462

1999 Hydrogen Sulfide Monitoring Report
Ryan Odenbach, Red Lake Watershed District

I. Purpose

The purpose of this study was to collect additional baseline data to help in future assessments of problems and solutions associated with hydrogen sulfide. Testing of hydrogen sulfide had only been done twice in 1996 and once in 1997. The 1997 data was discarded.

II. Monitoring Scheme

In 1999 the Red Lake Watershed District (RLWD) sampled eleven (11) sites for hydrogen sulfide and other water quality parameters. These included:

1) Red Lake River behind Slumberland (at the end of Greenwood Street), Site Kordel. This site was chosen because it is above the confluence of the Thief and Red Lake Rivers. The site shows amounts of parameters on the Red Lake River before mixing with the Thief River.
2) Red Lake River at First Street Bridge, Site 66. This site provides information on water quality just before aeration by the dam and after the confluence of the Thief and Red Lake Rivers.
3) Thief River at Long's Bridge, Site Long's Bridge. This site provides information on the water quality of the Thief River before the confluence of the Thief and Red Lake Rivers.
4) Outlet Channel at Good Lake, Site G.L. Channel. At the time of preparation for this project comments by RLWD staff were made about the strength of the hydrogen sulfide smell at the Good Lake outlet structure. Good Lake is an impoundment smaller but similar to impoundments found in the Thief River Watershed. It was decided to measure the amount of hydrogen sulfide entering the Red Lake River through the Good Lake outlet channel.
5) Outlet Structure at Good Lake, Site G.L. Structure. This was an added site to quantify the difference of hydrogen sulfide levels actually found in Good Lake. The difference between the channel measurements and the structure measurements quantifies how much is lost in aeration over the outlet structure.
6) Red Lake River above the USGS Rock Dam, Site Rock Weir. In order to try and quantify a load from the Good Lake Impoundment outlet this site was chosen above the outlet channel on the Red Lake River.
7) Red Lake River at Good's Bridge, Site Good's Bridge. This site is on the downstream side of the Good Lake Impoundment outlet channel.
8) County State Aid Highway #7 near the Agassiz Refuge, Site 40. A few sites were chosen on the Thief River below the Agassiz Pool outlet, to aid in determining where most of the hydrogen sulfide and other water quality parameters were originating. This site chosen as representative of water from the Agassiz Pool.
9) USGS Gage #05-0760 at the Hilyer Bridge, Site 760. This site is located downstream on the Thief River below several drainage ditch outlets and the Elm Lake outlet, before entering the City of Thief River Falls.

10) County Ditch 200, Site Ditch 200. This drainage ditch empties from the Elm Lake impoundment, the site was chosen at a point before entrance into the Thief River. This site would give an indication of the hydrogen sulfide contribution from Elm Lake.

11) County Ditch 20, Site Ditch 20. A few drainage ditches empty into the Thief River between the Agassiz Pool outlet and the City of Thief River Falls. County Ditch 20 is an example of one of these drainage ditches. This site quantifies what the drainage ditches may be contributing to hydrogen sulfide.

Maps of these sites are found in the appendix.

Other parameters along with hydrogen sulfide were measured. An association of other water quality parameters with hydrogen sulfide is important. A list with field methods, analysis methods, instruments used and laboratory used is found below. Era Laboratories, Inc., RMB Environmental Laboratories, Inc., and the University of Minnesota Crookston Laboratory are all certified by the Minnesota Department of Health for the respective analysis listed.

1) Dissolved H_2S (Hydrogen Sulfide): Analysis by Era Laboratories, Inc.; field collection involved using sterilized glass bottles with zinc acetate, holding them under water until filled then capping the bottle under water without any air bubbles, if air bubbles were seen another bottle was used, they were put in a cooler with ice to maintain at 4 degrees C and sent to lab; analysis EPA 376.2, Methylene Blue Method; minimum detection limit, 0.03 mg/L.

2) SO_4^{2-} (Sulfate Ion): Analysis by RMB Environmental Laboratories, Inc.; field collection involved putting sample water into sterile plastic bottles and preserving at 4 degrees C; analysis SM 4500-SO4 E; minimum detection limit, 10 mg/L.

3) Total PO_4^{3-} (Total Phosphorus): Analysis by RMB Environmental Laboratories, Inc; field collection involved putting sample water into sterile plastic bottles and preserving with sulfuric acid, keeping at 4 degrees C; analysis SM 4500-P E; minimum detection limit, 0.005 mg/L.

4) NH_3 (Ammonia): Analysis by RMB Environmental Laboratories, Inc.; field collection involved putting sample water into sterile plastic bottles and preserving with sulfuric acid, keeping at 4 degrees C; analysis SM 4500-NH3 F; minimum detection limit, 0.01 mg/L.

5) TKN (Total Kjeldahl Nitrogen): Analysis by RMB Environmental Laboratories, Inc.; field collection involved putting sample water into sterile plastic bottles and preserving with sulfuric acid, keeping at 4 degrees C; analysis EPA 351.2; minimum detection limit, 0.01 mg/L.

6) Alkalinity: Analysis by RMB Environmental Laboratories, Inc.; field collection involved putting sample water into sterile plastic bottles and preserving at 4 degrees C; analysis EPA 310.1; minimum detection limit, 10 mg/L.

7) Chemical Oxygen Demand: Analysis by RLWD staff at University of Minnesota Crookston water laboratory; field collection involved putting sample water into sterile plastic bottles and preserving at 4 degrees C; analysis SM 5220 D.

8) Turbidity: Analysis by RLWD staff at University of Minnesota Crookston water laboratory; field collection involved putting sample water into sterile plastic bottles and preserving at 4 degrees C; analysis was performed with Hach model 2100P Turbidimeter.

9) Conductivity, Dissolved Oxygen, pH, Water Temperature, and Total Dissolved Solids were measured using a Hydrolab model DataSonde 4 and Surveyor 4. The instrument was calibrated at the RLWD office.

The sites were sampled every week for a four (4) week period. Sample dates were March 9, March 18, March 26 and April 1. During ice conditions an ice auger was used to sample.

III. Results and Discussion

A column graph of each parameter is given at the end of this report along with a data sheet with each parameter on all sites. The data for Hydrogen sulfide showed that detectable levels were highest with site 40 and at site 760. At site 66, the main concern for the City of Thief River Falls, levels were still above detectable limits. Good Lake channel and structure both showed levels of hydrogen sulfide as well. Ditch 20 was never really flowing until runoff began in the last week of sampling. Ditch 200 from Elm Lake did not show any hydrogen sulfide.

Sites which were high in hydrogen sulfide also displayed high amounts of other parameters like: ammonia and TKN, total phosphorus, turbidity, sulfate, alkalinity, and conductivity. All of these parameters can point to the lack of oxygen in the water. Dissolved oxygen was very low and the chemical oxygen demand was very high pointing to near anoxic conditions in the water. The amount of dissolved oxygen in the Red Lake River may have been quite sufficient to react with the small amount of effluent from Good Lake. The outlet structure may also contribute dissolved oxygen to the Good Lake effluent.

Two questions arise when looking at the data: 1) Why did the Long's Bridge site show below detectable limits for three out of the four sample times? 2) Why did site 66 show any at all? If the Long's Bridge site is located on the Thief River before the confluence, it should have shown some measure of hydrogen sulfide during the first two sampling times. Also, since the Kordel site did not show any measure of hydrogen sulfide and a high amount of dissolved oxygen, the mixing at the confluence of the Thief and Red Lake Rivers should have been sufficient. Site 66, after the confluence, still showed a relatively high amount of hydrogen sulfide along with a high amount of dissolved oxygen. Ammonia and TKN, total phosphorus, sulfate and other parameters were noticeably lower at site 66 than at sites on the Thief River and actually compare to the water found in the Red Lake River above the confluence.

Hydrogen Sulfide

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	19	0.19	13	3.5	1.8	BDL	BDL	BDL	BDL	BDL
3/18/99	14	0.25	8.2	2.5	0.09	BDL	BDL	BDL	BDL	BDL
3/26/99	12	0.06	5.1	0.48	0.05	2	BDL	BDL	BDL	BDL
4/1/99	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Dissolved Oxygen

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	0.5	11.5	0.5	0.9	6.95	1.6	13.15	11.88	12.35	2.2
3/18/99	0.4	11.85	0.18	0.5	4.6	10.15	13.85	14.85	12.52	7.6
3/26/99	0.2	10	0.06	0.17	6.05	0.23	13.82	13.59	12.09	
4/1/99	11.69	16.75	11.78	15.63	13.65	12.22	11.65	11.33		14

Total Phosphorus

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	0.276	0.035	0.225	0.214	0.48	0.03	0.025	0.025	0.03	0.148
3/18/99	0.255	0.097	0.301	0.429	0.142	0.022	0.063	0.022	0.274	0.03
3/26/99	0.122	0.063	0.121	0.168	0.129	0.168	0.045	0.061	0.04	
4/1/99	0.158	0.234	0.262	0.03	0.05	0.272	0.061	0.038		0.17

Ammonia

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	3.68	0.102	3.03	2.46	2.3	0.106	0.049	0.036	0.636	1.08
3/18/99	3.72	0.142	2.84	2.21	2.18	0.129	0.058	0.067	0.073	0.612
3/26/99	3.46	0.238	2.69	3.93	2.18	1.98	0.111	0.118	0.131	
4/1/99	0.68	0.431	0.559	0.382	0.362	0.521	0.112	0.12		0.55

TKN

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	4.7	0.64	3.8	2.5	3.2	0.83	0.64	0.54	0.49	2.3
3/18/99	4.2	1	3	2.5	2.4	0.63	0.62	0.61	0.57	2.1
3/26/99	3.8	1.1	3.2	4.5	2.9	2.8	0.88	0.95	0.88	
4/1/99	1.1	1.8		0.81	0.92	1	0.67	0.78		1.1

Turbidity

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	231	3.7	142	21.2	18.1	2.41	1.99	2.3	3.48	12.2
3/18/99	166	4.21	131	23.5	14.8	1.88	11	2.98	4.41	28.3
3/26/99	138	8.27	108	5.66	9.02	64.8	13.2	3.2	4.89	
4/1/99	15.1	44.5	22.1	3.21	5.29	42.8	13.9	4.79		19.2

COD

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	117	32	100	70	80	35	34	34	40	57
3/18/99	110	37	88	73	68	35	43	34	31	29
3/26/99	91	29	74	92	67	50	34	36	28	
4/1/99	25	34	28	28	43	30	42	37		33

Sulfate

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	120	14	170	49	84	15	17	12	14	460
3/18/99	140	8.8	190	50	140	8.4	7.4	6.9	7.7	10
3/26/99	100	19	140	19	97	120	8.6	7.3	9.2	
4/1/99	56	18	24	18	37	55	13	8.8		20

Alkalinity

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	506	170	436	244	264	166	164	162	164	466
3/18/99	443	160	409	254	286	443	166	168	173	52
3/26/99	362	170	339	206	227	303	168	165	159	
4/1/99	75	53	55	64	65	51	74	90		44

Conductivity

Dates	Site 40	Site 66	Site 760	G.L. structure	G.L. channel	Long's Bridge	Good's Bridge	Rock Weir	Kordel	Ditch 200
3/9/99	1065	320	1067	516	630	958	367	368	304	1730
3/18/99	1053	312	989	567	709	320	300	297	288	156
3/26/99	878	343	857	520	570	833	310	303	302	
4/1/99	307	166	180	185	227	170	188	202		220