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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-N

July 18, 1978

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STATE OF MINNESOTA

For

Minnesota Pollution Control Agency
1935 West County Road B2
Roseville, Minnesota 55113

Attention: Loren Voigt

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May 1-
July
31

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

(2C) Midwest Research Institute

(2B)
Q U A R T E R L Y R E P O R T /
MRI Project No. 4558-N

(3) July 18, 1978

(4) 6/p. : ill. stat.

(5) (Consultant's report)

For

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Minnesota Pollution Control Agency
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STATE OF MINNESOTA

PREFACE

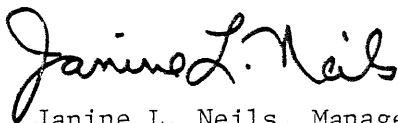
This report presents the activities of a project sponsored by the Minnesota Pollution Control Agency, "Assess Reserve Mining Company's Surface and Groundwater Monitoring and Quality Assurance Programs at Mile Post 7." The report covers the quarter beginning May 1, 1978 and ending July 31, 1978. The data 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 June 5, 1978. 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 Mr. Roscoe Colingsworth and Mrs. Jean Williams. The work of organizing, analyzing and reporting is performed at the North Star Division of Midwest Research Institute (MRI).

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 Dr. Lawrence Rust, Dr. Edwin Cook of the University of Minnesota, and Ms. Carole Green who acted as consultants on the project.

North Star Division
MIDWEST RESEARCH INSTITUTE



Janine L. Neils, Manager
Laboratory Services

Approved:



Arsen J. Darnay, Director
North Star Division

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North Star Division
MIDWEST RESEARCH INSTITUTE

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

May 1, 1978 through July 31, 1978

"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 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 June 5, 1978. Water sampling from both ground and surface stations was observed and several procedures were also witnessed within the laboratory.

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

All statistical analysis has been based on the "paired observation" concept. For analysis of the difference between Reserve and MDH data, the paired difference (D_i) was defined as:

$$D_i = (\text{Reserve Value} - \text{MDH Value})_i$$

where the subscript i indicates the pair number. For analysis of the difference between Reserve and certified values data, the paired difference (D_i) was defined as:

$$D_i = (\text{Reserve Value} - \text{Certified Value})_i$$

For a given water parameter (e.g., calcium), the individual paired differences are used to obtain the mean difference ($\bar{D}$) and standard deviation (S) of the difference from the relations:

$$\bar{D} = \frac{1}{N} \sum_{i=1}^N D_i$$

$$S^2 = \frac{1}{N-1} \sum_{i=1}^N (D_i - \bar{D})^2$$

After $\bar{D}$ and S are calculated, the t value is determined from:

$$t = \frac{\bar{D}}{\frac{S}{\sqrt{N}}}$$

which is compared with the critical t -values shown in Table 1. This comparison yields one of the following conclusions:

TABLE 1

N	Critical T-Value at Significance Level	
	5%	1%
2	12.706	63.657
3	4.303	9.925
4	3.182	5.841
5	2.776	4.604
6	2.571	4.032
7	2.447	3.707
8	2.365	3.499
9	2.306	3.355
10	2.262	3.250
11	2.228	3.169
12	2.201	3.106
13	2.179	3.055
14	2.160	3.012
15	2.145	2.977
16	2.131	2.947
17	2.120	2.921
18	2.110	2.898
19	2.101	2.878

1. If $t < -(\text{critical } t\text{-value})$, the Reserve data values are less than the MDH (or certified) values at the selected level of significance.
2. If $-(\text{critical } t\text{-value}) \leq t \leq (\text{critical } t\text{-value})$ the Reserve data values are equal to the MDH (or certified) values at the selected level of significance.
3. If $t > (\text{critical } t\text{-value})$, the Reserve data values are larger than the MDH (or certified) values at the selected level of significance.

The t-test summary table (Table 2) presents the number of data point pairs (N), average difference between Reserve and MDH data ($\bar{D}$), standard deviation of differences (S), associated t-value, and whether the Reserve values are greater than ($>$), equal to ($=$), or less than ($<$) the MDH values at both the 1- and 5-percent level of significance. T-test data for February and May are presented along with the combined results for the two months. The raw data used for comparison is tabulated in Tables 3 and 4.

Reserve's manganese and zinc data is smaller than the MDH data at both the 1- and 5-percent level of significance. Also, Reserve's pH data is larger than the MDH data at both of these significance levels.

In general, Reserve and MDH appear to obtain consistent results.

It should be noted that the number of data points for each parameter was insufficient to test the data for the assumption of normality. When 30 or more data points are available, we anticipate using a chi-square goodness of fit test for the assumption of normality.

If the assumption of normality is correct, then the t-test of paired differences is valid, even for sample sizes below 5. However, for small sample sizes, only very large differences will lead to the conclusion that the pair samples are different. If the differences in Reserve and MDH values

Table 2. t-Test Data from the Split Sample Program

Parameter	February					May					Combined					Units		
	N	D̄	S	T	RMC >, =, < MDH at Significant Level		N	D̄	S	T	RMC >, =, < MDH at Significant Level		N	D̄	S		T	
					1%	5%					1%	5%						
Calcium	9	1.578	1.260	3.7575	>	>	10	-2.680	3.105	-2.7290	=	<	19	-0.663	3.209	-0.9008	=	mg/l
Magnesium	8	1.025	0.797	3.6359	>	>	6	-0.180	2.386	-0.1848	=	=	14	0.509	1.707	1.1148	=	mg/l
Sodium	9	1.311	0.922	4.2645	>	>	10	0.394	3.057	0.4076	=	=	19	0.828	2.296	1.5729	=	mg/l
Potassium	3	-0.0067	0.124	-0.0930	=	=	10	-0.321	1.582	-0.6418	=	=	13	-0.362	1.350	-0.9676	=	mg/l
Sulfate	9	-1.089	2.335	-1.3988	=	=	10	-0.090	2.486	-0.1145	=	=	19	-0.563	2.402	-1.0222	=	mg/l
Chloride	7	0.071	0.472	0.4008	=	=	4	-7.075	12.027	-1.1765	=	=	11	-2.527	7.519	-1.1149	=	mg/l
Nitrate-N	3	-0.040	0.026	-2.6186	=	=	8	0.019	0.079	0.6728	=	=	11	0.003	0.072	0.1237	=	mg/l
Silica	9	0.633	0.778	2.4427	=	>	10	-1.430	1.581	-2.8612	=	<	19	-0.453	1.624	-1.2146	=	mg/l
Sol. O-PO ₄	8	0.0005	0.0026	0.5517	=	=	10	-0.0018	0.0055	-1.0324	=	=	18	-0.0008	0.0045	0.7345	=	mg/l
Iron	3	-0.006	0.022	-0.4804	=	=	5	0.052	0.091	1.2823	=	=	8	0.030	0.076	1.1300	=	mg/l
Manganese	7	-0.857	1.215	-1.8664	=	=	8	-2.500	1.690	-4.1833	<	<	15	-1.733	1.668	-4.0256	<	µg/l
Copper	7	-0.414	0.815	-1.3444	=	=	10	0.010	0.619	0.0511	=	=	17	-0.165	0.731	-0.9296	=	µg/l
Zinc	9	-0.942	0.985	-2.8700	=	<	10	-0.783	1.378	-1.7967	=	=	19	-0.858	1.178	-3.1766	<	µg/l
Cadmium	1	-0.300	--	--	--	--	5	0.099	0.209	1.0607	=	=	6	0.033	0.248	0.3213	=	µg/l
Chromium	2	-0.350	0.071	-7.0000	=	=	0	--	--	--	--	--	2	-0.350	0.071	-7.0000	=	µg/l
Barium	3	-5.333	12.097	-0.7636	=	=	2	-0.500	9.192	-0.0769	=	=	5	-3.400	10.065	-0.7554	=	µg/l
Fluoride	4	0.0125	0.0275	0.9078	=	=	3	0.050	0.036	2.4019	=	=	7	0.029	0.035	2.1715	=	mg/l
TDS	9	-0.133	27.919	-0.0143	=	=	10	17.780	31.670	1.7753	=	=	19	9.295	30.535	1.3268	=	mg/l
COD	3	0.500	3.727	0.2324	=	=	8	-1.625	4.518	-1.0173	=	=	11	-1.046	4.249	-0.8162	=	mg/l
Color	3	-15.000	8.660	-3.0000	=	=	4	-3.750	11.087	-0.6765	=	=	7	-8.571	11.073	-2.0480	=	units
pH	9	0.309	0.318	2.9124	=	>	10	0.483	0.566	2.7009	=	>	19	0.401	0.461	3.7837	>	units
Spec. Cond.	9	11.444	9.382	3.6594	>	>	10	4.800	34.538	0.4395	=	=	19	7.947	25.439	1.3617	=	µmhos/cm
Tot. Phosphorus	3	-0.0027	0.0012	-4.0000	=	=	4	-0.0495	0.0427	-2.3195	=	=	7	-0.0294	0.0392	-1.9855	=	mg/l
TSS	3	-0.667	0.787	-1.4669	=	=	4	0.375	2.142	0.3501	=	=	7	-0.071	1.669	-0.1132	=	mg/l
Turbidity	3	-1.733	1.069	-2.8077	=	=	4	1.225	0.991	2.4717	=	=	7	-0.043	1.837	-0.0617	=	units
Organic-N	0	--	--	--	--	--	4	-0.048	0.087	-1.1094	=	=	4	-0.048	0.087	-1.1094	=	mg/l

Table 3. Comparative Data Between Researve Mining (RMC) and the Minnesota Department of Health (MDH) from February 1978 (Surface Waters)

	107		109		110	
	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	13.6	11.6	19.9	18.8	10.1	10.0
Magnesium	4.75	4.1	6.65	5.8	3.82	3.6
Sodium	3.09	2.8	4.51	4.0	3.49	2.9
Potassium	0.32	<0.5	0.4	<0.5	0.21	<0.5
Sulfate	12.6	11.0	12.8	12.0	12.6	12.0
Chloride	1.6	1.7	2.8	3.4	2.4	2.7
Nitrate-N	0.25	0.26	0.24	0.31	0.34	0.39
Silica	14.5	13.0	14.7	13.0	15.4	15.0
Ammonia-N	0.057	<0.2	0.02	<0.2	0.06	<0.2
Sol. O-PO ₄	0.004	0.009	0.006	<0.008	0.003	0.004
Total PO ₄	0.011	0.013	0.009	0.011	0.005	0.009
Iron µg/l	460.0	490.0	400.0	400.0	242.0	230.0
Manganese µg/l	5.0	7.0	8.0	7.0	<1.0	<2.0
Copper µg/l	1.5	1.8	1.3	1.5	1.0	1.4
Zinc µg/l	1.0	1.5	1.0	1.5	1.1	1.9
Nickel µg/l	<2.0	<1.0	<2.0	1.1	<2.0	<1.0
Cadmium µg/l	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Lead µg/l	<2.0	0.2	<2.0	0.3	<2.0	0.3
Cobalt µg/l	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Chromium µg/l	<1.0	1.7	<1.0	<1.0	<1.0	2.5
Mercury µg/l	<0.2	<0.1	<0.2	<0.1	<0.2	<0.1
Silver µg/l	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Arsenic µg/l	<5.0	<1.0	<5.0	<1.0	<5.0	<1.0
Selenium µg/l	<5.0	<1.0	<5.0	<1.0	<5.0	<1.0
Barium µg/l	15.0	<13.0	22.0	<13.0	14.0	<13.0
Fluoride	<0.5	<0.2	<0.5	<0.2	<0.5	<0.2
TSS	1.9	2.0	0.9	2.4	0.4	0.8
TDS	69.6	100.0	98.8	130.0	57.9	88.0
Spec. Cond.	107.0	100.0	152.0	140.0	89.0	89.0
Turbidity	2.4	4.8	1.7	4.0	1.0	1.5
pH	7.62	7.3	7.74	7.3	7.58	7.3
Color	40.0	50.0	30.0	40.0	25.0	50.0
COD	23.2	25.0	15.8	11.0	19.5	21.0
Cyanide	<0.010	<0.001	<0.010	<0.001	<0.010	<0.001

Table 3. Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from February 1978 (Ground Waters) continued

	M2		M2A		M5		M5A		M5B		M10	
	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	24.5	21.2	37.5	34.0	11.6	11.6	19.7	18.4	23.7	21.6	56.8	56.0
Magnesium	5.65	5.3	12.8	12.0	2.87	<2.4	5.14	4.1	6.89	5.3	21.7	19.0
Sodium	23.35	22.0	5.94	5.4	26.8	24.0	18.6	16.0	15.6	14.0	8.12	6.6
Potassium	1.35	1.5	0.57	<0.5	0.25	<0.5	0.42	<0.5	0.71	0.65	1.97	1.9
Sulfate	17.4	21.0	11.0	13.0	29.0	34.0	18.6	18.0	15.1	15.0	15.1	18.0
Chloride	10.8	10.0	1.2	1.1	15.5	15.0	1.8	1.7	<1.0	0.75	<1.0	0.8
Nitrate-N	<0.1	0.02	<0.1	0.08	<0.1	0.01	<0.1	0.02	<0.1	0.08	<0.1	0.01
Ammonia-N	0.043	<0.2	<0.01	<0.2	<0.01	<0.2	0.012	<0.2	<0.01	<0.2	<0.01	<0.2
Silica	10.1	9.5	23.7	23.0	20.0	21.0	12.2	11.0	9.1	9.0	13.7	13.0
Sol. O-PO ₄	0.0009	0.006	0.007	0.004	0.003	0.002	0.005	0.004	0.005	0.004	0.002	0.001
Iron ug/l	9.0	<20.0	6.0	<20.0	11.0	<20.0	7.0	<20.0	14.0	<20.0	6.0	<20.0
Manganese ug/l	4.0	4.0	2.0	4.0	4.0	4.0	5.0	6.0	32.0	<2.0	27.0	29.0
Copper ug/l	1.7	1.5	1.9	4.1	<0.5	0.6	<0.5	0.6	1.2	1.3	3.7	3.6
Zinc ug/l	0.7	0.5	6.8	9.4	22.2	24.0	0.5	0.48	2.3	2.7	6.4	8.5
Nickel ug/l	<2.0	1.1	<2.0	2.2	<2.0	1.0	<2.0	<1.0	<2.0	1.2	<2.0	6.6
Cadmium ug/l	<0.2	<0.2	0.3	0.6	<0.2	0.02	<0.2	0.014	<0.2	0.18	<0.2	0.27
Lead ug/l	<2.0	0.2	<2.0	0.2	<2.0	0.3	<2.0	0.1	<2.0	0.2	<2.0	0.3
Cobalt ug/l	<1.0	<0.4	<1.0	<0.4	<1.0	<0.4	<1.0	<0.4	<1.0	<0.4	<1.0	<0.4
Chromium ug/l	1.0	1.4	2.0	2.3	<1.0	<0.2	<1.0	<0.2	<1.0	1.0	<1.0	0.5
Barium ug/l	20.0	<13.0	18.0	19.0	10.0	<13.0	17.0	<13.0	23.0	19.0	121.0	140.0
Fluoride	0.6	0.56	<0.5	<0.2	0.6	0.6	0.5	0.52	0.5	0.47	<0.5	<0.2
TDS	172.3	130.0	182.0	150.0	117.7	130.0	130.0	130.0	128.7	120.0	269.8	250.0
COD	4.8	<5.0	3.1	<5.0	2.0	<5.0	1.6	<5.0	2.2	<5.0	2.2	<5.0
Color	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
pH	8.98	8.4	7.26	7.5	8.75	7.9	8.46	8.3	7.99	7.6	8.00	8.0
Spec. Cond.	265.0	250.0	280.0	260.0	181.0	180.0	200.0	190.0	198.0	190.0	415.0	385.0

Table 4. Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from May 1978 (Surface Waters)

	Station 101		Station 102		Station 104		Station 105	
	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	3.9	4.8	4.5	6.4	7.1	9.2	4.9	6.4
Magnesium	1.35	<2	1.59	<2	2.69	<2	1.7	<2
Sodium	.6	.75	.69	.94	1.42	1.4	.92	1.0
Potassium	.47	1.2	.47	1.3	.55	1.3	.34	1.2
Sulfate	6	7	7	8	8.3	7.6	7.5	7.6
Chloride	<1	<.5	<1	.68	<1	.73	<1	<.5
Nitrate-N	.40	.36	.43	.35	.14	.11	.19	.17
Silica	7.1	13	7.1	9.1	5.1	6.5	6.4	8.7
Organic-N	.735	.85	.775	.69	.637	.69	.619	.72
Sol. O-PO ₄	.002	.008	.001	.010	.002	.010	.001	.009
Total PO ₄	.043	.043	.034	.123	.023	.041	.023	.051
Iron µg/l	291	270	593	390	593	600	605	540
Manganese µg/l	23	25	20	25	7	12	13	16
Copper µg/l	1.0	1.2	1.6	1.5	2.3	2.0	1.9	2.1
Zinc µg/l	1.7	4.4	2.7	4.0	1.0	2.5	1.1	2.4
Nickel µg/l	<2	<2	<2	<2	<2	<2	<2	<2
Cadmium µg/l	<.2	.025	<.2	.026	<.2	.020	<.2	.014
Lead µg/l	<2	.2	<2	.27	<2	.20	<2	.19
Cobalt µg/l	<1	<.5	<1	<.5	<1	.83	<1	<.5
Chromium µg/l	<1	<.5	<1	<.5	<1	<.5	<1	.6
Silver	<1	<.02	<1	<.02	<1	<.02	<1	<.02
Arsenic µg/l	<5	<.5	<5	<.5	<5	<.5	<5	<.5
Selenium µg/l	<5	<1	<5	<1	<5	<1	<5	<1
Barium µg/l	12	<15	10	<15	10	<15	<10	<15
Fluoride	<.5	.11	<.5	<.1	<.5	<.1	<.5	<.1
TSS	3.9	6.4	9.8	7.6	5.4	3.6	7.2	7.2
COD	37.8	37	37.1	37	30.1	25	32.5	41
Color	90	90	90	90	55	50	60	80
pH	6.63	6.6	6.65	6.7	7.07	6.7	7.04	6.8
TDS	22.8	34	26	34	40.9	46	28.6	40
Turbidity	1.8	.8	2.5	2.4	5.5	3.0	2.8	1.5
Ammonia	.106	<.2	.105	<.2	.060	<.2	.072	<.2
Spec. Cond.	35	35	40	45	63	65	44	45

Table 4. Comparative Data Between Reserve Mining (RMC) and the Minnesota Department of Health (MDH) from May 1978 (Ground Waters) continued

	M-1		M-1A		M-7		M-7A		M-7B		M-9A	
	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH	RMC	MDH
Calcium	24.4	26.4	31.8	34	18.3	18.8	15.1	21.6	14.4	24.8	29	28.8
Magnesium	3.37	3.16	6.94	6.32	7.92	10.69	11.3	7.53	4.57	7.05	4.43	4.86
Sodium	55.6	56	63.4	63	14.5	8.7	8.8	15	14.3	11	6.40	4.9
Potassium	1.56	2.2	1.83	2.2	.65	4.2	4.16	1.4	1.71	1.9	2.77	2.3
Sulfate	69.2	68	80.8	84	5.6	9.5	10	5.0	9	8.6	9.6	8.6
Chloride	85	88	85	110	<1	<.5	<1	1.3	1.0	1.4	1.2	1.1
Nitrate-N	.16	.17	.29	.22	<.1	.03	<.1	.02	1.44	1.6	.24	.16
Silica	6.6	7.9	6.6	7.9	10.9	9.9	9.0	10.7	13.9	13.7	12.4	13.0
Organic-N												
Sol. O-PO ₄	.001	.002	.007	.002	.004	.001	.002	.002	.003	.002	.007	.002
Total PO ₄												
Iron ug/l	6	<20	6	<20	8	<20	7	<20	8	<20	8	30
Manganese ug/l	3	4	7	8	6	7	3	5	<1	<3	<1	<3
Copper ug/l	8.3	7	5.5	5.5	1.2	1.9	1.3	1.6	3.8	3.2	2.6	3.4
Zinc ug/l	2.9	5	6.6	5.4	4.4	4.5	1.6	1.8	1.2	.37	1.1	.76
Nickel ug/l	2	<2	<2	<10	<2	<2	<2	<2	<2	<2	<2	<2
Cadmium ug/l	.7	.81	2.3	2.4	.4	.29	.4	.18	.4	.025	<.2	.041
Lead ug/l	<2	.29	<2	.20	<2	.45	<2	.27	<2	.13	<2	.15
Cobalt ug/l	<1	1.3	<1	1.6	<1	<.5	<1	.66	<1	.61	<1	.79
Chromium ug/l	<1	<.5	<1	<.5	<1	<.5	<1	<.5	<1	1.0	<1	1.1
Silver												
Arsenic ug/l												
Selenium ug/l												
Barium ug/l	12	19	33	27	<10	<15	12	<15	<10	<15	<10	<15
Fluoride	.8	.72	.9	.89	<.5	.38	<.5	.42	.5	.44	<.5	.11
TSS												
COD	8.8	<5	5.7	10.	2	8	2.8	<5	5.6	8	10.2	8
Color	<5	<5	<5	5	<5	5	<5	<5	<5	<5	<5	5
pH	9.41	7.9	9.3	7.9	8.25	8.4	8.83	8.4	9.04	8.6	9.41	8.8
TDS	308.8	240	364	290	133.3	120	133.3	100	126.7	120	127.4	110
Turbidity												
Ammonia	.106	<.2	.040	<.2	.026	<.2	.012	<.2	.042	<.2	.11	<.2
Spec. Cond.	475	480	560	460	205	220	205	210	195	220	196	190

remained at the same level as more data became available, then the t-test would eventually be able to discern a difference.

Comparison of Reserve Values with Certified Values

Table 5 lists the results of the Reserve Mining laboratory on performance evaluation samples. Due to the lack of similar data from the Minnesota Department of Health, variation data for only the Reserve laboratory can be calculated. This data is found in Table 6.

Table 5. Compilation of Reserve Laboratory's Performance Evaluation Samples

Parameter	10/6/77	12/5/77	3/3/78	ERA Value	ERA Acceptable Range	RMC 5/78	ERA Value	ERA Acceptable Range	RNC	EPA #1	RMC	EPA #2	RMC	EPA #3	RMC	EPA #4
Calcium	39	41.2	41.7	41	37-45	25.1	26	22-30	14.2	14.5						
Sodium	57.9	59	60	63	58-68	69.61	70	65-75	5.17	5.0	40.34	39.7				
Potassium	23.4	21	23.4	24	20-28	40.42	41	36-46	2.64	2.7						
Alkalinity	81.29	82	82.27	79	73-85	59.5	57	52-62	10.72	10.4						
Sulfate	56	53	56.5	55	50-60	--	--	--	12	12	101.6	102.4				
Nitrate	6.7	6.7	6.71	6.8	6.5-7.1	11.3	11.5	11-12	.19	.11	.41	.38				
Iron	.230	.275	.245	.250	.2-.3	.605	.63	.57-.69	.026	.033	.453	.417	.709	.678		
Manganese	.088	.092	.075	.100	.08-.12	.275	.250	.21-.29	.018	.026	.02	.045	.384	.397		
Cadmium	.0254	.024	.022	.0250	.015-.035	.065	.075	.06-.09	.005	.0052	.0231	.023	.059	.073		
Lead	.066	.032	.05	.063	.05-.076	.024	.025	.015-.035	.02	.022	.250	.298	.307	.352		
Chromium	.033	.042	.04	.042	.03-.054	.139	.125	.1-.15	.016	.012	.172	.154	.212	.209		
Mercury	.0039	.0037	.0037	.0033	.0023-.0043	.0016	.0013	.0008-.0018	.0017	.0008	.0023	.0045	.006	.0094		
Silver	.05	.062	.066	.067	.05-.084	<.0005	0	0-.2								
Arsenic	.076	.068	.092	.083	.070-.096	.032	.038	.028-.048	.025	.026	.109	.109	.139	.154		
Selenium	.028	.020	.024	.031	.021-.041	.032	.031	.021-.041	.005	.0052	.024	.026	.042	.044		
Barium	.847	1.08	.98	1.1	.9-1.3	.95	.69	.59-.79	.2	.236	1.12	1.1				
Fluoride	2.1	2.2	2.05	2.2	2-2.4	4.05	4.2	4.0-4.4	7.88	7.9	8.52	8.4				
pH	9.18	9.2	9.19	9.2	9.1-9.3	9.16	9.2	9.1-9.3								
Turbidity	3.6	3.9	3.6	4.0	3.5-4.5	2.0	2.3	1.8-2.8	155	157						
Spec. Cond.									2.9	3.0	14.2	14.4				
Magnesium									28.1	27.8						
Chloride									.0176	.017	.074	.0875	.407	.396		
Cobalt									.015	.016	.075	.072	.098	.102		
Copper									.028	.026	.047	.045	.117	.152		
Nickel									.012	.011	.0277	.03	.168	.174		
Zinc									.20	.23	1.605	1.59				
Ammonia									.051	.052	.186	.19				
O-Phosphorous													.42	.41	3.54	3.51
Tot. Kjeldahl													.205	.20	.70	.66
Tot. Phosphorous																
COD									15.2	15.4	210	231				
BOD									.48	2.9	40.42	146				

Table 6. t-Test on Performance Evaluation Results

Parameter	N	$\bar{D}$	S		Reserve $\begin{matrix} > \\ = \\ < \end{matrix}$ Cert. Value at Sig. Level		Units
					1%	5%	
Calcium	5	-0.460	1.046	-0.9838	=	=	mg/l
Sodium	6	-1.947	2.403	-1.9847	=	=	mg/l
Potassium	5	-0.968	1.159	-1.8673	=	=	mg/l
Alkalinity	6	1.978	1.259	3.8483	=	>	mg/l
Sulfate	5	-0.060	1.403	-0.0956	=	=	mg/l
Nitrate	6	-0.075	0.091	-2.0282	=	=	mg/l
Iron	7	0.0070	0.0246	0.7531	=	=	mg/l
Manganese	7	-0.0094	0.0168	-1.3704	=	=	mg/l
Cadmium	7	-0.0039	0.0057	-1.8007	=	=	mg/l
Lead	7	-0.0193	0.0214	-2.3854	=	=	mg/l
Chromium	7	0.0029	0.0098	0.7744	=	=	mg/l
Mercury	7	0.430	1.670	-0.6820	=	=	ug/l
Silver	3	-7.670	8.330	-1.5955	=	=	ug/l
Arsenic	7	-5.000	8.580	-1.5413	=	=	ug/l
Selenium	7	-2.030	2.560	-2.1003	=	=	ug/l
Barium	4	-0.033	0.218	-0.3061	=	=	mg/l
Fluoride	6	-0.057	0.086	-1.5322	=	=	mg/l
pH	6	0.005	0.058	0.2116	=	=	Units
Turbidity	4	-0.300	0.141	-4.2426	=	<	NTU

BIOLOGICAL MONITORING

The location of existing sampling stations and the existing procedures employed by Reserve's staff to monitor stream biota are generally appropriate. Several aspects of the monitoring program are well done. For example, the staff demonstrated considerable care in the location of sampling sites at each station, in the collection of the samples, and in the lab analyses. The sampling equipment and the records kept of field notes and lab analyses are also adequate.

However, there are several essential aspects of the monitoring program which need improvement. First, a control station should be added on the Beaver River; the addition of several more stations should be considered. Second, macroinvertebrate samples should be sent to another lab for confirmation of the identifications. Third, several essential steps in the pigment analysis should be added. Fourth, data on all replicates should be reported and a mean level calculated for each parameter at each station.

These aspects and several other points are discussed below.

Field Sampling

The selection of the actual sampling sites at each station and of the exact location of the replicate samples has been generally well done. Reserve's sampling personnel noted that they were attempting to have each sampling site as uniform as possible in terms of current velocity and substrate. The selection of identical sampling substrates will considerably facilitate comparison of samples between stations (e.g., comparisons between control stations, upstream, and downstream stations in potentially affected areas), particularly for those stations which are currently being sampled by a different means (the Ekman dredge is being used at Stations 103 and 104). The rubble-gravel-fine sand substrate might be preferred because macroinvertebrate diversity appears to be higher and this substrate is perhaps in the mid-range of the types of substrates common to streams in the area. However,

if substrates or collecting methods change, comparison with historical data is questionable unless a suitable "correction" factor can be determined.

The field sampling techniques, including how the sampler is used, how thoroughly the sampling is done, sieving, sample preservation, and note-taking are all acceptable. The sample identification sheet, chain-of-custody sheet, and field check list are very complete with regard to the information required. It may be advisable to include field measurements of dissolved oxygen at each station in addition to the data already being collected, because of the time differences of up to several weeks that sometimes occur between collection of the surface water quality and the macroinvertebrate samples.

The field sampling technique using the Surber sampler is satisfactory for stream sampling as is the Ponar dredge for collecting samples in Bear Lake. The use of the modified Hess sampler in place of the Surber is described in the May 11, 1978 letter from Mr. Tim Scherkenback of MPCA to Mr. Matthew Banovetz of Reserve. The point that loss of macroinvertebrates by organisms escaping around the net during sampling is well taken. However, several other points should also be considered. Though described in 1961, the Hess has not become widely used; the Surber sampler remains a standard sampling technique as described by EPA and Standard Methods. The drift of macroinvertebrates is greatest at night, and thus is not expected to be a large problem. Reserve's personnel are very careful in their sampling technique; thus sample loss from the substrate being ineffectively sampled or from around the edges of the Surber may be minimal. Finally, the modified Hess sampler appears to be awkward to use because it requires, in effect, samples to be collected at the bottom of a cylinder.

Nevertheless, it would be advisable to obtain some data on the magnitude of these losses. Reserve might use both types of samplers at several stations and compare the results. (It should be noted that at least six samples each would be needed for a statistical comparison.) A possible alternative would be to use a larger net downstream of the Surber to catch any organisms lost during sampling.

Relocating some of the stations in order to obtain substrates more similar to that at other stations may be desirable for interpreting the data. In examining the data from the October 1977 sampling, it appears that many of the differences in macroinvertebrate taxa and numbers of organisms found per square meter could be attributed to differences in current velocity and/or substrate type. For example, Table 7 shows much larger numbers of Diptera, Ephemeroptera, and Oligochaeta at Stations 102 and 105 than at Station 101; the major difference in substrate is the fine sand component at Stations 102 and 105, and organics at Station 101. That these differences are due to substrate is emphasized by the fact that the current velocity at Stations 101 and 105 are quite similar. The differences between Stations 102 and 105, which have similar substrates, are much less pronounced and are probably attributable to current. For example, Heptageniidae are clinging organisms in habit, and they are much more plentiful in the slower current of Station 105.

An alternative to finding uniform stations in terms of substrate and current velocity would be to use artificial substrates, such as the Hester-Dendy sampler. This sampler is approved by both EPA and Standard Methods. This alternative would help eliminate the variable of substrate type, and sampling sites could be selected more rapidly by using current velocity only. Suspended from floats, the samplers would remain at a constant depth as the stream rises and falls. Light effects thus would remain constant. Reserve's sampling personnel have indicated that they have had problems finding areas at each station with rubble-gravel substrates; artificial substrate samplers would eliminate the need for identical natural substrates. Also, artificial substrates are simpler to set and collect. Because all attached organisms can be retrieved, they are more efficient sampling tools.^(a)

For statistical purposes, at least five, and preferably more, if possible, replicates per station should be collected. This might be more easily accomplished if Hester-Dendy samplers were used. Sampling and sorting time would be considerably shortened with these samplers. The qualitative samples collected with the Surber and other techniques, in any case, should be retained; it is a very good procedure and is thoroughly done.

(a) Further communication with Reserve Mining Company indicates that this has been previously tried and proves to be an ineffective technique.

Table 7. Comparison of Macroinvertebrate Data for Stations 101, 102, and 105 (From Reserve's Monitoring Data, October 1977)

	Monitoring Stations		
	101	102	105
Current velocity (ft/sec)	1.90	2.24	2.07
Substrate Type	rubble-gravel- organics	rubble-gravel- fine sand	rubble-gravel- fine sand
<u>Organism</u>	<u>(Number/Square Meter)</u>		
Diptera			
Chironomidae	330	1650	1903
Empididae	11	0	11
Heleidae	0	0	0
Simuliidae	33	88	55
Tipulidae	0	11	0
Trichoptera			
Hydropsychidae	0	22	0
Lepidostomatidae	33	0	0
Rhyacophilidae	0	0	0
Hydroptilidae	0	0	0
Plecoptera			
Nemouridae	0	0	22
Perlidae	11	0	22
Pteronarcidae	0	0	11
Unidentified	198	0	66
Ephemeroptera			
Baetidae	22	165	286
Heptageniidae	0	33	495
Coleoptera			
Elmidae	11	77	220
Annelida			
Unidentified Oligochaeta	44	528	0
Erpobdellidae	22	0	0
Megaloptera			
Sialidae	0	0	0
Gastropoda			
Ancylidae	0	0	33
Planorbidae	0	0	0
Valvatidae	0	0	0
Pelecypoda			
Sphaeriidae	0	0	11
Hydracarina	<u>0</u>	<u>0</u>	<u>11</u>
TOTAL	715	2574	3146

Reserve's biological monitoring could be improved with regard to control stations. A control station is necessary on the Beaver River for comparison with downstream stations in potentially disturbed areas (See Figure 1). This station should be located upstream from the diversion canal and in a habitat as similar as possible to the downstream stations.

Other control stations might also be useful, including a station each on Big and Little Thirtynine Creeks, Kit Creek, an unnamed tributary (flowing from the east) joining the Beaver between Kit Creek and the West Branch of the Beaver, and a station on the West Branch of the Beaver River. Also useful for comparisons might be another station on the East Branch of the Beaver.

Periphyton pigment samples are required to be frozen if they cannot be analyzed soon after they are collected, according to standard methodology. There is some ambiguity about the length of time allowed, however. Reserve ices their samples in the field. In about two to three hours the samples are in the labs and placed in a freezer. Although this delay is short, it would be useful to compare the effects of this delay with freezing the samples in the field. Access to dry ice, however, may be a significant impediment to field freezing.

Analysis

The initial lab handling of the samples is being done in a satisfactory manner--this includes logging them in the master log book, sieving, and transferring to the ethanol-water-glycerine preservative of macroinvertebrate samples. The sorting of the macroinvertebrates from the debris in the sample is also very thorough, as is the supervision and checking of the lab techniques. Procedures for determining periphyton pigments and dry and wet weight-biomass are also generally well carried out.

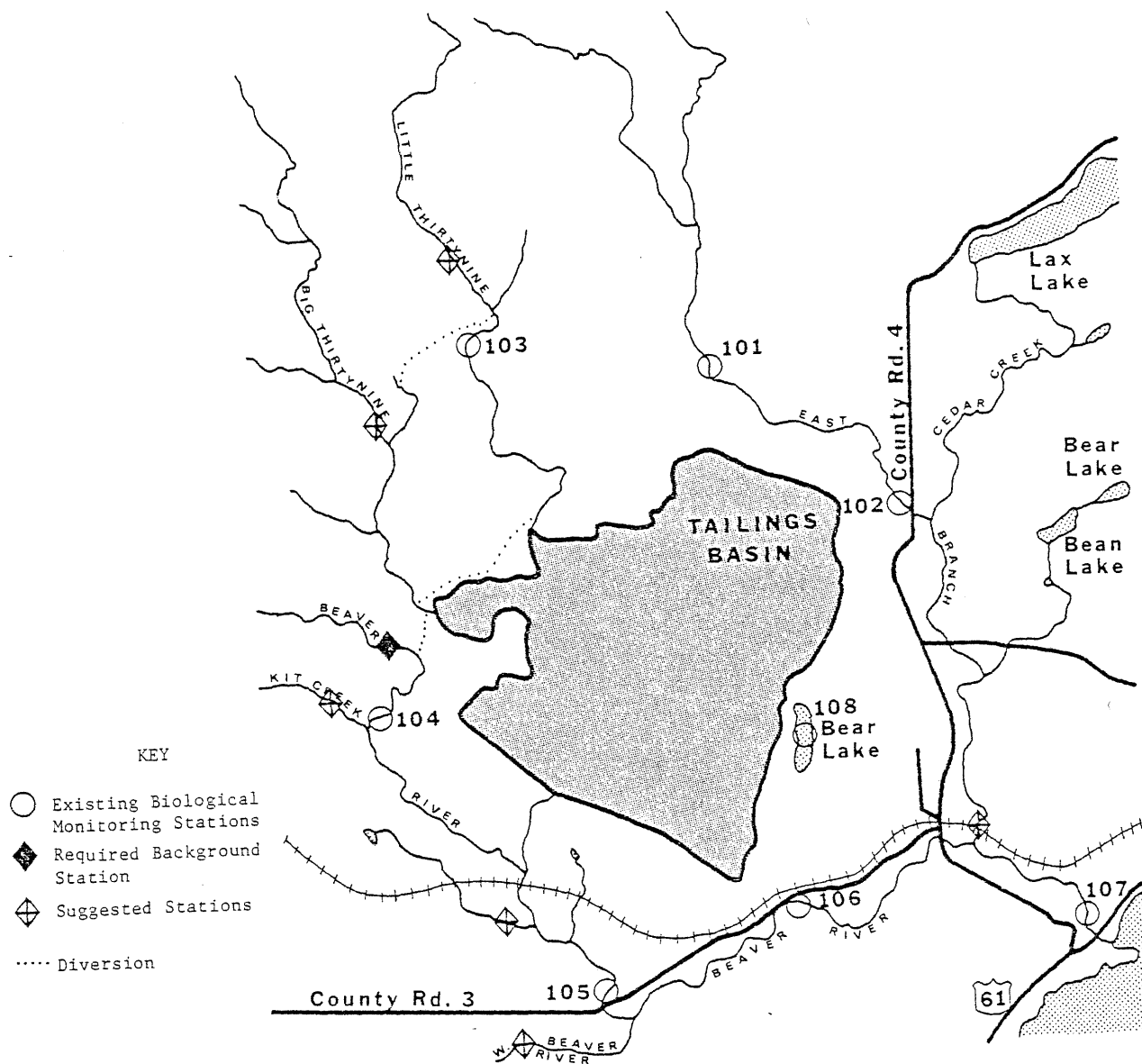


Figure 1

The taxonomic work is being done by people who have some background and training in macroinvertebrate taxonomy. Reserve's taxonomists have an excellent reference collection, which they use to assist them in their identifications. There was substantial disagreement in only one major taxonomic group between Reserve's identification of the macroinvertebrates in two of the Spring 1978 samples sent to MRI and the results obtained by MRI's taxonomist. The samples sent to MRI were the only ones for which Reserve personnel have completed identifications on the 1978 data; they were both Surber net samples from Station 105. Since Reserve's monitoring also includes Ekman dredge samples and qualitative samples, further verification on MRI's part of these types of samples is warranted.

In the order Diptera, Reserve's taxonomist noted only the presence of the family Chironomidae; however, we also found the family Simuliidae, which comprised about one-third to one-fourth of all the Diptera in each sample. Because these two families are substantially different in appearance, it is not expected that this error will recur in future taxonomic work. The only other identification problem was observed with the beetle Stenelmis. Dr. Edwin Cook of the University of Minnesota (who verified MRI's identifications) identified all Coleoptera found as Optioservus. This is an understandable error; Coleoptera are difficult to identify.^(a) Several pupae and one Lepidoptera larva that had not been noted on Reserve's data sheets were also found. These types of macroinvertebrates should be noted on the lab sheets, even when identification is not possible. Tables 8 and 9 show the macroinvertebrates as they were identified by Reserve and MRI taxonomists. As can be seen from these tables, the exact numbers of macroinvertebrates found, particularly the Diptera, are different between MRI's and Reserve's taxonomic work. These differences are not serious, however, because counts of individuals would be expected to vary when a large number of very small Diptera and damaged specimens are present, as they were in these samples.

(a) Subsequently found to be transcription errors by Reserve Mining Company.

Table 8. Comparison of Identifications of Macroinvertebrates Collected by Reserve on May 18, 1978, at Station 105--Sample A1

<u>Organism</u>	<u>RMC</u> <u>Number</u>	<u>Genera Observed</u>	<u>Organism</u>	<u>MRI</u> <u>Number</u>	<u>Genera Observed</u>
Diptera			Diptera		
Chironomidae	122		Chironomidae	96	
			Chironomidae pupae	6	
			Simuliidae	30	
Tricoptera			Tricoptera		
Leptoceridae	1	<u>Oecetis</u>	Leptoceridae	1	<u>Oecetis</u>
Ephemeroptera			Ephemeroptera		
Baetidae	14	Caenis	Caenidae	1	Caenis
		*Pseudocloeon?	Ephemerellidae	14	*Ephemerella?
		*Paraleptophlebia			
Plecoptera			Plecoptera		
Pteronarcidae	1	<u>Pteronarcys</u>	Pteronarcidae	1	<u>Pteronarcys</u>
Coleoptera			Coleoptera		
Elmidae	5	<u>Optioservus</u>	Elmidae	5	<u>Optioservus</u>
		<u>Stenelmis</u>			
Oligochaeta	3		Lepidoptera		
			Pyrilidae	1	
Copepoda	3		Oligochaeta	5**	
Hydracarina	1		Copepoda	3	
			Hydracarina	1	
Total Individuals	148		Total Individuals	164	

*Early instars.

*Early instars.
**Three whole, two pieces.

Table 9. Comparison of Identifications of Macroinvertebrates Collected by Reserve on May 18, 1978, at Station 105--Sample A2

<u>Organism</u>	<u>RMC</u> <u>Number</u>	<u>Genera Observed</u>	<u>Organism</u>	<u>MRI</u> <u>Number</u>	<u>Genera Observed</u>
Diptera			Diptera		
Chironomidae	394		Chironomidae	293	
			Chironomidae pupa	1	
			Simuliidae	102	
Trichoptera			Trichoptera		
Hydroptilidae	2	?	Hydroptilidae	2	<u>Stactobiella?</u>
Ephemeroptera			Ephemeroptera		
Baetidae	23	<u>Paraleptophlebia</u>	Leptophlebiidae	1	<u>Paraleptophlebia</u>
		** <u>Ephemerella?</u>	Ephemerellidae	20	* <u>Ephemerella</u>
	4	** <u>Stenonema</u>	Heptageniidae	5	<u>Stenonema</u>
Plecoptera			Plecoptera		
Perlodidae	1	* <u>Isogenus</u>	Perlodidae	1	*** <u>Alloperla</u> or <u>Chloroperla (?)</u>
Coleoptera			Coleoptera		
Elmidae	4	<u>Stenelmis</u>	Elmidae	4	<u>Optioservus</u>
Oligochaeta	9		Oligochaeta	8**	
Ostracoda	2		Ostracoda	2	
Hydracarina	9		Hydracarina	8	
			Hemiptera(?) embryo		
			Corixidae?	1	
Total Individuals	448		Total Individuals	448	

*In reference collection.
**Damaged specimen.

*Nineteen were very early instars.
**Pieces.
***Immature Form

Reserve presently has not established a verification program whereby samples are regularly sent to an outside taxonomist. This should be implemented along with the protocol for selecting the samples to be verified. Dr. Charles Wirtz, a consultant from Philadelphia who has previously worked with Reserve's taxonomists, would be a satisfactory choice to do the verification. Another person to consider is Dr. Edwin Cook of the University of Minnesota in St. Paul; he is also familiar with the macroinvertebrates of northern Minnesota.

Three essential steps in the standard procedure for pigment analysis have been omitted from Reserve's procedures: a) mechanical disruption of the sample using a tissue grinder; b) addition of a small amount of magnesium carbonate; and c) steeping ground sample for 24 hours in a dark refrigerator at 4°C.

Algal cells, especially the blue-green filament types of periphyton such as Oscillatoria, require disruption for efficient removal of the algal pigments. A tissue grinder consisting of a teflon pestle and glass mortar is recommended for mechanically disrupting algal cells. Steeping the extract in the refrigerator further assures complete extraction. A saturated aqueous solution of magnesium carbonate in the amount of about 10 percent of the volume of the extract in the tissue grinder should be added to each sample in the tissue grinder to control pH.

Statistics and Reporting

The statistical analyses Reserve's staff presently plan to perform on the biological data, determination of the standard deviation and coefficient of variation, probably will be of little value to interpreting their data. The number of replicates (three) is too small to obtain a reliable estimate of a taxon or chlorophyll a concentration, for example. A doubling of the number of replicates would provide a useful estimate of the means for a t-test of the significance of the difference between two stations; more than six replicates would improve this estimate. This statistical approach would be best used to assess differences in each sampling date, although it would also

seem to be quite sensitive to differences in the data due to substrate types. Variability in the data due to seasonal effects would probably limit the usefulness of this approach for comparisons of current data with historical data.

Another approach, using Reserve's historical data from most of the sampling stations, employs calculations of the percent difference between pairs of stations. For example, comparison could be made of the percent differences of the means of the abundances of a taxon or chlorophyll a concentrations in replicate samples collected from 1974 through 1977 between Stations 107 and 109 (See Table 10). The mean and standard deviation of the percent differences could then be calculated. This approach may be less sensitive to substrate differences than the other approach described above. It has the advantage of canceling out variations in the data due to common factors, such as weather.

Similarly, the percent differences of the other parameters could be calculated for this station pair, and for other station pairs such as between 107 and 110, and 109 and 110. These statistics would provide a reasonable estimate of the pre-project relationship between the stations mentioned above--the mouth of the Beaver River (Station 107) and the mouth of the Split Rock (Station 109) and Baptism (Station 110) Rivers.

If the percent difference of the means of replicates of most of the parameters between Station 107 and 109 and/or 110 collected during the project (for example Spring 1978) were to fall outside of two standard deviations from the mean, while those between 109 and 110 were to remain within, it could be concluded with 95 percent probability that Station 107 was affected by a factor not common to the other two stations.

Continuing these comparisons upstream (i.e., between Stations 107 and 106, 106 and 105, etc.) the area in which the disturbance occurred might be narrowed. Alternatively, if no effects are observed at Station 107, a comparison with upstream stations might show that a disturbance of lesser impact did or did not occur.

Table 10. Example of Statistical Analysis of Reserve's Biological Monitoring Program

Sampling Periods	Sampling Stations		Difference	Percent
	107	109		
Spring 1974	$\bar{x}_1^{(1)}$	$\bar{x}_1'^{(1)}$	d_1	$\frac{d_1}{\bar{x}_1} \times 100$
Fall	$\bar{x}_2$	$\bar{x}_2'$	d_2	$\frac{d_2}{\bar{x}_2} \times 100$
Spring 1975	$\bar{x}_3$	$\bar{x}_3'$	d_3	$\frac{d_3}{\bar{x}_3} \times 100$
Fall	$\bar{x}_4$	$\bar{x}_4'$	d_4	$\frac{d_4}{\bar{x}_4} \times 100$
Spring 1976	$\bar{x}_5$	$\bar{x}_5'$	d_5	$\frac{d_5}{\bar{x}_5} \times 100$
Fall	$\bar{x}_6$	$\bar{x}_6'$	d_6	$\frac{d_6}{\bar{x}_6} \times 100$
Spring 1977	$\bar{x}_7$	$\bar{x}_7'$	d_7	$\frac{d_7}{\bar{x}_7} \times 100$
Fall	$\bar{x}_8$	$\bar{x}_8'$	d_8	$\frac{d_8}{\bar{x}_8} \times 100$
				$\sum_{i=1}^N \frac{d_i}{\bar{x}_i} \times 100$

Note: 1. $\bar{x}_1$ and $\bar{x}_1'$ are the means of the replicates collected during Spring 1974 for Stations 107 and 109, respectively.

Calculate mean of the percent differences between stations:

$$\bar{d}_N = \frac{\sum_{i=1}^N \frac{d_i}{\bar{x}_i} \times 100}{N}$$

Calculate standard deviation of the mean: $s =$

$$\sqrt{\frac{\sum_{i=1}^N \left(\frac{d_i}{\bar{x}_i} \times 100 - \bar{d}_N \right)^2}{N - 1}}$$

In earlier tabulations of the biological data, only a single biological observation was reported, such as one Surber sample, according to Reserve personnel. However, they plan to report the data on all replicates and calculate the means of the observations for 1978 and subsequent data. This latter method of reporting should be satisfactory. It is suggested, however, that when macroinvertebrate specimens are identified to genus, counts of the number of organisms per genus be made and tabulated on the laboratory data sheets. This probably would require minimal additional effort.

Chlorophyll a which has been corrected for pheophytin a interference, is measured but not reported; chlorophyll a concentrations, as calculated by the trichromatic method, are reported but an overestimate periphyton biomass, particularly when the chlorophyll a : pheophytin a ratio approaches 1. The sampling method used by Reserve (horizontally oriented slides located on the stream bottom) is probably more susceptible to adverse growing conditions for periphyton because of more favorable conditions for sediment deposition. The onset of adverse growing conditions leads to increases in the amount of pheophytin. Also, the data reported are not identified as to whether they are single observations or the mean of several observations.

Recommended Improvements to Reserve's Biological Monitoring Program

1. Establishment of a control station on the Beaver River upstream from its confluence with the low-water diversion (or any other project activity) is highly desirable.
2. Consideration should be given to establishing control stations on Big and Little Thirtynine Creeks, Kit Creek, and on an unnamed tributary upstream from Station 105, on the West Branch of the Beaver River, and another station on the East Branch of the Beaver River downstream from its confluence of with Cedar River.

3. Consider relocating some stations, such as Stations 103 and 104, so that all have a rubble-gravel-fine sand substrate, or alternatively, use artificial substrates such as the Hester-Dendy sampler.
4. Consider either increasing to six the number of replicates per station and testing for significance the means of replicates or maintaining the number of replicates and substrates for analysis by comparison of percent differences of parameters between station pairs.
5. Measure dissolved oxygen concentrations when collecting biological samples.
6. Consider comparing the results of several macroinvertebrate collections made by the Surber sampler with the modified Hess sampler.
7. Assess the need to freeze periphyton pigment samples in the field.
8. Establish a program to confirm Reserve's macroinvertebrate data.
9. Include the following essential steps in pigment analysis:
 - a. Mechanical disruption of periphyton samples using a tissue grinder consisting of a teflon pestle and glass mortar;
 - b. Addition of a small amount of magnesium carbonate (about 10 percent of the volume of the extract to be ground of a saturated solution) to the pigment sample; and
 - c. Steeping the ground sample for 24 hours in a dark refrigerator at 4°C.

10. Report all the macroinvertebrate, pigment, and dry and organic weight biomass data on all replicates collected at each station, and calculate the mean of these observations.
11. When the macroinvertebrates are identified to genus, include count of organisms per genus on the lab sheets.

INTRA-LAB QUALITY ASSURANCE PROGRAM

MRI - Reserve Data Comparison

MRI conducted surface water sampling and analyses in and around the Mile Post 7 site during the summer of 1975. This was in conjunction with the preparation of the EIS on the selection of an on-land tailings basin. Comparative data from the Reserve Mining laboratories during the same time period are listed in Table 11.

In this table the comparisons are made using data collected from similar locations. The MRI and Reserve locations are shown in Figures 2 and 3. Station R-2 is located on Big Thirty-Nine Creek and corresponds to Reserve's station #3. Station R-4 corresponds to Reserve's Station #2 and is located on the East Branch of the Beaver River. MRI station R-5 is located on the West Branch of the Beaver and corresponds to Reserve's Station #5. The last comparison is between MRI's station R-8 and Reserve's Station #6. This station is located above Avon Falls on the Beaver River. Although these sites and sample collection times are not identical, the comparisons of data should be valid with only small variations expected.

Most of the data in Table 11 compares favorably taking into account the fluctuations occurring because of differences in sampling locations and time. Discrepancies occur consistently in solids (both suspended and dissolved), sulfate, fluoride, nitrate, chloride, sodium, potassium and zinc analyses.

In an effort to correlate 1975 data to present laboratory practices, Table 12 compares 1975 data to 1978 data. The two stations chosen (1 and 2) have not changed over the past three years, thus the data should reflect analytical changes that affect results (e.g., lowering of detection limits due to instrumentation changes). Also stations one and two were chosen because they are relatively unaffected by the construction on Mile Post 7. Again, small variations will occur due to the seasonal differences between 1975 and 1978. The data consistently compares well. The fluctuations are

Table 11. Comparison of MRI and Reserve Mining Data

	Sta. #3 Big 39 (R-2) 6/29/75 MRI	Sta. #3 Big 39 (R-2) 7/1/75 MRI	Sta. #3 Big 39 (R-2) 7/1/75 RMC	Sta. #3 Big 39 (R-2) 8/4/75 MRI	Sta. #3 Big 39 (R-2) 8/4/75 RMC	Sta. #3 Big 39 (R-2) 8/29/75 MRI	Sta. #3 Big 39 (R-2) 8/29/75 RMC	Sta. #3 Big 39 (R-2) 7/1/75 MRI	Sta. #3 Big 39 (R-2) 7/1/75 RMC	Sta. #2 Beaver R. East 6/29/75 MRI	Sta. #2 Beaver R. East 7/1/75 RMC	Sta. #2 Beaver R. East 7/7/75 MRI	Sta. #2 Beaver R. East 7/7/75 RMC	Sta. #2 Beaver R. East 7/16/75 MRI	Sta. #2 Beaver R. East 8/4/75 RMC	Sta. #2 Beaver R. East 8/29/75 MRI	Sta. #2 Beaver R. East 9/3/75 RMC
pH	6.71	7.56	7.56	7.05	7.56	7.05	7.56	7.05	7.56	6.76	7.55	7.36	7.55	6.60	7.4	7.55	7.5
DO	7.8	7.2	7.2	4.6	7.2	4.6	7.2	4.6	7.2	7.4	7.2	6.25	7.2	6.8	7.1	10.15	8.3
Temperature	22	--	--	26	--	26	--	21	--	21	--	24	--	19	24	15	17
Alkalinity	24.5	45.8	45.8	44	45.8	44	45.8	56	80	32	31	22	31	32	48	36	50
Total Hardness	53	--	--	56	--	70	--	70	--	45	--	41	--	57	--	49	--
Calcium	12	13.9	13.9	15.5	13.9	17	22	17	22	10.5	10.2	10	10.2	10.5	14.2	--	14
Magnesium	3.6	3.75	3.75	3.9	3.75	4.6	6.1	4.6	6.1	2.9	2.9	2.7	2.9	3.6	4.4	--	4.4
Solids - TSS	5	1.8	1.8	2	1.8	4	5.8	4	5.8	6	1.0	2.5	1.0	1	6.0	1.5	3.8
TDS	63.5	58	58	123	58	117	--	117	--	106	44	116	44	113	--	81.5	--
Iron	1.1	1.1	1.1	1.3	1.1	1.3	1.4	1.3	1.4	.8	.84	.95	.84	3.0	.48	.8	.55
Copper	.05	.002	.002	<.05	.002	<.05	.0015	<.05	.0028	.1	.002	<.05	.002	<.05	.002	.0004	.002
Manganese	.09	.05	.05	.09	.05	.12	.41	.12	.18	.06	.02	.06	.02	.09	.07	.035	.19
Ammonia	<.1	.08	.08	<.1	.08	<.1	.06	<.1	.04	<.1	.06	<.1	.06	<.1	.04	--	<.01
Nitrate	3.99	<.1	<.1	1.75	<.1	.11	<.1	.11	<.1	.92	.11	.745	.11	.045	<.1	--	<.1
Zinc	.03	.006	.006	.1	.006	.07	.006	.07	.007	.49	.006	.055	.006	.1	.0055	.002	.0042
Cyanide	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	--	<.01
Lead	.005	.001	.001	--	.001	.00045	.001	.00045	<.001	.0008	.003	.00065	.003	.00045	.001	.0003	<.001
Total Chromium	.05	<.001	<.001	.075	<.001	.10	<.001	.10	<.001	.1	<.001	.05	<.001	<.05	<.001	.0003	<.001
Cadmium	<.02	<.0002	<.0002	<.02	<.0002	<.02	<.0002	<.02	<.0002	.02	<.0002	<.02	<.0002	<.02	<.00002	.00006	<.00002
Arsenic	<.002	--	--	<.002	--	<.002	--	<.002	--	<.002	--	<.002	--	<.002	--	.001	--
Silver	.24	<.001	<.001	<.04	<.001	<.04	<.001	<.04	<.00004	<.28	<.001	<.04	<.001	<.04	<.001	<.00004	<.001
Chloride	1	.5	.5	1	.5	1.5	1.1	1.5	1.6	1	.5	1	.5	1	1.1	--	1.0
Silica	3.5	6.6	6.6	9	6.6	9	8.3	9	9.4	4.5	6.8	10	6.8	10	9.0	--	7.6
Potassium	<.2	.52	.52	.4	.52	.2	.65	.2	.68	.2	.52	.2	.52	.2	.63	--	.53
Sodium	2.75	1.65	1.65	.75	1.65	1.5	3.3	1.5	3.8	3.25	1.65	.75	1.65	1.7	2.8	--	2.8
Barium	.005	.008	.008	.007	.008	.007	.013	.007	--	.006	.007	.008	.007	.006	.001	.006	--
Selenium	<.003	<.005	<.005	<.003	<.005	<.003	<.005	<.003	--	<.003	<.005	.003	<.005	.003	<.005	<.002	--
Phenol	.007	<.005	<.005	<.002	<.005	<.002	<.005	<.002	<.005	<.004	<.005	.002	<.005	<.004	<.005	--	<.005
Sulfate	<.1	4.0	4.0	<.1	4.0	4.5	5.2	4.5	6.5	<.1	4.8	<.1	4.8	1	5.6	--	6.5
Oil	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	--	<.1
Fluoride	.4	.19	.19	.3	.19	.4	<.5	.4	<.5	.52	.24	.55	.24	.5	<.5	--	<.5

Table 11. Comparison of MRI and Reserve Mining Data (Continued)

	Beaver R. West (R-5) 6/29/75 MRI	Sta. #5 Beaver R. West 7/1/75 RMC	Beaver R. West (R-5) 7/16/75 MRI	Sta. #5 Beaver R. West 8/4/75 RMC	Beaver R. West (R-5) 8/29/75 MRI	Sta. #5 Beaver R. West 9/3/75 RMC	Beaver R., Avon Falls (R-8) 7/9/75 MRI	Sta. #6 Above Avon Falls 7/1/75 RMC	Beaver R., Avon Falls (R-8) 8/29/75 MRI	Sta. #6 Above Avon Falls 9/3/75 RMC
pH	6.71	7.6	7.30	7.6	6.70	7.7	7.98	7.8	7.95	8.2
DO	5.8	7.8	7.05	7.8	5.2	7.8	8.78	8.1	9.78	11.9
Temperature	22	21	26	21	22	21	15	20	15	17
Alkalinity	77	45	60	45	73	72.6	93	50	74	81
Total Hardness	71	--	71	--	84	--	105	--	84	--
Calcium	17.5	13.9	18.5	13.9	21	19.8	--	17	--	21.7
Magnesium	5.1	3.9	4.8	3.9	7.0	6.1	--	4.2	--	6.8
Solids - TSS	20.5	4	6.5	4	7.5	3.2	2.5	7.2	5	9.2
TDS	99.5	61.5	138	61.5	161.5	--	174.5	64	109	--
Iron	1.55	1.37	1.0	1.37	3.0	.33	.75	1.7	.6	.42
Copper	.075	.0036	<.05	.0036	<.05	.0024	.0012	.003	.0011	.002
Manganese	.06	.02	.06	.02	.12	.05	.04	.02	.04	.07
Ammonia	<.1	.08	.17	.08	<.1	.025	--	.068	--	<.01
Nitrate	1.1	<.1	.86	<.1	.01	<.1	--	<.1	--	<.1
Zinc	.68	.008	.09	.008	.05	.005	.005	.002	.002	.004
Cyanide	<.01	<.01	<.01	<.01	.025	<.01	--	<.01	--	<.01
Lead	.0015	.001	--	.001	.0010	.001	.0004	.001	.0005	<.001
Total Chromium	.075	<.001	<.05	<.001	<.05	<.001	.0008	<.001	.0011	<.001
Cadmium	<.02	<.0002	<.02	<.0002	<.02	<.0002	.00006	<.0002	<.00004	<.0002
Arsenic	<.002	--	<.002	--	<.002	--	.002	--	.001	--
Silver	<.04	<.001	<.04	<.001	<.04	.001	<.00004	.001	<.00004	<.001
Chloride	1	.5	<.5	.5	1	.9	--	.5	--	2.2
Silica	4	7.3	7	7.3	6.5	7.5	--	6.8	--	6.0
Potassium	.3	.66	.4	.66	.4	.75	--	.87	--	.8
Sodium	3.1	1.8	.75	1.8	1.75	3.2	--	2.0	--	4.1
Barium	.01	.009	.015	.009	.012	.009	.012	.012	.011	--
Selenium	.0077	<.005	.003	<.005	<.003	<.005	<.002	<.005	<.002	--
Phenol	<.002	<.005	<.002	<.005	.008	<.005	--	<.005	--	<.005
Sulfate	<1	5.8	<1	5.8	4	6.3	--	7	--	7.7
Oil	<1	<1	<1	<1	<1	<1	--	<1	--	<1
Fluoride	.3	.18	.4	.18	.4	<.5	--	.17	--	<.5

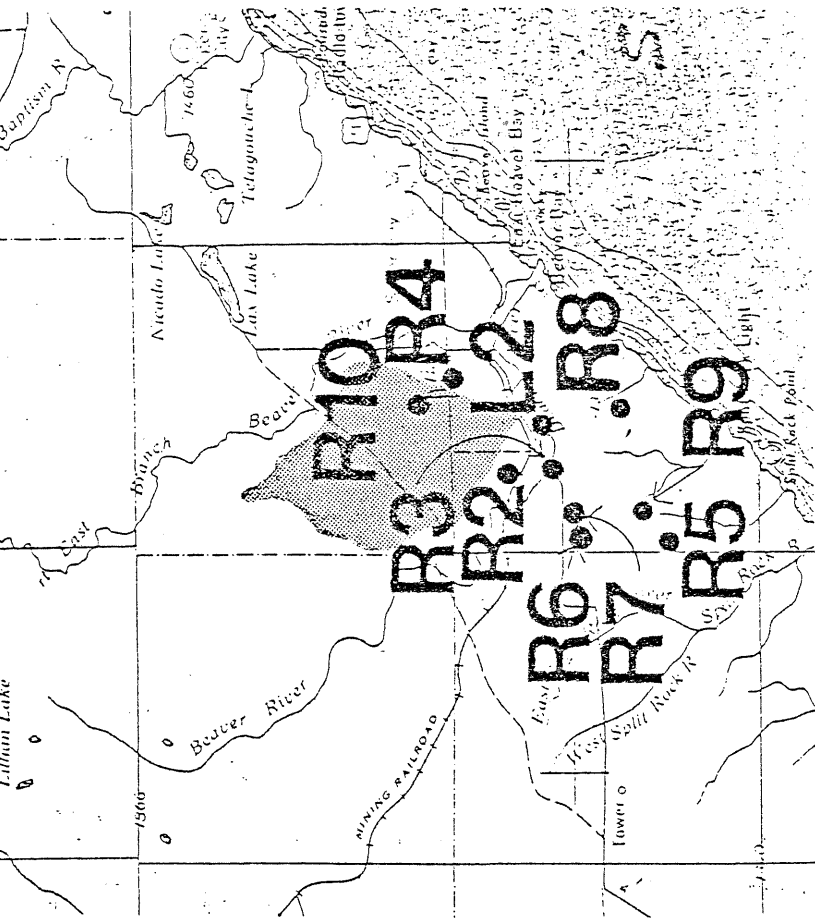


Figure 2. MRI Sampling Stations

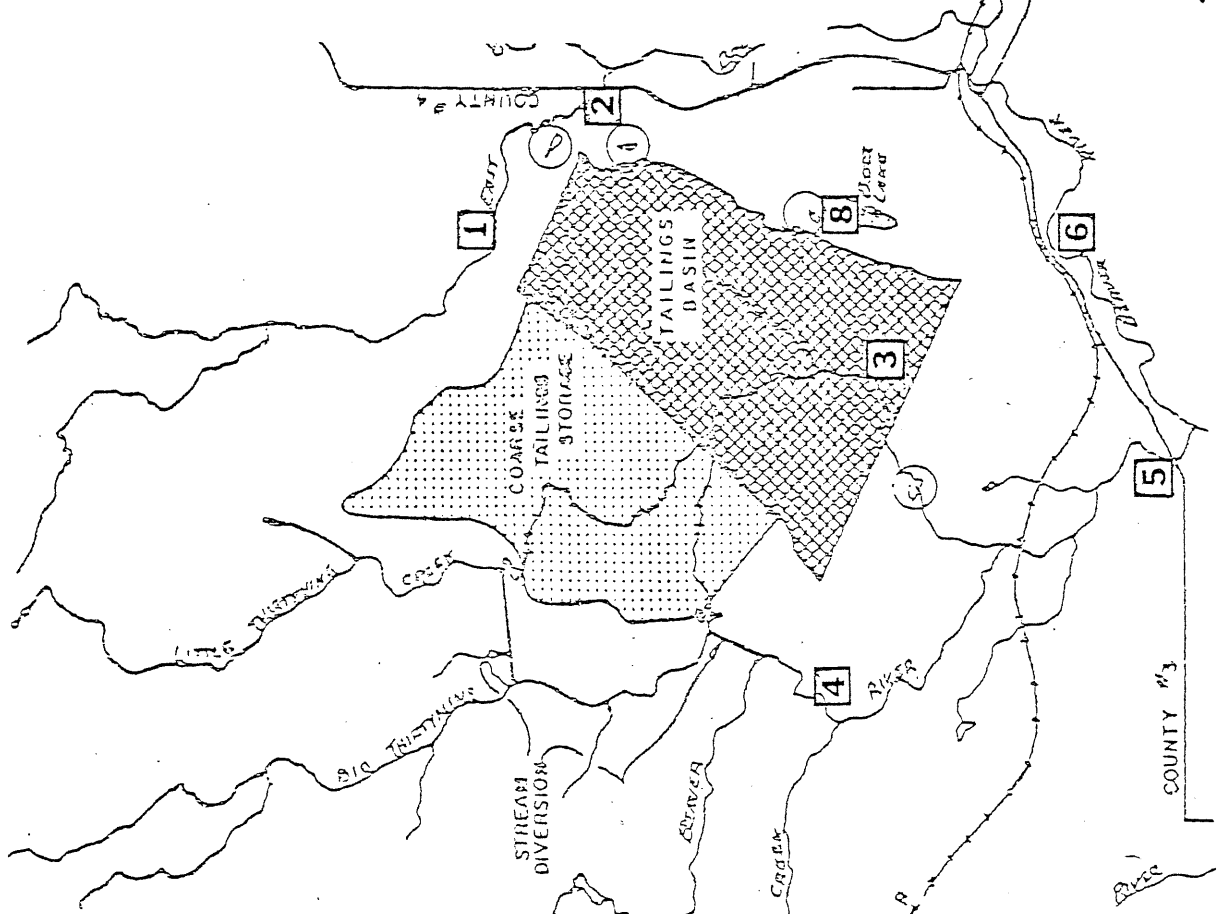


Figure 3. Reserve Mining Company Sampling Stations

Table 12. Comparison of Data Between 1975 and 1978 During the Month of May

Minnesota State Permit Analysis	Station 1 5/6/75	Station 101 5/1/78	Station 2 5/6/75	Station 102 5/1/78
Calcium	4.7	3.9	4.0	4.5
Magnesium	1.45	1.35	1.3	1.59
Sodium	1.0	.60	.9	.69
Potassium	.47	.47	.5	.47
Alkalinity	10.07	8.68	8.53	10.18
Sulfate	10.6	6.0	8.5	6.0
Chloride	<.5	<1	.5	<1
Silica	6.6	7.1	6.7	7.1
Nitrate	.12	.4	.35	.43
Nitrite	.002	.003	.002	.003
Ammonia	.021	.106	<.01	.105
Organic Nitrogen	.674	.735	.760	.775
Sol. O-PO ₄		.002		.001
Total PO ₄	.014	.043	.009	.034
Phenol	<.0005	<.0005	<.0005	<.0005
Iron µg/l	315	291	720	593
Manganese µg/l	4	23	14	20
Copper µg/l	1.9	1.0	2.6	1.6
Zinc µg/l	6.4	1.7	8.6	2.7
Nickel µg/l	2	<2	2	<2
Cadmium µg/l	<.2	<.2	<.2	<.2
Lead µg/l	<1	<2	1	<2
Cobalt µg/l	.6	<1	1.5	<1
Chromium µg/l	<1	<1	<1	<1
Mercury µg/l	<.2	<.2	<.2	<.2
Silver µg/l	<1	<1	<1	<1
Arsenic µg/l	<5	<5	<5	<5
MDAS	--	--	--	
Hydrogen Sulfide	--	<.1		<.1
Cyanide	<.01	<.01	<.01	<.01
Fluoride	.15	<.5	.12	<.5
TSS	1.8	3.9	14	9.8
TDS		22.8		26
Total Solids	31.8		41.1	
BOD ₅	.7	1.1	1.2	1.5
COD	43.9	37.8	36.2	37.1
Oil & Grease	<1	<1	<1	<1
Color		90		90
pH	6.97	6.6	6.78	6.6
DO	9.7	13.3	12.4	11.9
Temperature, °C	6.1	1.0	6.3	1.0
Spec. Cond.	36	35	36	40
Turbidity	.9	1.8	4.5	2.5
Fecal Coliforms	15	4	<1	1
Total Coliforms	360	28	260	64
Fecal Strep.	750	4	27	6
Fibers	--	--	--	--
Amines	--	<.01	--	<.01
Selenium µg/l	<5	<5	<5	<5
Barium µg/l	--	12	--	10

all within expected yearly differences. One noticeable change is the detection limit for fluoride. This suggests that a change in the analytical technique occurred. Except in the case of fluoride, these data suggest that the discrepancies that existed in 1975 would still exist.

Sampling Procedures

All the information in this section was gathered from data provided by Reserve Mining Company or by observation made by MRI staff during a site visit June 5-9, 1978.

A summary of the Reserve Mining laboratory's collection and handling of surface and ground water samples is found in Figures 4 and 5. The container type along with its preparation are also included. The bottle preparation for the various parameters meet EPA guidelines. When new bottles are being used (as in the case of the general chemistry and x-ray bottles) special care must be taken by the sampling crews to assure that they are rinsed three times with the sample water. It was observed, particularly in the case of well waters that were hand sampled, that this was not always practiced. Contamination from bottles could produce erroneous results.

Fiber bottles are containers rinsed three times with distilled/deionized water that has been filtered through a .45 μm pore filter. By contacting the Minnesota Department of Health, which will be analyzing the fiber samples, it was ascertained that this procedure is barely adequate. EPA suggests that either .45 μm or .1 μm pore size filtering techniques may be used successfully on fiber samples. The Health Department uses either .22 μm (for historical data) or .1 μm pore size filters and thus the bottle preparation should include three rinses with distilled/deionized water that has been filtered through a maximum .22 μm pore size filter.

Several options exist to accomplish this filtering without added effort. Cellulose acetate filters are commercially available with a .2 μm pore size that can be connected directly to the distilled/deionized water line.

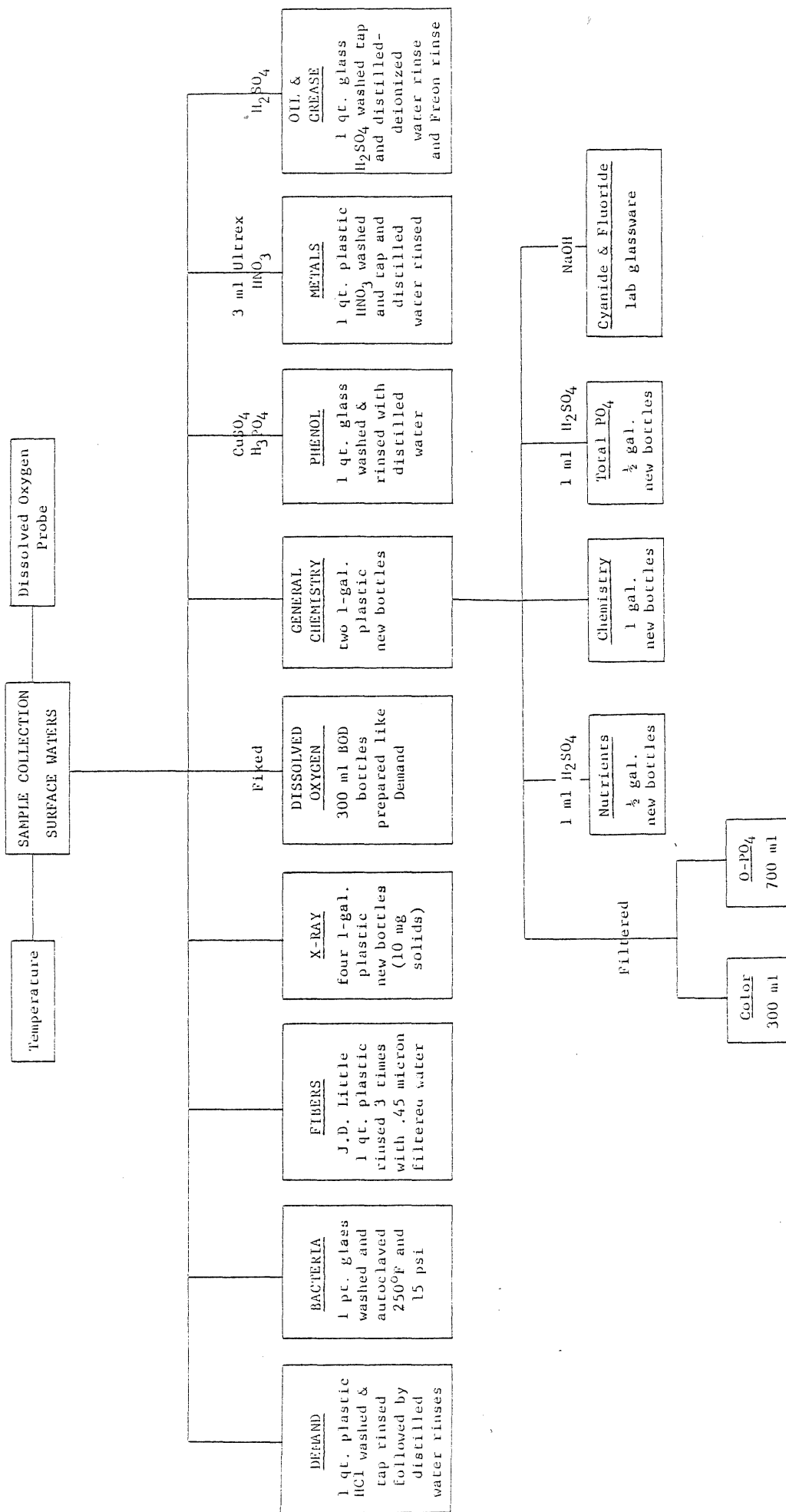


Figure 4. Schematic of Splitting and Preservation of Surface Water Samples

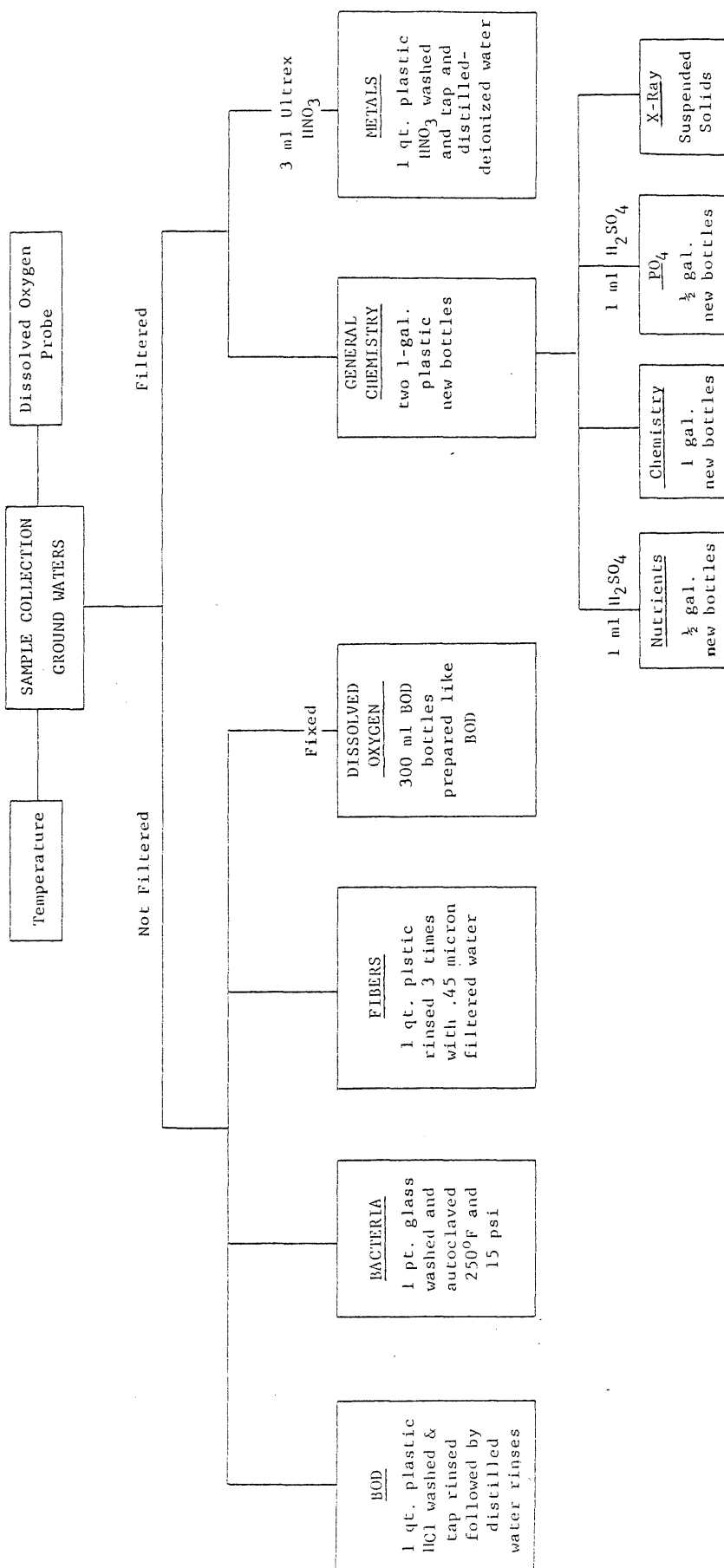


Figure 5. Schematic of Splitting and Preservation of Ground Water Samples

MRI has used this type of laboratory water for several years in all analyses with no background rise. Data are available that show that water treated in this manner has acceptable background levels for both crysotile and amphibole fibers. Another option is to replace the .45 μm pore size filters with .22 μm pore size filters. Although this would slow down the filtration process, it would achieve the desired results.

Sampling techniques were observed for surface water samples at sites 106 and 107 and for groundwater samples at well site 10. Consistent procedures need to be practiced when sampling to insure sample integrity. At the surface stations it was observed that some of the sampling personnel were rinsing bottles less than the three required times and collecting the samples off the surface. To obtain a consistent sample when grab sampling, all sampling personnel should take samples approximately the same distance below the surface. EPA suggests that grab samples taken in streams should be collected from mid-depth in a well mixed section of the stream.

During the observation at well 10, the same problem occurred in bottle rinsing. When new, unwashed bottles are used, in the case of general chemistry and x-ray samples, care must be taken to rinse the bottles to avoid the inclusion of foreign materials.

The length of times that the deep wells are purged is sufficient and the all plastic Kemmler sampling apparatus (see Figure 6) used on the shallow wells prevents the inclusion of trace metal contaminants. Again, care must be taken to avoid contamination of the sample from excess handling of the parts of the sampler that come into contact with the liquid.

Once the samples are collected they are labeled with prenumbered water-proof labels as found in Figure 7. These labels contain all the information required by the EPA: sample number, date and time of sampling, source of sample, point of sampling, type and quantity of preservation, and the sampler's initials.



Figure 6. All Plastic Kemmler Sampler for Well Sampling

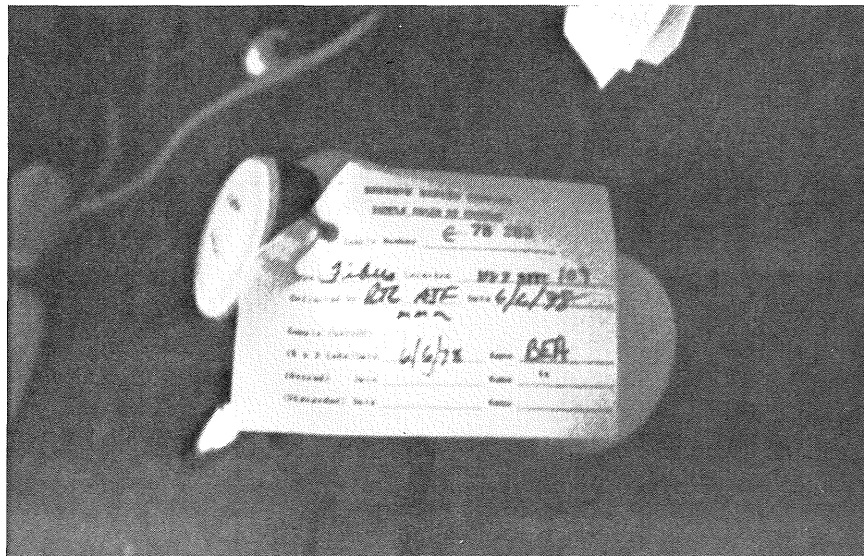


Figure 7. Sample Bottle Labeling Techniques

Field conditions, field analyses results, sampling personnel involved, and site numbers are logged into a permanently bound field notebook. These data are transferred to the lab with the samples. The information included in the notebook meets EPA requirements and helps correlate data to field conditions.

No sample preservation occurs in the field except the fixing of DO samples. All samples are kept on ice and are transported to the laboratory within six hours. EPA prefers the preservation of samples to occur in the field. Constituents within a sample can subtly alter concentrations within a short period of time. The sample matrix which the Reserve Mining laboratory is handling (surface and ground water) can probably withstand the six hour transportation time with no appreciable change in constituent concentration. These samples must be kept at or below 4°C during transport and must be preserved immediately upon receipt at the laboratory, which should be a maximum of six hours following collection.

Preservation techniques practiced for most of the parameters are satisfactory (See Table 13). The type of techniques used are found in Figures 4 and 5. All samples are stored at 4°C until analyzed. The quantity of acid added should be sufficient to lower the pH to <2 except in the case of phenol samples which need to be acidified to a pH ≤ 4 . The one constituent that wasn't preserved for properly was cyanide. At the same time as all the other preservation techniques (within six hours of collection) an aliquot (at least 500 ml) should be removed for CN analysis in which the pH is adjusted to >12 with sodium hydroxide.

All sample containers are in accordance with EPA recommendations as found in Table 3 except the phenol bottles. EPA suggests that amber glass bottles be used to decrease the photo-decomposition of the phenol compounds. Photo-decomposition has proven to be a problem during studies conducted by MRI.

Table 13. EPA Recommendations for Sampling and Preservation of Samples (1)

Measurement	Volume Required (ml)	Container	Perservative	Holding Time ^c
Acidity	100	P,G ^a	Cool, 4°C	24 hours
Alkalinity	100	P,G	Cool, 4°C	24 hours
Arsenic	100	P,G	HNO ₃ to pH <2	6 months
BOD	1000	P,G	Cool, 4°C	6 hours ^b
Bromide	100	P,G	Cool, 4°C	24 hours
COD	50	P,G	H ₂ SO ₄ to pH <2	7 days
Chloride	50	P,G	None Required	7 days
Chloride Req.	50	P,G	Cool, 4°C	24 hours
Color	50	P,G	Cool, 4°C	24 hours
Cyanides	500	P,G	Cool, 4°C NaOH to pH 12	24 hours
Dissolved Oxygen				
Probe	300	G only	Det. on site	no holding
Winkler	300	G only	Fix on site	no holding
Fluoride	300	P,G	Cool, 4°C	7 days
Hardness	100	P,G	Cool, 4°C	7 days
Iodide	100	P,G	Cool, 4°C	24 hours
MBAS	250	P,G	Cool, 4°C	24 hours
Metals				
Dissolved	200	P,G	Filter on site HNO ₃ to pH <2	6 months
Suspended			Filter on site	6 months
Total	100		HNO ₃ to pH <2	6 months
Mercury				
Dissolved	100	P,G	Filter HNO ₃ to pH <2	38 days (glass) 13 days (hard plastic)
Total	100	P,G	HNO ₃ to pH <2	38 days (glass) 13 days (hard plastic)
Nitrogen				
Ammonia	400	P,G	Cool, 4°C H ₂ SO ₄ to pH <2	24 hours ^c
Kjeldahl	500	P,G	Cool, 4°C H ₂ SO ₄ to pH <2	24 hours ^c
Nitrate	100	P,G	Cool, 4°C H ₂ SO ₄ to pH <2	24 hours ^c
Nitrite	50	P,G	Cool, 4°C	24 hours ^c
NTA	50	P,G	Coo, 4°C	24 hours
Oil & Grease	1000	G only	Cool, 4°C H ₂ SO ₄ to pH <2	24 hours
Organic Carbon	25	P,G	Cool, 4°C H ₂ SO ₄ to pH <2	24 hours
pH	25	P,G	Cool, 4°C Det. on site	6 hours ^b
Phenolics	500	G only	Cool, 4°C H ₃ PO ₄ to pH <4 1.0 g CuSO ₄ /l	24 hours

Table 13. EPA Recommendations for Sampling and Preservation of Samples⁽¹⁾ (Continued)

Measurement	Volume Required (ml)	Container	Preservative	Holding Time ^e
Phosphorus				
Orthophosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	24 hours ^c
Hydrolyzable	50	P,G	Cool, 4°C H ₂ SO ₄ to pH <2	24 hours ^c
Total	50	P,G	Cool, 4°C	24 hours ^c
Total, Dissolved	50	P,G	Filter on site Cool, 4°C	24 hours ^c
Residue				
Filterable	100	P,G	Cool, 4°C	7 days
Nonfilterable	100	P,G	Cool, 4°C	7 days
Total	100	P,G	Cool, 4°C	7 days
Volatile	100	P,G	Cool, 4°C	7 days
Settleable Matter	1000	P,G	None required	24 hours
Selenium	50	P,G	HNO ₃ to pH <2	6 months
Silica	50	P only	Cool, 4°C	7 days
Specific Conductance	100	P,G	Cool, 4°C	24 hours ^d
Sulfate	50	P,G	Cool, 4°C	7 days
Sulfide	50	P,G	2 ml zinc acetate	24 hours
Sulfite	50	P,G	Cool, 4°C	24 hours
Temperature	1000	P,G	Det. on site	no holding
Threshold Odor	200	G only	Cool, 4°C	24 hours
Turbidity	100	P,G	Cool, 4°C	7 days

- a. Plastic or glass.
- b. If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.
- c. Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/l, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.
- d. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.
- e. It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

It was also observed that within the laboratory all the filtered samples are placed into bottles that have not been previously rinsed with the sample. Some of these bottles (e.g., metals) have had previous special treatment and are satisfactory. The general chemistry bottles for the filtered samples should either be rinsed three times with filtered sample or should go through a cleaning consisting of a phosphate-free detergent wash followed by several rinses of tap and then distilled water.

Compliance to Time Limits Upon Initiation of Analysis

It was observed that in the Reserve Mining laboratory, pH, dissolved oxygen (Winkler method), alkalinity, color, specific conductance, turbidity, fecal coliform, total coliform, and fecal streptococci are analyzed for on the day that the samples are collected. Amines are also fixed on the first day. Nitrate, nitrite, and surfactants are analyzed for as soon as possible (usually 1 to 2 days from collection). All BOD's for a sampling trip are batched and are set up following the receipt of the last samples for that month (usually on Wednesday if sampling begins on a Monday). All other analyses are initiated in random order as analyst time permits.

Table 14 lists the holding time from collection to analysis for six parameters during the month of May. These figures are typical of the lag times encountered when scanning data going back to the first of the year. It is evident that the holding times vary greatly from the EPA guidelines.

Table 14

Parameter	Date Collected	Date Analyzed	Time Lapse	EPA(1) Time Limit
Silica	5/1	5/5	4 days	7 days
Total Phosphorus	5/1	5/11	10 days	24 hours
Ortho Phosphorus	5/1	5/12	11 days	24 hours
Sulfate	5/1	5/15	14 days	7 days
Nitrate	5/1	5/16	15 days	24 hours
Chloride	5/1	5/4	3 days	7 days

The EPA has set forth guidelines for the ideal lapse time between sampling and analysis. It is stressed that these are ideal numbers and with proper storage and preservation the integrity of the sample will be retained longer than the limits. These limits are listed in Table 13.

It is impossible to predict how much time can be allowed to lapse between sampling and analysis. Many factors come into play that affect different matrices. The rule of thumb is to order the analysis following the EPA guidelines and get to them as soon as possible.

Certain analyses should be done in the field. Dissolved oxygen should be either fixed in the field or read with a DO meter and probe. The Reserve Mining sampling personnel do both. Temperature and pH should also be done at the sampling site. If it can be proven that there is not change in pH between the times of the sample collection and its receipt at the laboratory it can be analyzed for when the samples are returned to the laboratory as it is currently being done.

BOD's should be set up within six hours of receipt rather than batching them. If more than twenty-four hours have elapsed, significant changes in the sample will cause erroneous BOD values.

Methods for Analysis

A comparison of Reserve Mining's methods of analyses and the EPA approved methods (according to the Federal Register, Title 40, Chapter 1, Part 136⁽²⁾ and its amendments.⁽³⁾) is found in Table 15. All methods except those for sodium, potassium, chromium, arsenic, silver, barium, selenium, chloride, nitrate, total dissolved solids and amines conform to federally approved methods.

Table 15. Comparison of Methods of Analysis

Minnesota State Permit Analysis	Reserve Method			Approved Methods (2,3)				
	Description	Reference	Page	Description	1974 EPA Methods (1)	14th Edition Std. Methods (2)	Pt. 31 ASTM (4) 1975	USGS Methods
Calcium	Dig. AA	Std. Methods	148	Dig. AA	103	148	345	66
Magnesium	Dig. AA	Std. Methods	148	Dig. AA	114	148	345	109
Sodium	Dig. AA	Perkin-Elmer	EN-1	Dig. AA	147			143
Potassium	Dig. AA	Perkin-Elmer	EN-1	Dig. AA	143			134
Alkalinity	Elec. Tit.	Std. Methods	278	Elec. Tit.	3	278	111	41
Sulfate	Turbidimetric	Std. Methods	496	Turbidimetric	277	496	425	
Chloride	Colorimetric	ASTM	269	Colorimetric	31	613		
Silica	Colorimetric	Std. Methods	487	Filtration Colorimetric	274	487	398	139
Nitrate	UV Spectro.	Std. Methods	420	Bruc. Color	197	427	358	119
				Cadmium Radiation	201	423		
				Colorimetric	215	434	--	121
Nitrite	Diazo-Color	Std. Methods	434	Diazo Color	215	434		121
Ammonia	Dist. Nessler. photo	Std. Methods	412	Dist. Nessler.	159	412	237	116
Org. Nitrogen	Dig. Dist. Nessler. Photo	Std. Methods	437	Dig. Dist. Nessler.	175	437		122
Sol. O-PO ₄	Ascorbic Acid	Std. Methods	481	Ascorbic Acid Red	249	481	384	131
Total PO ₄	Dig. Ascorbic Acid	Std. Methods	476	Dig. Asc. Acid	249	476	384	133
Phenol	CHCl ₃ Ext. Color 4AAP	Std. Methods	577	Colorimetric 4AAP	241	577	545	
Iron	Dig. AA	Std. Methods	148	Dig. AA	140	148	345	102
Manganese	Dig. AA	Std. Methods	148	Dig. AA	144	148	345	109
Copper	Dig. AA	Std. Methods	148	Dig. AA	408	148	345	83
Zinc	Dig. AA	Std. Methods	148	Dig. AA	155	148	345	159
Nickel	Dig. AA	Std. Methods	148	Dig. AA	141	148	345	115
Cadmium	Dig. AA	Std. Methods	148	Dig. AA	401	148	345	62
Lead	Dig. AA	Std. Methods	148	Dig. AA	142	148	345	105
Cobalt	Dig. AA	Std. Methods	148	Dig. AA	407	148	345	80
Chromium	Dig. AA	Perkin-Elmer	EN-4	Dig. AA	105	148	345	78
Mercury	Flameless AA	Std. Methods	156	Fless AA	143	156	338	51
Silver	Dig. AA	Perkin-Elmer	EN-2	Dig. AA	146	148		142
Arsenic	Dig. AA	Perkin-Elmer	EN-4	Dig. AA	95	150		31
Surfactants	Colorimetric	Std. Methods	600	Colorimetric	157	600	494	
Cyanide	Dist. Color	Std. Methods	361	Dist. Color	40	361	503	85
Fluoride	Spec. Ion Elec.	Std. Methods	391	Spec. Ion Elec.	65	391	307	93
TSS	Glass Filter	Std. Methods	94	Glass Filter	268	94		
TDS	Calculation	Upper Great Lakes	--	Glass Filter	266	92		
Total Solids	Gravimetric	Std. Methods	91	Gravimetric	270	91		
BOD ₅	Electrode	Std. Methods	543	Electrode	543			
COD	Dichromate Reflux	Std. Methods	550	Dichromate Reflux	20	550	472	124
Oil & Grease	Ext. L-L	Std. Methods	515	Ext. L-L	229	515		
Color	Colorimetric (Visual)	Std. Methods	64	Colorimetric (Visual)	36	64		82
pH	Electronic	Std. Methods	460	Electronic	239	460	178	129
DO	Probe	Std. Methods	450	Probe	56	450		
	Winkler Tit.	Std. Methods	443	Winkler Tit.	51	443	363	126
Temperature	Glass Thermometer	Std. Methods	125	Glass Thermometer	286	125		31
Spec. Cond.	W. Bridge Conductimetry	Std. Methods	71	W. Bridge Conductimetry	275	71	120	148
Turbidity	Nephelometric	Std. Methods	132	Nephelometric	295	132	223	156
Fecal Col.	Membrane Filter	Std. Methods	937	Membrane Filter		937		
Total Col.	Membrane Filter	Std. Methods	928	Membrane Filter		928		
Fecal Strep.	Membrane Filter	Std. Methods	944	Membrane Filter		944		
Amines	Colorimetric	ASTM	491					
Selenium	Dig. AA	Perkin-Elmer	EN-5	Dig. AA	145	159		
Barium	Dig. AA	Perkin-Elmer	EN-2	Dig. AA	97	152		52

The method from the Perkin Elmer handbook for alkali metals, including sodium and potassium, varies from approved methods by the addition of lanthanum oxide for all the required alkali metals rather than for just cadmium and magnesium. This difference will not affect the results obtained for potassium or sodium.

The Perkin Elmer methods for chromium and arsenic (EN-4), silver and barium (EN-2), and selenium (EN-5) are recognized as legitimate methods for graphite furnace analyses. In the last few years, the EPA has required the low detection limits that only graphite furnace atomic absorption can provide. In the priority pollutant protocols being issued by the EPA, the method found in the "Atomic Absorption Newsletter," 14, page 111 (1975) is referred to as the method of choice for the flameless atomic absorption analysis of arsenic, selenium, silver and barium. This compares favorably with the methods in use.

The method used by the Reserve Mining laboratory for the analysis of chlorides is technically not an approved method. It is basically the approved automated colorimetric method without the automation. EPA has not officially approved this method as it is being practiced but the ASTM manual (1975)⁽⁴⁾ recognizes this technique. It is a good method for analyzing for low concentrations of chloride ion.

The ultraviolet technique now being employed by the Reserve Mining laboratory is classified by the EPA as a screening method.⁽⁵⁾ This method is used to choose a final analytical procedure which will be most sensitive for that concentration range (usually cadmium reduction or brucine methods). It is not meant to be used as a final analytical procedure. Although the bulk of the samples analyzed by the laboratory are relatively free from interference, this method has several interference problems that can severely alter the results. The data comparison between the Minnesota Department of Health and the Reserve Mining laboratories could be better. The discrepancies that exist in the nitrate analyses are probably due to differences in methods.

It is MRI's recommendation that one of the approved methods (see Table 15) for nitrate be chosen. Although the ultraviolet method has performed satisfactorily, one of its main interferences is any dissolved organic material. This type of interference can occur sporadically, influencing results.

The method being used for total dissolved solids by the Reserve Mining laboratory is also not an approved method. Due to the low level of dissolved solids in the surface waters collected by Reserve, analysis by conventional means leads to erroneous results. At such low levels, errors incurred by the method overshadow the results. The data being produced by calculation appear more reasonable and if this method is adopted, it is recommended that all agencies conform so that all the data are comparable.

The conversion factor of .65 adopted by the Upper Great Lakes Reference Group of the International Joint Commission is a reasonable one. For surface waters, MRI recommends that this system be adopted.

Ground water samples present a different situation. Dissolved solids levels are higher, hence less error occurs. Table 16 summarizes the comparative data gathered for May. The ratios between dissolved solids and specific conductivity are incongruent for surface waters but are reasonable for ground waters. It is not a valid assumption that the calculations would give accurate results for ground waters. The recommended gravimetric method is the method of choice for these samples. Calculating dissolved solids, different methods should be adopted for each class of sample.

TABLE 16

	RMC Specific Cond.	MDH Specific Cond.	RMC Calc. TDS	MDH TDS	MDH TDS ÷ Spec. Cond.	MDH Calc.TDS Spec. Cond.x .65
Station 101	35	35	22.8	34	.97	22.8
Station 102	40	45	26	34	.76	22.8
Station 104	63	65	40.9	46	.71	42.2
Station 105	44	45	28.6	40	.89	29.2
Well M-1	475	480	308.8	240	.50	312
Well M-1A	560	460	364	290	.63	299
Well M-7	205	220	133.3	120	.55	143
Well M-7A	205	210	133.3	100	.48	136.5
Well M-7B	195	220	126.7	120	.57	143
Well M-9A	196	190	127.4	110	.58	123.5

There is only one method in any of the standard methods manuals for amines. This is found in the ASTM (1975)⁽⁴⁾ standards. EPA has no recommended method, and this fact should be taken into account when reviewing the data.

Although the remainder of the methods are approved in the Federal Register, small discrepancies exist between actual practices and some of the referenced methods. This diversion occurs mainly with metals analyses. During the digestion of the heavy metals fraction, sulfuric acid is added. Lead is analyzed for out of this fraction, and when sulfuric acid is used, lead sulfate forms which is insoluble in all acids. Low lead results will occur. Sulfuric acid is not used in any of the methods referenced by

Reserve Mining. In another case, the reagent quantities and concentrations used in the cold vapor mercury determination do not correspond to that in any of the references. The digestion method being implemented is not rigorous enough to digest any organically-bound mercury. MRI recommends using the approved technique from Standard Methods to assure total digestion.

The analysis of performance evaluation samples is an indicator as to the effectiveness of the methods used for analysis. A compilation of the results produced by the Reserve Mining laboratory and the acceptable ranges are found in Table 5. Good agreement exists for most of the parameters. The discrepancy in some of the lead results could be due to the use sulfuric acid in the digestion step. Variations in the metals currently being run by the personnel in the laboratory along with MRI personnel. A graphic presentation of the metals analyses as understood by MRI is found in Figure 8. Because of time considerations, actual observation of the analytical technique did not take place during the visit to Reserve Mining Company in June.

Biochemical oxygen demand procedures were observed by MRI personnel. The method used by the Reserve Mining laboratory is unsatisfactory. The surface waters found in northern Minnesota do not make a suitable seed. Raw sewage should be used. Samples should be set up within six hours of collection and if more than six hours elapse between collection and analysis, (not more than 24 hours), the samples should be kept at 4°C until analysis. Samples should not sit overnight at room temperature. This practice causes radical changes in sample constitution which lead to erroneous results.

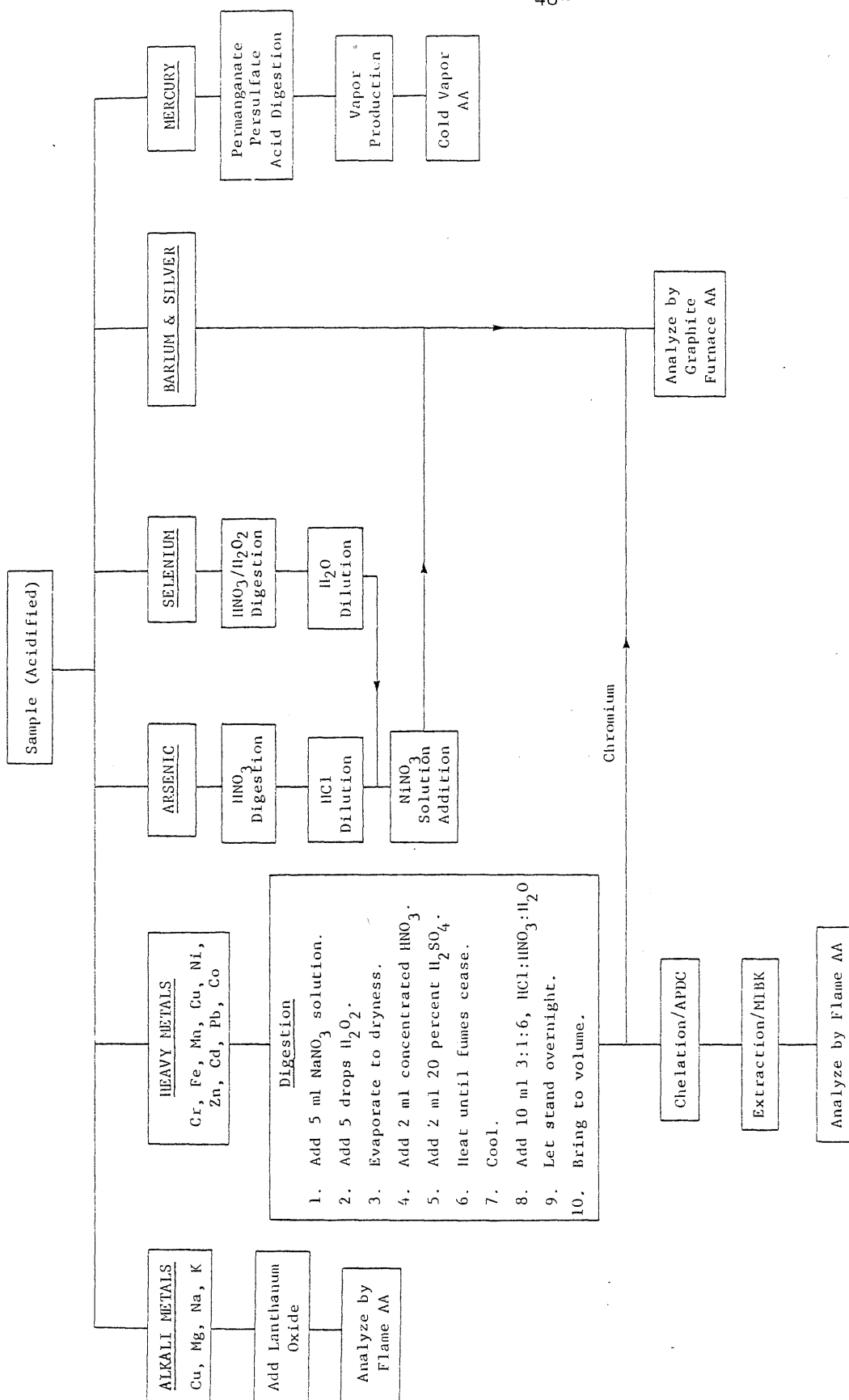


Figure 8. Schematic of the Metals Procedures

Maintenance and Calibration of Instruments

The Reserve Mining laboratory has a rigorous preventative maintenance program for a number of their instruments. The atomic absorption spectrophotometers and gas chromatograph are routinely checked semiannually by the manufacturer. This is accomplished under a standing agreement. Semi-annual checks are sufficient to assure proper performance. During the checks, the instrument is cleaned and the optics are aligned. Standards are run as a check on sensitivity. The analytical balances in the laboratory are cleaned and calibrated annually. This practice is accomplished by an independent servicing company. This program is within guidelines required by the EPA.⁽⁶⁾ The x-ray diffraction unit is also on a yearly preventative maintenance contract. This is sufficient to meet standards. All other instrumentation is serviced as necessary by the manufacturer.

A set of standards is on order to calibrate the spectrophotometers in the laboratory. These standards should be used monthly to assure accurate performance of all the spectrophotometric instruments.

Calibration of the instrumentation occurs prior to all analyses. Dissolved oxygen probes and meters are calibrated in the field using a water saturated air technique. When measuring pH, the meters are calibrated using buffer solutions. Analytical balances are zeroed. Atomic absorption and spectrophotometric equipment are calibrated, with standards of varying concentrations prior to analysis (which bracket the expected results). These techniques correspond with federally approved laboratory practices.

Laboratory Quality Assurance

The Reserve Mining laboratory's quality assurance program consists of a minimum 10 percent duplicate analyses for all parameters and the analysis of synthetic samples prepared either by the EPA or by an independent company. No graphic representation of duplicate data exists within the laboratory and results are not compared to any quality assurance criteria. Documented

records should exist to prove that the variance of the duplicate analyses are within expected precision ranges. Rather than accumulating precision data and in view of the timing and quantity of analyses run by the laboratory, special quality assurance runs of at least fifteen duplicate sets of samples within the expected concentration ranges should be run and confidence limits established for each type of analysis. This will provide a base of information with which to compare the variance of the data, indicating when a particular analysis is out of control. Without these special quality assurance procedures, there is no way of knowing what the expected variance of a particular analysis is within an individual laboratory. At this time, there is no documented information regarding precision of each analysis performed within the Reserve Mining Company laboratory. The most recent guidelines regarding quality assurance, published by the EPA, can be found in Appendix A. This gives a complete description of the quality assurance programs that should be initiated by the Reserve Mining laboratory.

Accuracy is ascertained by running synthetically spiked blanks. These samples consist of laboratory grade water spiked with the particular component (or components) of interest. These components should be at levels expected in the samples. Standards of this nature should be run 5 percent of the time or one with each group of analyses performed at any given time, whichever is greater. Again a basis of comparison must exist. At least fifteen runs at two different levels must be analyzed to provide baseline variance information. This is used to judge when an individual analysis is out of control. As with precision procedures, the most efficient way to acquire the baseline data would be through an intensive quality assurance run. The data acquired from this run can then be statistically converted to a basis for comparison for the 5 percent data collected from each run of a particular constituent. This technique must be practiced for each parameter analyzed for by the laboratory.

The same techniques exist for the collection and comparison of recovery data as for the accuracy data. The only difference is that synthetic spikes are added to actual samples rather than laboratory distilled/deionized water. The same methods are used to acquire baseline data. Also, the required number of assurance analyses run along with each batch of sample is the same (see Appendix A). This practice of fortifying samples is essential to all types of analyses, but is crucial for the metals analyses where matrix effects can substantially alter results.

In summary, laboratories that analyze environmental samples must confirm their results by using the three methods described above (precision, accuracy and recovery); and this corroboration must be fully documented. The requirement for and the implementation of these procedures are clearly detailed in the EPA protocol in Appendix A and in the "Handbook for Analytical Quality Control in Water and Wastewater Laboratories."⁽⁶⁾

Certified performance evaluation samples (those provided by EPA or other laboratories) are required only when a new procedure is initiated; otherwise, they are recommended annually. This type of sample will indicate only if the method being used and the analyst are operating correctly. Once proven, this quality assurance parameter will change only when analyst or method vary. The performance ascertained from these samples has little bearing on how accurately the methods will behave on actual samples. Other quality assurance practices are necessary to properly define the variance seen daily.

During the past year, eight performance evaluation samples have been analyzed for various constituents. This is more than necessary, and their value is somewhat questionable due to the fact that they do not test the variations in results that sample matrix and concentration present.

Recommendations for Reserve's Intra-Laboratory Quality Assurance Project

In conclusion, MRI personnel make the following recommendations with regard to intra-laboratory quality assurance:

1. Consistent sampling procedures should be practiced by Reserve Mining Company personnel when collecting both ground and surface waters. This includes both bottle rinsing and collection depths.
2. Fiber bottles should be rinsed with a maximum .22 μ m filtered distilled/deionized water for analysis by the Minnesota Department of Health.
3. The fraction of sample to be analyzed for cyanide should be preserved with sodium hydroxide immediately upon receipt at the laboratory.
4. New bottles should either be rinsed with sample or previously washed when they are used as containers for filtered samples.
5. Time limits between sample collection and the initiation of analysis for all but the first day should be ordered according to the EPA guidelines⁽¹⁾ and started as soon as possible. BOD's should be set up the day that they are collected.
6. A method for nitrates should be chosen from the federally approved methods. The current method being employed can lead to erroneous results.
7. The calculation from specific conductivity of total dissolved solids results for surface waters should be adopted but standard methods should be used on groundwater.
8. The methods used for the digestion steps for metals should conform to the methods referenced by Reserve Mining Company. Sulfuric acid should not be used in the digestion technique.

9. The quality assurance techniques of precision, accuracy, and recovery should be initiated as soon as possible following the federal guidelines set forth in Appendix A and in the EPA Handbook for Quality Assurance. (6)

REFERENCES

1. "Methods for Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, Methods Development and Quality Assurance Research Laboratory, Cincinnati, Ohio 45268 (1974).
2. "Environmental Protection Agency Regulations on Test Procedures for the Analysis of Pollutants," 40 CFR 136; *Federal Register*, 38, p. 28758 (October 15, 1973).
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4. Annual Book of ASTM Standards, Part 31, Water (Annually revised), p. 529, American Society for Testing and Materials, Philadelphia, Pennsylvania, 19103 (1975).
5. Standard Methods for Examination of Water and Wastewater, 14th Edition; American Public Health Association, Washington, D.C. 20036 (1975).
6. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," U.S. Environmental Protection Agency, Analytical Quality Control Laboratory, National Environmental Research Center, Cincinnati, Ohio (1972).

APPENDIX A

Quality Assurance Program for the Analyses of
Chemical Constituents in Environmental Samples

QUALITY ASSURANCE PROGRAM FOR THE ANALYSES OF
CHEMICAL CONSTITUENTS IN ENVIRONMENTAL SAMPLES*

The following program of quality assurance is for use by laboratories engaged in the analysis of organic and inorganic chemicals, metals, and general analysis parameters in environmental samples.

Each laboratory is responsible for maintaining a continuing record of the data from all quality control checks and for using these data to make decisions on the acceptability of the analytical results as they are acquired. All quality control data generated, problems identified, and corrective actions taken to resolve the problems are to be recorded and provided to the responsible authority when reporting the analytical results. As available, quality control (QC) check samples of known value and performance evaluation (PE) samples should be analyzed by the laboratory prior to initiation of the analytical program.

A. Intralaboratory Quality Control

As a part of its intralaboratory analytical quality control program, the laboratory must develop single laboratory precision and accuracy criteria for each parameter that it is required to measure. These criteria must compare favorably with published data. Initially, these data may be applied over a broad concentration range. As more data accumulate, the precision and accuracy of the method should be updated and criteria developed for multiple narrower ranges.

1. Precision - To determine the precision of the method, a regular program of analyses of replicate aliquots of environmental samples must be carried out. The precision criterion should be developed from 15 sets of replicate results accumulated over a period of time during the routine analysis program. At least two replicate aliquots of well mixed sample must be analyzed with each set of 20 samples or less analyzed at a given time. These replicate data must be obtained for each parameter of interest.

*U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1978.

Initially, samples selected for replicate analyses should be those that are most representative of the interference potential of the sample type. For example, in the current Effluent Guidelines Verification Program, the influent to the treatment process would be appropriate. As the program progresses, samples representing the entire range of concentrations and interference potential should be designed into the replicate analyses program.

After 15 replicate results have been obtained, calculate the range (R_i) of these results as follows:

$$R_i = | X_{i1} - X_{i2} |$$

where R_i is the difference between the results of the pair (X_{i1} and X_{i2}) from sample $i=1$ through n . The concentration of each sample is represented by the mean:

$$\bar{X}_i = \frac{(X_{i1} + X_{i2})}{2}$$

where $\bar{X}_i$ is the average of the results of the replicate pair. A preliminary estimate of the critical difference (R_c) between replicate analyses for any specific concentration level (C) can be calculated as:

$$R_c = 3.27 \left(C \sum_{i=1}^n R_i \right) / \left(\sum_{i=1}^n \bar{X}_i \right).$$

From these data develop a table of such R_c values for various C values that span the concentration range of interest.

These preliminary critical difference values may be used to judge the acceptability of the succeeding replicate results. To do this, calculate the mean ($\bar{X}$) and difference (R) between the replicate results. Referring to the table of critical

range values developed above, find the C nearest to $\bar{X}$ and use its R_c to evaluate the acceptability of R. If the R is greater than R_c , the system precision is out of control and the source of this unusual variability should be identified and resolved before continuing with routine analyses. Record the results of all replicate analyses and periodically (after 25 to 30 additional pairs of replicate results are obtained) revise, update, and improve the table of critical range values.

2. Accuracy - In addition to the initial determination of the precision of the method, a program must be maintained to verify that the laboratory accuracy continues under control. This program is concurrent to the spiked sample analysis program outlined below and is carried out by preparing check standards and analyzing them according to the method. The check standards should be approximately equal to the concentration found in routine samples. Alternately, one standard above and one standard below the midpoint of the range of the method should be used. Analyze the standard and calculate O_i (the observed value). The percent recovery (P_i) is then calculated as follows:

$$P_i = \frac{100 (O_i)}{T_i} ,$$

where T_i = the true value.

After determining the P_i for approximately 15 check standards, calculate the mean ($\bar{P}$) and standard deviation (S_p) of the percentages as follows:

$$\bar{P} = \frac{\sum_{i=1}^n P_i}{n}$$

and:

$$S_p = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^n P_i^2 - \frac{(\sum_{i=1}^n P)^2}{n} \right]}$$

where n = the number of results available.

If the percent recovery for succeeding check standards is not within the interval of $\bar{P} \pm 2 S_p$, the system should be checked for problems. If problems exist, they must be resolved before continuing with routine analysis. This criteria is tighter than the generally accepted $\bar{P} \pm 3 S_p$ but will result in more accurate data for real samples if these check standards are used to adjust the calibration curve.

At least one check standard must be analyzed along with each set of 20 samples or less that is analyzed at a given time. This check standard data must be obtained for each parameter of interest.

Record the recovery of all check standards and periodically revise, update and improve the accuracy criteria.

3. Recovery - Determine the recovery of the method for the analysis of environmental samples by adding a spike (T_i , true value) sufficient to approximately double the background concentration level ($\bar{X}_i$) of the sample selected earlier for replicate analysis (Section A1). If the original concentration is higher than the midpoint of the standard curve (range of the method), then the concentration of the spike should be approximately one-half the original concentration. If the concentration of the original sample was not detectable, the concentration of the spike should be five to fifteen times the lower limit of detection. The volume of standard added in aqueous solution should not

dilute the sample by more than ten percent. The volume of standard added in an organic solvent solution should be kept small (100 μ l/l or less), so that the solubility of the standard in the water will not be affected.

Analyze the sample, calculate the observed value (O_i), and then calculate the recovery for the spike as follows:

$$P_i = 100(O_i - \bar{X}_i)/T_i$$

where P_i is the percent recovery. If the sample was diluted due to the addition of the spike, adjust $\bar{X}_i$ accordingly.

After determining P_i for at least 15 spike results, calculate the mean percent recovery ($\bar{P}$) and standard deviation (S_p) of the recovery as follows:

$$\bar{P} = \frac{n}{\sum_{i=1}^n P_i} / n$$

$$S_p = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^n P_i^2 - \frac{(\sum_{i=1}^n P_i)^2}{n} \right]}$$

where n - the number of percent recovery values available.

If the percent recovery of the spike is not within the interval of $\bar{P} \pm 3 S_p$, the system accuracy is out of control and the source of this systematic error should be identified and resolved before continuing with routine analysis.

At least one spiked sample must be analyzed along with each set of 20 samples or less that is analyzed at a given time. This spiked data must be obtained for each parameter of interest. Record the recovery data of all spiked analyses and periodically (every 25 to 30 data points) revise, update, and improve the accuracy criteria.

B. Additional Routine Quality Control Practices

In addition to the foregoing formal quality control program, certain other practices must be included during routine analyses by the laboratory to eliminate determinate errors and to insure the quality of the data. These practices include: instrument calibration and performance checks, preparation and daily check of calibration curves, method blank analyses, and field blank analyses. Some of these operations are common to all analytical methods and some are unique to specific methods.

For additional information and guidance in analytical quality control practices refer to the U.S. Environmental Protection Agency's "Analytical Quality Control Handbook".

1. Operations Common to all Methods

- a. Standard Curve - Prior to the analysis of samples, a standard curve that covers the entire working range of the method must be constructed with at least five standards, including one near the upper limit of the concentration range and one near the lower limit of the concentration range. The other standards should be equally spaced throughout the operating concentration range.

Each day, if operation is continuous, or prior to analyzing each group of samples, if operation is non-continuous, analyze a minimum of two standards to establish the validity of the original standard curve. These standards should represent the range of the standard curve, i.e., one above and one below the midpoint of the standard curve. If these standards fall outside the established limits, a new standard curve must be constructed. These limits should be established by the analyst as a part of his ongoing quality control program.

- b. Method Blank - A method blank must be determined for each set of samples analyzed and whenever a new source (new container) of reagent or solvent is introduced into the analytical scheme. (NOTE: the individual solvents and reagents should be checked for purity prior to use in determining the method blank or in the analysis of samples.)

To determine the method blank, take a quantity of reagents equivalent to that used in the analysis of the sample and carry them through the entire analytical procedure including all glassware and other materials that come into contact with the sample. Determine a method blank for each class of compounds to be determined, i.e., pesticides, base-neutrals and acids, metals, phenolics, cyanides, etc.

Reagents having background levels that interfere with the compounds to be determined must be purified and shown to be acceptable or replaced with some that are acceptable prior to proceeding with the analyses. Problems encountered and corrective actions taken should be reported to the responsible authority for information and possible resolution of problems encountered by other analysts.

- c. Field Blanks - A field blank must be analyzed with each set of samples from a given source. This is particularly important whenever automatic samplers are used for collection of samples as in the current Effluent Guidelines Program. The blanks must be analyzed in the same manner as the sample. Preparation of field blanks is described in the sampling and analysis protocol. Field blanks for purgeables are sent from the laboratory to the sampling site and returned as a check on possible contamination of the sample by permeation of volatiles through the septum seal.

When interferences occur, the analytical results must be discarded unless sufficient data from these blanks is available to permit correction of the results.