MIDWEST RESEARCH INSTITUTE

MRI REPORT

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

F I N A L R E P O R T

MRI Project No. 4558-A

October 17, 1980

For

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

Attention: Loren Voigt

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PREFACE

This is the final report for 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." All data were collected from documents and samples supplied by the Minnesota Pollution Control Agency and Reserve Mining Company. Observations from several on-site visits are also included. The Technical Project Officer was Mr. Loren Voigt.

Ms. Janine L. Neils served as project leader. The work of organizing, analyzing and reporting was performed at the North Star Analytical Laboratories (NSAL). The NSAL is in the Analytical Chemistry Department of Midwest Research Institute.

The cooperation of personnel from MPCA and Reserve Mining Company made this project possible and 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 project.

Chemical Sciences Division
MIDWEST RESEARCH INSTITUTE

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North Star Analytical Laboratories

Approved:

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

INTRODUCTION

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

Midwest Research Institute personnel were 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 were also made by MRI personnel which substantially improved the quality of these programs.

This is the final report for this project and contains summaries of a) results from eight sets of monthly data collected during 1978 and 1979; and b) the recommendations concerning the biological monitoring and intra-laboratory quality assurance programs made by MRI during the previous four reports and the actions taken by MPCA and Reserve in response to these suggestions.

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

Results of Paired Sample Analysis for Eight Sets of Monthly Data

Six sets of monthly data have previously been compared (February, May, August, and November 1978 and February and May, 1979). Data for the months of August and November, 1979 have been made available and have been statistically analyzed to examine differences between test results from Reserve and MDH. These data are summarized in Tables 1 through 4. The test for differences for each parameter has been completed for data obtained in each of the eight months as well as for composite cumulative data for all of the eight 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 eight 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 said to be inconsistent with one another. A summary of the five parameters is presented in Table 6. To date, all data pairs for these parameters have been consistent.

3. Sixteen parameters exhibit no significant difference between Reserve and MDH when all eight months of data are combined. However, significant differences do exist for one or more of the monthly data sets. The data for the sixteen

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

	Station 109		Station 111		Station 112	
	RMC	MDH	RMC	MDH	RMC	MDH
Nitrate-N + Nitrite-N	.21	.06	.28	.09	.26	.08
Silica	8.7	7.7	8.6	7.4	9.3	8.1
Sol. O-PO_4	.007	.006	.008	.005	.011	.006
Total PO_4	.027	.024	.043	.012	.043	.012
Iron µg/l	500	890	1190	890	3600	1200
Manganese µg/l	12	30	96	140	62	100
Copper µg/l	6.4	2.9	4.2	1.3	6.8	1.5
Zinc µg/l	2.5	1.8	3.8	2.5	2.9	2.1
Nickel µg/l	3	<1	<2	<1	<2	<1
Cadmium µg/l	<.2	.02	<.2	.02	<.2	.03
Lead µg/l	<2	.26	<2	.40	2	.36
Cobalt µg/l	<1	<.5	<1	<.5	<1	<.5
Chromium µg/l	2	.89	1	.52	<1	<.5
Silver µg/l	<1	<.02	<1	<.02	<1	<.02
Arsenic µg/l	<5	2.0	<5	1.6	<5	1.2
Selenium µg/l	<5	<1	<5	<1	<5	<1
Barium µg/l	14	12	<10	<5	<10	6
Fluoride	<.5	.13	<.5	.16	<.5	.13
TSS	3.8	.8	11.8	8.0	6.2	9.2
COD	49.7	49	48.1	50	50.2	62
Color	120	120	60	100	100	100
pH	7.55	8.2	7.74	7.6	7.53	7.7
TDS	76	120	71.5	110	61.7	95
Turbidity	4.5	3.2	3.0	2.3	2.5	1.6
Ammonia-N	.130	.11	.153	.09	.122	.15
Spec. Cond.	117	120	110	110	95	100
Mercury	<.2	<.1	<.2	<.1	<.2	<.1
Organic-N	.850	.63	1.008	.71	.910	.60
TKN	.979	.74	1.161	.80	1.033	.75

Table 2. Ground Water Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) for August 1979

	Well M-1		Well M-2A		Well M-2		Well M-60		Well M-1A		Well M-6	
	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Nitrate-N + Nitrite-N	<.10	.03	.12	.06	<.10	.05	.17	.08	.27	.18	.57	.53
Silica	6.5	7.0	20.9	21	8.4	8.8	16.3	16	6.7	6.8	21.2	20
Sol. O-PO_4	<.001	<.001	.005	.001	<.001	<.001	<.001	<.001	.005	.003	.003	<.001
Iron µg/l	7	<20	6	<20	8	<20	7	<20	15	<20	11	<20
Manganese µg/l	9	7.3	14	30	33	27	13	8.4	14	15	3	13
Copper µg/l	1.1	3.2	6.3	8.1	5.5	4.8	2.7	3.4	7.7	5.8	3.9	5.4
Zinc µg/l	1.8	3.2	18.5	27	9.3	3.6	7.7	5.2	22.2	20	5.2	4.3
Nickel µg/l	<2	<1	<2	<1	<2	<1	<2	2	<2	<1	<2	<1
Cadmium µg/l	.4	.12	.6	1.4	.3	.14	.3	.16	1.2	.75	.2	.18
Lead µg/l	<2	--	<2	--	3	--	<2	--	2	--	<2	--
Cobalt µg/l	<1	<.5	<1	<.5	<1	<.5	<1	<.5	<1	<.5	<1	<.5
Chromium µg/l	<1	.4	2	1.3	1	.52	<1	<.5	<1	<.5	2	1.9
Barium µg/l	15	14	27	12	11	10	32	30	25	27	23	21
Fluoride	.8	.82	<.5	.14	6	.58	<.5	.22	.9	.92	<.5	.17
COD	5.0	<5	2.6	<5	2.7	<5	4.0	6	4.9	5	4.3	<5
Color	<5	5	<5	5	<5	5	--	5	<5	5	<5	5
pH	9.08	8.8	8.94	7.8	7.40	8.7	8.00	8.3	8.02	8.1	7.77	8.0
TDS	312	260	204.8	170	162.5	120	299	210	357.5	300	396.5	320
Ammonia-N	.037	.06	<.010	.02	<.010	<.02	.047	.08	.015	.03	.021	.05
Spec. Cond.	480	460	315	290	250	220	460	440	550	540	610	600

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

	Station 101		Station 102		Station 103	
	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	8.7	8.4	9.9	10	12	12
Magnesium	2.91	3.2	3.13	3.4	3.35	3.6
Sodium	2.31	2.1	2.35	2.3	2.07	2.1
Potassium	.57	<.5	.46	<.5	.51	<.5
Sulfate	6.4	13	8.0	13	6.8	10
Chloride	1.1	1.8	1.1	1.6	1.2	1.2
Nitrate-N + Nitrite-N	.29	.23	.31	.20	.13	--
Silica	9.2	11	9.2	11	8.6	10
Sol. O-PO_4	.002	<.001	.002	<.001	.001	<.001
Total PO_4	.010	.055	.011	.047	.011	.048
Iron µg/l	430	390	570	510	420	450
Manganese µg/l	7	9	17	18	59	62
Copper µg/l	1.3	1.1	1.3	1.3	<.5	1.0
Zinc µg/l	2.4	1.9	4.4	3.0	<.5	.83
Nickel µg/l	3	<1	3	<1	<2	<1
Cadmium µg/l	.3	.024	.2	.034	<.2	.058
Lead µg/l	<2	.2	<2	<.2	<2	<.2
Cobalt µg/l	<1	<.5	<1	<.5	2	<.5
Chromium µg/l	<1	8.9	<1	.6	<1	<.5
Silver µg/l	<1	<.02	<1	<.02	<1	<.02
Arsenic µg/l	<5	<1	<5	<1	<5	<1
Selenium µg/l	<5	<1	<5	<1	<5	<1
Barium µg/l	13	<5	<10	6.0	10	<5
Fluoride	<.5	.18	<.5	.18	<.5	.11
TSS	.7	8.0	1.3	1.2	.5	.8
COD	27.5	51	25.9	47	7.7	35
Color	90	130	80	130	45	80
pH	7.44	6.8	7.44	7.2	7.05	7.2
TDS	55.2	74	53.9	59	61.1	59
Turbidity	1.0	1.0	1.9	1.9	1.1	1.4
Ammonia-N	.051	.02	.048	<.02	.051	.02
Spec. Cond.	85	72	83	78	94	92
Mercury	<.2	<.1	<.2	<.1	<.2	<.1
Organic-N	.601	.65	.587	.66	.452	.55
TKN	.652	.67	.635	.66	.503	.57

Table 4. Ground Water Comparative Data Between Reserve Mining (RMC) and The Minnesota Department of Health from November 1979

	Well M-9		Well M-7A		Well M-3		Mell M-9A		Well M-7		Well M-7B	
	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	35.8	34.8	28.5	27.2	108.8	441	33.8	32.4	23.4	22.8	16.9	18.8
Magnesium	7.92	8.01	12.33	12.6	<.01	<2	8.00	8.01	9.47	9.96	1.57	3.16
Sodium	5.03	4.1	8.97	8.1	19.81	22	5.23	4.4	11.26	10	12.2	12
Potassium	.25	<.5	.83	.85	1.41	3.2	.78	.96	.35	<.5	7.43	5.4
Sulfate	9.0	11	9.4	11	7.4	7.0	10.8	11	8.8	9.2	16.2	14
Chloride	<1.0	.5	<1.0	<.5	1.6	2.8	<1.0	.6	<1.0	<.5	1.5	1.1
Nitrate-N + Nitrite-N	.16	.14	<.10	.01	.23	.08	.18	.18	<.1	<.01	.44	.34
Silica	15.7	20	10.9	12	8.4	3.5	15.5	16	10.6	12	12.3	13
Sol. O-PO_4	.004	.002	.002	<.001	<.001	<.001	.004	<.001	.004	.001	.004	.002
Iron µg/1	2	<20	3	<20	3	90	3	<20	3	<20	7	42
Manganese µg/1	<1	<3	12	6	<1	<3	<1	<3	59	11	<1	<3
Copper µg/1	.5	3.3	.6	2.5	19.7	18.0	4.6	5.0	3.8	2.3	15.2	20
Zinc µg/1	1.0	.25	2.3	1.2	1.5	<.2	1.2	.96	40.2	3.6	.8	.92
Nickel µg/1	<2	<1.0	<2	<1.0	5	4.9	<2	<1.0	<2	<1	<2	4.5
Cadmium µg/1	.2	.035	<.2	.097	<.2	.043	.3	.077	.6	.23	<.2	.075
Lead µg/1	<2	<.2	<2	.30	6	<.2	2	<.2	<2	.5	<2	.3
Cobalt µg/1	<1	<.5	<1	<.5	1	<.5	<1	<.5	<1	<.5	<1	<.5
Chromium µg/1	<1	<.5	<1	<.5	4	2.5	<1	.50	2	<.5	<1	.7
Barium µg/1	<10	<5	20	15	996	10	10	10	<10	5.0	13	9.0
Fluoride	<.5	.1	<.5	.44	<.5	.20	<.5	.11	<.5	.44	<.5	.30
COD	2.9	9	1.5	9	10.9	14	3.6	5	.6	39	18.8	22
Color	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	18	<5
pH	8.07	8.1	8.24	8.2	11.94	12.1	8.23	8.4	8.31	8.3	9.61	9.6
TDS	178.8	140	182	130	1625	870	175.5	140	162.5	120	109.2	120
Ammonia-N	<.01	.02	<.01	.05	.123	.17	<.01	.05	<.01	<.02	.016	.05
Spec. Cond.	275	240	280	250	2500	4300	270	240	250	220	168	170
Mercury	<.2	--	<.2	--	.4	--	<.2	--	<.2	--	<.2	--

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	August 1979	November 1979	Total
Potassium	3	10	1	2	3	2	0	4	25
Copper	7	10	10	9	8	6	9	8	67
Suspended Solids	3	4	4	2	3	3	3	3	25
Nickel	0	0	1	2	1	0	0	1	5
Cobalt	0	0	0	3	0	0	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	22	0
Silver	26	0
Arsenic	26	0
Selenium	26	0
Cyanide	7	0

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 ≠ M: Significant difference exists between Reserve and MDH.

4. Ten parameters exhibit significant differences between samples analyzed by Reserve and MDH when all eight 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 Agust and November 1979 are summarized in Tables 9 and 10 respectively.

In reviewing the comparative data for parameters for which significant differences are indicated over the eight months that MRI has conducted the t-test analysis (Table 8), some observations are noteworthy. The quality of comparisons for COD data has been sporatic over the eight months. At times the comparisons are very good, while for other months the comparison shows statistically significant differences. For example, for the data from August and November of 1979, the August comparison shows no significant differences, while the November comparison indicates a significant difference between MDH and Reserve, with the results from MDH being greater in all cases than those from Reserve. This discrepancy has also appeared in the comparisons for other months.

The comparison for the orthophosphate and total phosphate analyses indicate significant differences. However, the levels are so low that meaningful comparisons are questionable. No trends are indicated when comparing the data.

Barium analyses have indicated some significant differences. When the results don't compare the Reserve result is higher than the MDH result (i.e., well M-3 for November '79; RMC, Ba = 996 mg/l and MDH, Ba = 10 mg/l).

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

	Type of Difference For:														
Parameter	February 1978	May 1978	Cumulative	August 1978	Cumulative	November 1978	Cumulative	February 1979	Cumulative	May 1979	Cumulative	August 1979	Cumulative	November 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	---	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	---	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	---	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	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	R=M	R=M	R=M	R=M
Cadmium	---	R=M	R=M	---	R=M	R≠M	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	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	R=M	R=M	R=M	R=M
Lead	---	---	---	R≠M	R≠M	---	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	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	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	---	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	---	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	R≠M	R=M	R=M	R=M
TKN	---	---	---	---	---	R=M	R=M	---	R=M	R≠M	R=M	R≠M	R≠M	R=M	R=M
Chromium	R=M	---	R=M	R=M	R=M	---	R=M	R=M	R=M	R=M	R=M	R≠M	R=M	R=M	R=M

Table 8. Parameters for Which Composite of Eight 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	August 1979	Cumulative	November 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	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	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	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	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	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	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	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	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	R=M	R≠M	R=M	R≠M
Ammonia-N	--	--	--	--	--	R=M	R=M	R≠M	R≠M	R=M	R≠M	R=M	R≠M	R=M	R≠M

Table 9. T-Test Data From the Split Sample Program
Cumulative and August 1979 Comparisons

	August 1979					Cumulative				
Parameter	N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5% Significance Level	N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5% Significance Level
Potassium	0	-	-	-	-	21	-0.193	1.701	-0.520	R=M
Copper	9	0.911	2.640	1.035	R=M	59	-0.194	5.229	-0.285	R=M
Chromium	5	0.574	0.369	3.476	R≠M	20	1.534	3.795	1.807	R=M
Suspended Solids	3	1.267	3.717	0.590	R=M	22	-0.023	2.154	-0.049	R=M
Nickel	0	-	-	-	-	4	4.650	6.279	1.481	R=M
Cobalt	0	-	-	-	-	3	0.333	0.751	0.769	R=M
Calcium	0	-	-	-	-	54	-0.337	8.693	-0.285	R=M
Magnesium	0	-	-	-	-	42	0.508	1.700	1.937	R=M
Sodium	0	-	-	-	-	56	-0.177	2.455	-0.539	R=M
Silica	9	0.422	0.728	1.741	R=M	64	0.189	1.695	0.892	R=M
Iron	3	0.770	1.453	0.918	R=M	32	0.026	0.473	0.315	R=M
Cadmium	6	0.042	0.437	0.234	R=M	16	0.090	0.311	1.153	R=M
Manganese	9	-12.744	18.232	-2.097	R=M	48	-3.765	50.689	-0.515	R=M
Zinc	9	0.467	3.864	0.362	R=M	58	-0.393	4.341	-0.689	R=M
Lead	1	1.640	-	-	-	7	0.717	1.316	1.441	R=M
Ph	9	-0.130	0.665	-0.587	R=M	65	0.098	0.537	1.468	R=M
Organic-N	3	0.276	0.049	9.783	R≠M	20	0.042	0.139	1.355	R=M
Sulfate	0	-	-	-	-	56	0.248	2.471	0.752	R=M
Chloride	0	-	-	-	-	22	-1.351	5.391	-1.176	R=M
Turbidity	3	0.967	0.306	5.480	R≠M	23	-0.704	3.411	-0.990	R=M
TKN	3	0.294	0.062	8.250	R≠M	9	0.130	0.147	2.643	R≠M
COD	5	-3.020	5.044	-1.339	R=M	42	-2.952	4.340	-4.409	R≠M
Color	3	-13.333	23.094	-1.000	R=M	23	-19.565	19.183	-4.891	R≠M

Table 9. T-Test Data From the Split Sample Program Cumulative and August 1979 Comparisons (Continued)

	August 1979					Cumulative				
Parameter	N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5% Significance Level	N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5% Significance Level
Soluble Orthophosphorus	5	0.0030	0.0016	4.243	R≠M	47	-0.0022	0.0052	-2.941	R≠M
Fluoride	3	-0.0067	0.0231	-0.500	R=M	14	0.0236	0.0369	2.389	R≠M
Total Phosphorus	3	0.022	0.016	2.321	R=M	23	-0.043	0.085	-2.415	R≠M
Specific Conductivity	9	11.889	12.683	2.812	R≠M	64	18.391	57.829	2.544	R≠M
Barium	7	3.000	5.477	1.449	R=M	27	5.370	7.914	3.526	R≠M
Nitrate-Nitrite	7	0.114	0.059	5.115	R≠M	38	0.087	0.182	2.934	R≠M
Total Dissolved Solids	9	26.311	51.385	1.536	R=M	65	22.334	69.960	2.574	R≠M
Ammonia-N	7	-0.0064	0.0355	-0.480	R=M	18	-0.0674	0.0778	-3.676	R≠M

Table 10. T-Test Data From the Split Sample Program
Cumulative and November 1979 Comparisons

	November 1979					Cumulative				
Parameter	N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5% Significance Level	N	$\bar{D}$	S	T	RMC =, ≠ MDH at 5% Significance Level
Potassium	4	0.010	1.566	0.013	R=M	25	-0.160	1.651	-0.486	R=M
Copper	8	-0.813	2.222	-1.034	R=M	67	-0.268	4.959	-0.442	R=M
Chromium	2	0.500	1.414	0.500	R=M	22	1.440	3.636	1.857	R=M
Suspended Solids	3	-2.500	4.162	-1.041	R=M	25	-0.320	2.485	-0.644	R=M
Nickel	1	0.100	-	-	-	5	3.740	5.806	1.440	R=M
Cobalt	0	-	-	-	-	3	0.333	0.751	0.769	R=M
Calcium	8	0.325	1.061	0.867	R=M	62	-0.252	8.114	-0.244	R=M
Magnesium	8	-0.408	0.499	-2.312	R=M	50	0.362	1.603	1.595	R=M
Sodium	9	0.237	1.017	0.698	R=M	65	-0.120	2.309	-0.417	R=M
Silicon	9	-0.900	2.438	-1.107	R=M	73	0.055	1.818	0.258	R=M
Iron	5	-0.010	0.060	-0.388	R=M	37	0.021	0.440	0.295	R=M
Cadmium	5	0.240	0.086	6.240	R≠M	21	0.126	0.280	2.054	R=M
Manganese	5	9.600	21.756	0.987	R=M	53	-2.504	48.726	-0.374	R=M
Zinc	7	5.781	13.599	1.125	R=M	65	0.272	6.152	0.357	R=M
Lead	0	-	-	-	-	7	0.717	1.316	1.441	R=M
Ph	9	0.048	0.257	0.559	R=M	74	0.092	0.510	1.547	R=M
Organic-N	3	-0.073	0.025	-5.184	R≠M	23	0.027	0.135	0.959	R=M
Sulfate	9	-1.822	2.754	-1.985	R=M	65	-0.039	2.591	-0.120	R=M
Chloride	5	-0.400	0.621	-1.442	R=M	27	-1.175	4.865	-1.255	R=M
Turbidity	3	-0.100	0.173	-1.000	R=M	26	-0.635	3.206	-1.009	R=M
TKN	3	-0.031	0.032	-1.663	R=M	12	0.090	0.146	2.132	R=M
COD	9	-14.622	13.268	-3.306	R≠M	51	-5.012	7.988	-4.481	R≠M
Color	3	-41.667	7.638	-9.449	R≠M	26	-22.115	19.503	-5.782	R≠M

The nitrate-nitrite comparative data also indicates significant differences for data collected in August and November 1979. In all the results for August, the Reserve result is greater than the MDH result. In light of the differences of the method used for analysis and the lack of EPA approval of Reserve's method, careful scrutinization of these data are indicated.

MRI is not in a position to make a judgment on the accuracy of any results but we recommend, especially in the case of the COD analyses where the data have not compared well during this program and the observed differences are large, that MPCA test the validity of the results. Two mechanisms could be used. First, a blind sample prepared by an independent third party could be submitted to each laboratory for analysis. This could be done on a periodic basis. The sample should be of the same matrix as normally encountered. Secondly, the precision quality assurance data accumulated by the laboratories could be reviewed by MPCA, to ascertain the range of comparability of individual results.

ASSESSMENT OF THE BIOLOGICAL MONITORING PROGRAM

Since the last report (August 31, 1979) no macroinvertebrate samples from Reserve Mining have been received by MRI for confirmation of the counts and identification. Therefore, no comparative taxonomic data are included in this report.

This section summarizes the suggestions made by MRI personnel and the resulting action taken by Reserve Mining and the Minnesota Pollution Control Agency (MPCA). Several items have been suggested in the quarterly reports. It was recommended that Reserve Mining establish control stations on the Beaver River upstream from its confluence with the low-water diversion and on Big Thirtynine Creek. These recommendations were supported by MPCA and biological sampling stations have been established at these locations. The recommendation to place biological control stations on some of the other streams was found to be unnecessary by MPCA personnel.

MRI personnel recommended that stations 103 and 104 be relocated so that all sampling sites would have the same substrate. MPCA and Reserve Mining agreed to this change and the stations have been relocated.

Subsequently, MRI recommended that collection of six macroinvertebrate samples per site would give a better mean value for the macroinvertebrate population than the three which were collected at each site. A study conducted by Reserve Mining established that there is little improvement in the estimate of the mean of the macroinvertebrate population when more than three samples are collected at each site.

Another study conducted by Reserve Mining provided data on the periphyton analyses. Two of MRI's recommendations were incorporated into their analytical scheme. These were the addition of a small amount of magnesium carbonate to the pigment sample and steeping the macerated sample for 24 hours in a dark refrigerator at 4° C. Other sample-handling recommendations made by MRI (see Quarterly Report, July 18, 1978) were found to be unncessary. These included

freezing the periphyton sample in the field and using a tissue grinder to mechanically disrupt the cells. Reserve has also acted on MRI's recommendation to analyze EPA check samples for chlorophyll a. Reserve has made it part of its annual monitoring plan to analyze these samples. Also, the narrow bandpass Bausch and Lomb Spectronic 710 spectrophotometer is being used for chlorophyll a analysis.

Three of MRI's recommendations for the biological monitoring program were found to be unnecessary when reviewed by MPCA personnel. Hester-Dendy samplers will not be used by Reserve Mining for sample collection. This method of sample collection had been tried by Reserve with very little success. MPCA personnel also decided that using a Surber net is sufficient to collect representative macroinvertebrate samples. Lastly, it was decided by mutual agreement between MPCA and Reserve that it was unnecessary to measure dissolved oxygen levels while collecting biological samples. This action was taken since the DO levels at these sampling locations are usually measured as part of the monthly water quality monitoring program.

MRI personnel recommended that Reserve Mining test for the statistical significance of their biological data by using the station-pair comparison technique (Quarterly Report, July 18, 1978). Reserve Mining concurred with this recommendation and will use this technique in the future.

Dr. Edwin Cook from the University of Minnesota will act as consultant to Reserve Mining and has confirmed Reserve's macroinvertebrate reference collection. MRI recommends that Reserve send macroinvertebrate samples to Dr. Cook for confirmation on a periodic basis. Dr. Cook has also reviewed Reserve's taxonomic keys for applicability to regional species identification.

Throughout the project there has generally been good agreement, both quantitatively and qualitatively, between Reserve's and MRI's macroinvertebrate identifications.

ASSESSMENT OF THE INTRA-LABORATORY QUALITY ASSURANCE PROGRAM

Several recommendations have been made by MRI personnel in their quarterly reports regarding intra-laboratory quality assurance. These recommendations concern sample collection and analytical procedures, sample preservation and quality assurance.

The recommendations concerning sampling were made to assure that consistent and representative samples were collected for analysis. It was recommended that care is taken in the collection of samples as to the depth of collection and also that bottles are properly rinsed with the sample matrix prior to actual sample collection. Reserve Mining has agreed to incorporate these recommendations into its monitoring program. Also, in accordance with a recommendation made by the Minnesota Department of Health, Reserve Mining agreed to rinse the bottles which are used for fiber collection with deionized/distilled water which had been filtered through a 0.2 micron filter.

It was recommended by MRI personnel that all samples which are analyzed for cyanide be preserved in the field by adjusting the pH to 12 with sodium hydroxide. It was also suggested that holding times be observed in accordance with appropriate EPA protocol. MPCA and Reserve Mining have agreed with these recommendations and Reserve has added them to their monitoring program.

Several recommendations concerning analytical procedures have been made by MRI during the two years of the program. Nitrate analyses are currently being performed by Reserve with a non-approved method. The United States Environmental Protection Agency in the Federal Register published on Monday, December 3, 1979 entitled "Guidelines Establishing Test Procedures for the Analysis of Pollutants: Proposed Regulations" lists all test procedures approved by the USEPA for analysis of water and wastewater samples. The ultraviolet spectrophotometric procedure used by Reserve Mining is not included there. Although MPCA personnel agree that an approved method for analysis is preferable, they have allowed Reserve Mining to utilize this method. Analytical data for matrices normally

encountered in Reserve Mining's monitoring program and which are spiked with nitrate and analyzed according to the ultraviolet method will be of interest. This will indicate whether the waters analyzed by this method contribute any interferences, and thereby require that an approved alternative method be used for nitrate analysis. Reserve Mining has ceased using sulfuric acid during the digestion of samples for metals analyses. This was done in response to MPCA agreement with MRI's recommendation.

Total dissolved solids (TDS) analyses have been dropped from the list of analyses required of Reserve Mining. This was done as a result of the discrepancy that existed between Reserve's method of calculating from specific conductivity and the approved gravimetric method for determination of TDS. Due to the low level of total dissolved solids in the surface water samples collected by Reserve Mining, it was decided by MCPA personnel that this analysis is not of use as an indicative tool.

As with the total dissolved solids analysis, MPCA and Reserve Mining have agreed that BOD analyses are of little value for assessing water quality changes. MPCA has suggested that a formal application to drop these measurements be made by Reserve Mining. In the interim, the procedures which are used have undergone several changes in order to conform with recommended procedures for BOD determination.

Initiation and continuing operation of an active quality assurance program has been one of MRI's main recommendations to Reserve Mining and MPCA. The program as outlined in MRI's July 18, 1978 report has been approved by MPCA. The quality assurance program stated in Reserve Mining's "Milepost 7 Water Monitoring and Quality Assurance Programs" include proper chain of custody and field recordkeeping procedures, spiking of 10 percent of all samples collected from ground and surface waters, the analysis of a spiked reagent blank with every 20 samples, the analysis of replicate samples, equipment maintenance procedures, proper quality of reagent chemicals, proper analytical record keeping, and collection and analysis of approximately 10 percent replicate

samples for submission to Minnesota Department of Health. The performance of these quality assurance practices will insure the accuracy of the results produced in the laboratory as well as pinpoint analytical problem areas and trends.

In general, the Reserve Mining intra-laboratory quality assurance programs conform to federally-approved methods. The recommendations made by MRI have resulted either in a change of procedure by Reserve, an agreement between MCPA and Reserve on the methods of choice, or as in the case of quality assurance, the initiation of a recognized program. Reserve Mining has proven competence in the performance of sampling and analysis of the environmental samples required by MPCA for the Milepost 7 monitoring program.