	R=M	R=M
pH	R≠M	R≠M	R≠M	R=M	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	R≠M	R=M	R≠M	R=M
Sulfate	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R≠M	R=M	R≠M	R=M
Chloride	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R≠M	R=M
Turbidity	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R≠M	R=M	R=M	R=M
TKN	---	---	---	---	---	R=M	R=M	---	R=M	R≠M	R=M

Table 8. Parameters for Which Composite of Four Months of Data Indicate Significant Differences Between Reserve and MDH

Parameter	Type of Difference For:										
	February 1978	May 1978	Cumulative	August 1978	Cumulative	November 1978	Cumulative	February 1979	Cumulative	May 1979	Cumulative
COD	R=M	R=M	R=M	R≠M	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	R=M	R≠M	R≠M	R≠M
Soluble Orthophosphorus	R=M	R=M	R=M	R=M	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	---	R≠M	R=M	R≠M
Total Phosphorus	R=M	R=M	R=M	R=M	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	R≠M	R≠M	R=M	R≠M
Barium	R=M	R=M	R=M	---	R=M	R≠M	R=M	R≠M	R≠M	R=M	R≠M
Nitrate-Nitrite	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R≠M
Total Dissolved Solids	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R=M	R≠M	R=M	R≠M
Ammonia-N	---	---	---	---	---	R=M	R=M	R≠M	R≠M	R=M	R≠M

Table 9. T-Test Data from the Split Sample Program Cumulative and February 1979 Comparisons

Parameter	February 1979 N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5 Percent Significance Level	Cumulative N	$\bar{D}$	S	T	RMC =, = MDH at 5 Percent Significance Level
Potassium	3	0.033	0.471	0.123	R=M	19	-0.338	1.718	-0.859	R=M
Copper	8	-0.013	1.934	-0.018	R=M	44	0.426	5.937	0.476	R=M
Chromium	4	0.450	0.370	2.435	R=M	13	2.185	4.613	1.708	R=M
Suspended Solids	3	-1.733	1.159	-2.590	R=M	16	-0.769	1.458	-2.110	R=M
Nickel	1	2.60	---	---	---	4	4.65	6.279	1.481	R=M
Cobalt	0	---	---	---	---	3	0.333	0.751	0.769	R=M
Calcium	9	-1.733	11.528	-0.451	R=M	47	-0.377	9.321	-0.277	R=M
Magnesium	8	0.420	0.595	1.996	R=M	38	0.390	1.539	1.563	R=M
Sodium	9	0.339	0.311	3.274	R≠M	47	-0.019	2.584	-0.050	R=M
Silica	9	1.733	0.970	5.363	R≠M	47	0.168	1.949	0.591	R=M
Iron	9	-0.085	0.204	-1.243	R=M	26	-0.076	0.168	-2.309	R≠M
Cadmium	0	---	---	---	---	10	0.119	0.230	1.633	R=M
Manganese	4	-43.75	85.50	-1.023	R=M	33	-1.061	60.474	-0.101	R=M
Zinc	8	0.254	3.703	0.194	R=M	40	-0.543	4.127	-0.832	R=M
Lead	1	-2.0	---	---	---	4	0.460	1.732	0.531	R=M
pH	9	0.101	0.421	0.721	R=M	47	0.130	0.504	1.768	R=M
Organic-N	3	0.086	0.010	14.261	R≠M	14	-0.029	0.085	-1.282	R=M
Sulfate	9	1.211	1.495	2.430	R≠M	47	-0.057	2.420	-0.163	R=M
Chloride	2	-0.650	0.495	-1.857	R=M	20	-1.412	5.664	-1.115	R=M
Turbidity	3	-8.567	0.153	-97.136	R≠M	17	-1.247	3.842	-1.338	R=M
TKN	0	---	---	---	---	3	-0.019	0.082	-0.401	R=M
COD	9	-5.467	2.547	-6.440	R≠M	33	-3.261	4.173	-4.488	R≠M
Color	3	-43.333	25.658	-2.925	R=M	17	-20.294	20.727	-4.037	R≠M
Soluble Orthophosphorus	3	-0.0087	0.0119	-1.258	R=M	34	-0.0022	0.0051	-2.531	R≠M
Fluoride	0	---	---	---	---	9	0.033	0.040	2.481	R≠M
Total Phosphorus	3	-0.0057	0.0021	-4.715	R≠M	17	-0.055	0.094	-2.407	R≠M
Specific Conductivity	8	12.50	12.49	2.831	R≠M	46	20.91	66.44	2.135	R≠M
Barium	7	10.14	6.01	4.464	R≠M	18	5.61	8.47	2.810	R≠M
Nitrate-Nitrite	7	0.270	0.349	2.047	R=M	27	0.077	0.213	1.888	R=M
Total Dissolved Solids	9	34.78	103.89	1.004	R=M	47	24.13	78.20	2.115	R≠M
Ammonia-N	4	-0.141	0.054	-5.184	R≠M	6	-0.126	0.051	-6.096	R≠M

Table 10. T-Test Data from the Split Sample Program Cumulative and May 1979 Comparisons

Parameter	May 1979 N	May 1979 $\bar{D}$	May 1979 S	May 1979 T	May 1979 RMC =, ≠ MDH at 5 Percent Significance Level	Cumulative N	Cumulative $\bar{D}$	Cumulative S	Cumulative T	Cumulative RMC =, ≠ MDH at 5 Percent Significance Level
Potassium	2	1.19	0.735	2.289	R=M	21	-0.193	1.701	-0.520	R=M
Copper	6	-0.150	0.459	-0.800	R=M	50	-0.393	5.564	-0.499	R=M
Chromium	2	-0.300	0.990	-0.429	R=M	15	1.853	4.367	1.644	R=M
Suspended Solids	3	2.667	1.079	4.282	R=M	19	-0.226	1.886	-0.523	R=M
Nickel	0	---	---	---	---	4	4.65	6.279	1.481	R=M
Cobalt	0	---	---	---	---	3	0.333	0.751	0.769	R=M
Calcium	7	-0.071	1.130	-0.167	R=M	54	-0.337	8.693	-0.285	R=M
Magnesium	4	1.628	2.907	1.120	R=M	42	0.508	1.700	1.937	R=M
Sodium	9	-1.001	1.463	-2.052	R=M	56	-0.177	2.455	-0.539	R=M
Silica	8	0.050	0.444	0.319	R=M	55	0.151	1.807	0.619	R=M
Iron	3	0.169	0.084	3.471	R=M	29	-0.051	0.177	-1.540	R=M
Cadmium	0	---	---	---	---	10	0.119	0.230	1.633	R=M
Manganese	6	-5.167	4.309	-2.937	R≠M	39	-1.692	55.537	-0.190	R=M
Zinc	9	-0.584	5.941	-0.295	R=M	49	-0.551	4.441	-0.868	R=M
Lead	2	0.770	0.523	2.081	R=M	6	0.563	1.371	1.006	R=M
pH	9	0.158	0.579	0.817	R=M	56	0.135	0.511	1.968	R=M
Organic-N	3	0.141	0.047	5.161	R≠M	17	0.001	0.103	0.035	R=M
Sulfate	9	1.844	2.210	2.503	R≠M	56	0.248	2.471	0.752	R=M
Chloride	2	-0.750	0.071	-15.000	R≠M	22	-1.351	5.391	-1.176	R=M
Turbidity	3	0.700	0.361	3.363	R=M	20	-0.955	3.599	-1.187	R=M
TKN	3	0.114	0.043	4.578	R≠M	6	0.047	0.093	1.241	R=M
COD	4	-0.325	5.243	-0.124	R=M	37	-2.943	4.316	-4.148	R≠M
Color	3	-21.667	2.887	-13.000	R≠M	20	-20.50	19.050	-4.813	R≠M
Soluble Orthophosphorus	8	-0.0055	0.0044	-3.529	R≠M	42	-0.0028	0.0051	-3.604	R≠M
Fluoride	2	0.025	0.007	5.000	R=M	11	0.032	0.036	2.907	R≠M
Total Phosphorus	3	-0.037	0.012	-5.557	R≠M	20	-0.052	0.087	-2.695	R≠M
Specific Conductivity	9	12.00	34.84	1.033	R=M	55	19.46	62.21	2.320	R≠M
Barium	2	11.50	10.61	1.533	R=M	20	6.20	8.57	3.236	R≠M
Nitrate-Nitrite	4	0.101	0.077	2.610	R=M	31	0.081	0.200	2.241	R≠M
Total Dissolved Solids	9	8.98	33.36	0.808	R=M	56	21.70	72.86	2.228	R≠M
Ammonia-N	5	-0.083	0.094	-1.982	R=M	11	-0.106	0.073	-4.852	R≠M

BIOLOGICAL MONITORING

The biological monitoring program being carried out by Reserve Mining Company was reviewed and the collection of periphyton samples was observed. All of the recommendations given in MRI's Quarterly Report of 20 December 1978 have been followed or taken under consideration. One macroinvertebrate sample taken during the spring sample collection was analyzed by a consultant to MRI. Both the counts and identification are generally the same.

Field Sampling

As indicated in the 20 December 1978 Quarterly Report, the sampling sites at some of Reserve's stations have been relocated so that they are more similar to the ones found to be satisfactory earlier in 1978 in terms of stream velocity and substrate. The two new control stations that were established by Reserve (Stations 112 and 114) were visited early in July. The macroinvertebrate sampling had been completed, but the portions of the rivers where the sampling was performed were observed and were found to be satisfactory, as were the areas where periphyton sampling was performed. Station 103 (one of the relocated stations) was also visited; this new location also has a stream velocity and substrate that are more consistent with those at other sites.

Only collection of the periphyton samples was observed during the July visit; the spring macroinvertebrate sample collection had been completed. The periphyton sampling procedure was the same as that observed in the autumn of 1978; it was carefully and thoroughly done.

Analysis--Macroinvertebrates

A quantitative sample from Station 101 was sent to MRI for verification of Reserve's taxonomic analysis. The agreement between Reserve's and MRI's taxonomic identifications is generally quite good.

The primary difference in macroinvertebrate counts occurred in the Chironomidae, where Reserve's taxonomist found 231 and MRI's consultant found 218 (see Table 11). There were four Chironomid exuviae in the sample, which MRI's consultant did not count as specimens. This may account for part of the difference. In addition, the two Oligochaete pieces and the tenth Simuliid found by MRI's consultant may have been included as Chironomidae by Reserve. Another possibility is that some of the smallest Chironomidae may have been lost as the macroinvertebrates were transferred during identification. This difference in macroinvertebrate counts is not considered to be one that should give rise to serious concern; the same is true of other minor differences in count that can be noted in Table 11. The correlation between taxonomic identifications is very good.

Reserve personnel visited Dr. Edwin Cook of the University of Minnesota in St. Paul in the spring of 1979. Dr. Cook reviewed Reserve's reference collection and agreed to assist Reserve's taxonomists with difficult identifications and do taxonomic verification on selected samples. Dr. Cook also gave Reserve personnel a list of taxonomic keys that he would recommend if they would wish to expand their collection.

Analysis--Periphyton

During this quarter's visit to Reserve, the periphyton analysis procedures were not observed. This has been done during other visits, however. Reserve personnel did indicate that they are now using a narrow-band spectrophotometer (Bausch and Lomb Spectronic 710) for measuring pigment concentrations. Due to the lack of an inter-laboratory check on the data produced for chlorophyll *a* analyses, it is suggested that an EPA check sample be completed to verify procedures.

Table 11. Comparison of Identification of Macroinvertebrates Collected by Reserve on May 2, 1979, at Station 101--Surber 1

RMC			MRI		
Organism	Number	Genera Observed	Organism	Number	Genera Observed
Diptera			Diptera		
Chironomidae larvae	231	Not identified	Chironomidae larvae	218	Not identified
Simuliidae	9	Not identified	Simuliidae	10	Not identified
Pupae	5	Mostly Chironomidae	Pupae	5	Mostly Chironomidae
eggs in Chironomid sand case			eggs in Chironomid sand case		
Trichoptera			Trichoptera		
Hydropsychidae	3	*Hydropsyche;* one in stone case	Hydropsychidae	3	*Hydropsyche;* one very early pupa
Rhyacophilidae larvae	1	*Glossosoma*	Rhyacophilidae larvae	1	*Glossosoma*
Rhyacophilidae pupae	4	*Glossosoma*	Rhyacophilidae pupae	4	Possibly *Glossosoma*
Ephemeroptera			Ephemeroptera		
Heptageniidae	1	Not identified*	Heptageniidae	1	Not identified*
	1	*Epeorus*		1	*Epeorus*
Leptophlebiidae	1	*Paraleptophlebia*	Leptophlebiidae	1	*Paraleptophlebia*
Ephemerellidae	2	*Ephemerella*	Ephemerellidae	2	*Ephemerella*
Plecoptera			Plecoptera		
Chloroperlidae	1	*Hastaperla*	Chloroperlidae	1	*Hastaperla*
Gastropoda	1	Soft anatomy; probably *Ferrisia*	Gastropoda	1	Soft anatomy; possibly *Ferrisia*
Coleoptera			Coleoptera		
Elmidae larvae	4	*Optioservus*	Elmidae larvae	4	*Optioservus*
Hydracarina	8	Not identified	Hydracarina	7	Not identified
Ostracoda	1	Not identified	Ostracoda	1	Not identified
Copepoda	no count	Not identified	Copepoda	3	Not identified
			Oligochaeta	2	Not identified; pieces
TOTAL	273		TOTAL	265	

*Missing parts.

Comments and Recommendations

1. The two control stations (Stations 112 and 114) and one of the relocated stations (Station 103) have all been visited and have been found to be satisfactory with regard to stream velocity and substrate.

2. There is good agreement between Reserve's and MRI's counts and identification of the qualitative sample taken at Station 101. Efforts should be made by Reserve personnel to provide a qualitative sample from the spring collection for verification by MRI's consultant.

3. Reserve has had their reference collection checked by Dr. Edwin Cook of the University of Minnesota and has also made arrangements with Dr. Cook for assistance with difficult identifications and confirmation of selected samples.

4. Reserve is now using the narrow-band Bausch and Lomb Spectronic 710 spectrophotometer for measuring pigment concentrations.

5. MRI recommends the analysis of a chlorophyll *a* check sample, which is provided free by EPA, as a verification of their procedures as no other program currently exists.

INTRA-LAB QUALITY ASSURANCE PROGRAM

Methods for Analysis

A comparison of analytical chemical methods used by Reserve Mining and the Minnesota Department of Health for the parameters that are compared in these reports is found in Table 12. Most methods are comparable and are found in one of these approved manuals: *Standard Methods for Water and Wastewater Analysis,*[1] *EPA Methods,*[2] *Perkin Elmer Graphite Furnace Manual,*[3] *Perkin Elmer Flame AA Manual,*[4] or *ASTM.*[5] For a number of analyses there is a variance in the detection limit. Although the method may be the same, the detection limit may vary due to instrumentation differences and individual technique.

It has been noticed in the February 1979 groundwater comparisons listed in Table 2 that there is a large discrepancy between Reserve Mining and Minnesota Department of Health in their results for iron. Although the t-test data shows no significant differences when the ground and surface water pairs are combined, when the criteria is applied to only the groundwater samples, inequality is indicated. The results reported by the Minnesota Department of Health Laboratory are exceptionally high for groundwater samples. The accuracy of the results should be checked by both laboratories.

At this time, we have compared six sets of paired results from Reserve and the Minnesota Department of Health using t-test criteria. The number of samples which has been analyzed is now of a sufficient size which, in some cases, will allow the analysis of differences between data points. By inspection of the data in Table 8, which summarizes those parameters obtained from the two laboratories for which the cumulative data indicate a significant difference in results and comparison of these data to discrepancies in data from the two laboratories. Significant differences have been observed for chemical oxygen demand data in February 1979. Inspection of the data reveals that discrepancies exist in groundwaters with low COD levels.

Table 12. Comparison of Analytical Methods Used by Reserve Mining Company Laboratory and the Minnesota Department of Health Laboratory

Parameter	Reserve Mining Company		Minnesota Department of Health	
	Method	Detection Limit	Method	Detection Limit
Calcium	Flame AA[1]	.1 mg/l	Flame AA, as $CaCO_3$[2]	4 mg/l
Magnesium	Flame AA[1]	.01 mg/l	Flame AA, as $CaCO_3$[2]	2 mg/l
Sodium	Flame AA[4]	.05 mg/l	Flame AA[2]	.5 mg/l
Potassium	Flame AA[4]	.05 mg/l	Flame AA[2]	.5 mg/l
Sulfate	Turbidimetric[1]	1 mg/l	Turbidimetric[1]	5 mg/l
Chloride	Colorimetric[5]	1 mg/l	Hg SCN Method[2]	.5 mg/l
Nitrate	UV Spectrophotometric[1]	.1 mg/l	Automated Cadmium Reduction[2]	.01 mg/l
Silica	Molybdosilicate[1]	.1 mg/l	Molybdosilicate[1]	.5 mg/l
Organic-N	Digestion, Distillation, Nesslerization[1]	.01 mg/l	Digestion, Distillation, Nesslerization[2]	.3 mg/l
Sol. $O-PO_4$	Ascorbic Acid	.001 mg/l	Single Reagent Heteropoly Blue[2]	.001 mg/l
Total PO_4	Digestion, Ascorbic Acid[1]	.001 mg/l	Automated Digestion Heteropoly Blue[2]	.001 mg/l
Iron	Chelation, Extraction, Flame AA[1]	1 µg/l	Furnace AA[3]	20 µg/l
Manganese	Chelation, Extraction, Flame AA[1]	1 µg/l	Furnace AA[3]	3 µg/l
Copper	Chelation, Extraction, Flame AA[1]	.5 µg/l	Furnace AA[3]	.2 µg/l
Zinc	Chelation, Extraction, Flame AA[1]	.5 µg/l	Furnace AA[3]	.05 µg/l
Nickel	Chelation, Extraction, Flame AA[1]	2 µg/l	Furnace AA[3]	2 µg/l
Cadmium	Chelation, Extraction, Flame AA[1]	.2 µg/l	Furnace AA[3]	.01 µg/l
Lead	Chelation, Extraction, Flame AA[1]	2 µg/l	Furnace AA[3]	.1 µg/l
Cobalt	Chelation, Extraction, Flame AA[1]	1 µg/l	Furnace AA[3]	.5 µg/l
Chromium	Furnace AA[3]	1 µg/l	Furnace AA[3]	.5 µg/l
Silver	Furnace AA[3]	1 µg/l	Furnace AA[3]	.02 µg/l
Arsenic	Furnace AA[3]	5 µg/l	+, Furnace AA[3]	1 µg/l
Selenium	Furnace AA[3]	5 µg/l	+, Furnace AA[3]	1 µg/l
Barium	Furnace AA[3]	10 µg/l	Furnace AA[3]	15 µg/l
Mercury	Cold Vapor AA[1]	.2 µg/l	Cold Vapor AA[2]	.1 µg/l
Fluoride	Specific Ion Electrode[1]	.5 mg/l	Selective Ion Electrode[1]	.1 mg/l
TSS	Gravimetric[1]	---	Gravimetric[1]	.5 mg/l
COD	Reflux Titration[1]	.1 mg/l	•, Reflux Titration[1]	5 mg/l
Color	Visual Comparison with Standards[1]	5 mg/l	Visual Comparison with Standards[1]	5 JTU
pH	Glass Electrode[1]	---	Glass Electrode[1]	---
TDS	Calculation	---	Gravimetric 180°[1]	.5 JTU
Turbidity	Nephelometric[1]	---	Nephelometric[1]	.2 NTU
Ammonia-N	Distillation, Nesslerization[1]	.01 mg/l	*, Distillation, Nesslerization	.2 mg/l*
Spec. Cond.	Wheatstone Bridge[1]	---	Wheatstone Bridge[1]	---
Cyanide	Distillation, Barbituric Acid-Pyridine[1]	.01 mg/l	Distillation Barbituric Acid-Pyridine[1]	.001 mg/l
TKN	Digestion, Distillation, Nesslerization[1]	.2 mg/l	Automated Phenate[1]	.1 mg/l

+: Hydride generation method if matrix problems occur.
*: Beginning 3/1/79 .02 mg/l--Automated Hypochlorite Oxidation Method
•: Beginning 7/1/79--Ampule Digestion and Spectrophotometry.

Cumulative t-test data for phosphorus analyses also exhibit significant differences. These differences occur for ortho-phosphate in November 1978 and May 1979 and for total phosphorus in the months of November 1978, February, and May 1979. The MDH results for ortho-phosphate were considerably higher in November 1978 than the Reserve data for that month. However, data from both laboratories before and after November 1978 have shown good agreement.

Discrepancies in total phosphorus data were observed in comparisons of data for November 1978 and May 1979. Data were scattered and showed the same general relationship to each other (MDH results > RMC results). However, the February 1979 data show better agreement than data obtained in either November 1978 and May 1979.

The data for fluoride and specific conductivity are other examples of data comparisons which show a statistical difference. However, with respect to fluoride, upon reviewing the data, there is no single month in which significant differences exist between data. Also, for specific conductivity the cumulative data appear to indicate statistically significant differences. However, inspection of monthly data shows that no significant differences are apparent for any given month and the cumulative data are biased considerably by several pieces of data for which there is poor agreement (e.g., Well Location M-3 for February 1979).

For barium, however, small differences in the individual data sets are accumulated and significant statistical differences are found in comparison of barium data for November 1978 and February 1979. The Reserve Mining laboratory has, in general, reported higher results for barium than MDH. The methods used by each laboratory should be evaluated by analysis of fortified blanks and fortified samples to evaluate the potential differences in analytical data.

In most cases nitrate/nitrite results compare well, but at certain stations these data show significant differences. Whenever there is a significant difference in results, the RMC laboratory reports higher values than MDH. This

may be attributed to interferences to the UV method that do not affect the cadmium reduction method. This occurs at surface stations 103, 106, 107, 109, 110, and 112 and groundwater station 3M.

Due to the limited data (one pair) available for these stations, no conclusive comparisons can be made. Data from the two laboratories for the above referenced stations compare poorly and the reasons for these differences need to be resolved. This can be accomplished by analysis of fortified blanks and fortified samples by both laboratories and comparison of the results. This should be done either before the next split sample program or at the same time as the analysis of split samples.

For most of the months for which data were compared, the ammonia values showed consistently good agreements, but the February 1979 data compared so poorly that is biased the cumulative comparisons. For the month of February 1979 no data less than 0.09 mg/liter were reported which is inconsistent with available detection limits previously provided to MRI by MDH. At the time of the February sampling, the MDH laboratory was changing to an automated system, so that the poor agreement between laboratories may have been the result of a method error in the changeover. The data from Reserve Mining from February 1979 compares favorably with data collected in February 1978, although the specific sampling stations differ.

For total dissolved solids (TDS), all the comparative data for the individual months show no significant difference between data from MDH and RMC. However, when data for February 1979 and May 1979 are included, the cumulative t-test shows significant differences between pairs. In this case, approximately 45 pairs were compared. The methods used by RMC and MDH laboratories for measuring TDS are different enough to warrant further examination.

In August and September of 1978, Reserve Mining conducted a study comparing results for TDS obtained by a gravimetric procedure to those calculated by multiplying the specific conductivity of the sample by the conversion factor (using a uniform conversion factor of 0.65). The results of this study are

summarized in Table 13. The precision of the triplicate gravimetric analyses is within 1 percent at all TDS levels. The 14th edition of *Standard Methods* states that when 18 laboratories analyzed an unknown containing 134 mg/liter filterable residue (TDS), the analytical precision was 10 percent with the recommended gravimetric method (when the residue was dried at 103-105°C). This level of TDS is equivalent to the average found in most waters from Mile Post 7.

It is not legitimate to assume that a uniform conversion factor will apply to all waters. All the stations included in the current sampling program have waters containing varying concentrations of ionic species, each of which contributes differently to the specific conductivity. As shown in Table 13 the experimentally determined conversion factors vary greatly, ranging from 0.5 to 1.11. The relative difference (expressed as a percentage) between the gravimetric and calculated values of TDS are listed in the final column of this table. Inspection of the final column indicates a highly variable different between TDS values calculated from specific conductivity and those measured gravimetrically. This makes any comparison between data obtained from Reserve and MDH laboratories inconclusive.

The use of the 0.65 conversion factor is highly suspect because the factor seems to vary randomly around the value calculated by comparing TDS with specific conductivity and appears to be dependent on whether the sample is a surface or groundwater sample. The TDS for groundwater is generally higher when calculated using the conversion factor than when measured gravimetrically. However, TDS data for surface water samples are generally just the opposite. In addition to the variation of the value of the conversion factor with sample matrix, it also appears to be site dependent. This is demonstrated by the variance in factors among the various sampling sites for similar sample types (i.e., groundwater or surface water). Because of the uncertainties involved in calculating TDS from specific conductivity, MRI recommends that the Reserve Mining laboratory adopt the approved gravimetric method for TDS analysis.

Table 13. Total Dissolved Solids Study by Reserve Mining Company
August 1978--Triplicate Analysis

Sample Type	Sample Number	Gravimetric TDS mg/l	Average	Conductivity	Factor	TDS Calculation (0.65 x Specific Conductivity)	Percent Difference
Groundwater	E-78-348	236.0 243.0 243.0	241	480	0.50	312	30
Groundwater	E-78-349	291.5 301.5 303.5	298	540	0.55	351	18
Groundwater	E-78-352	161.2 160.8 161.0	161	280	0.58	182	13
Groundwater	E-78-356	303.1 302.9 303.0	303	510	0.59	331	9
Surface Water	E-78-342	84.5 87.5 90.5	87	90	0.97	58.5	33
Surface Water	E-78-338	110.4 110.6 110.5	110	100	1.11	65	41
Surface Water	E-78-341	87.5 87.5 87.6	87	100	0.87	65	25

In summary, it is the recommendation of MRI personnel that consideration be given to the discrepancies found in the data for chemical oxygen demand, barium, nitrate/nitrite, and phosphorus determination. This evaluation should include analysis by both laboratories of spiked blanks and spiked samples for all the parameters for which significant discrepancies exist. It is also recommended that the Reserve Mining Company laboratory adopt the gravimetric method for determination of TDS for the next set of interlaboratory comparisons.

Laboratory Quality Assurance

The quality assurance program suggested by MRI personnel has been agreed to by Reserve Mining personnel. The collection and analysis of samples has started and the data are being calculated. MRI personnel would appreciate receiving copies of this information so that it may be included in future reports. Fortified samples of ground and surface waters and spiked blank samples will be analyzed by RMC as soon as time permits. MRI recommends that this be done immediately so that all data produced can be verified on a daily basis. Recoveries from spiked blanks and samples will be helpful in defining problems encountered when significant differences appear in data obtained in the split sample program. Problems with reagent quality, contamination of dilution water, operator errors or instrument malfunctions can be recognized and corrected.

The draft of the Reserve Mining Company Mile Post 7 Water Monitoring and Quality Assurance Programs (July 3, 1979) was reviewed by MRI. MRI recommendations are:

1. Total dissolved solids should be measured using the accepted gravimetric method. This should be required by the Minnesota Pollution Control Agency.
2. The water monitoring quality assurance program should include fortification and analysis of 10 percent of all ground and surface water samples which are collected. The recoveries for these fortifications should be reported along with the analytical data. Once the method recovery has been established, a spiked reagent blank should be analyzed with every 20 samples.

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