428
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Comments/Summary:

WQ-47

An Analysis of Hydrogen Sulfide Generation at Elephant Butte Reservoir Sierra County, New Mexico

A report by;

Christopher M. Canavan

Prepared for:

The United States Department of the Interior
Bureau of Reclamation
Elephant Butte Field Division
Truth or Consequences, NM

July 11, 1999

Introduction

Elephant Butte Reservoir is located on the Rio Grande in the Chihuahuan Desert of south central New Mexico, just north of the town of Truth or Consequences. Although the reservoir was created to provide the southern New Mexico agricultural region with a stable water supply for irrigation and to reduce the effects of flooding, it is used for recreational boating and fishing as well. The U.S. Bureau of Reclamation (USBR) also operates a 24,300-kilowatt hydroelectric power generating station at Elephant Butte Dam.

Elephant Butte Reservoir has been described as a modified dimictic lake with no true thermocline, but periods of thermal uniformity from September to October and April to May (Kidd 1974). However, recent studies clearly describe a monomictic lake with a distinct thermocline and a period of thermal stratification from July to October. This is then followed by mixis and isothermal conditions from December through March when surface waters begin to heat and start the process over again. This is common to deep water bodies of the temperate zone where ice cover is absent in the winter, and extreme summer heat warms the surface water. As the water is heated in the summer, circulation with the colder, denser water at depth decreases until the lake, or in this case, reservoir, eventually stratifies into a warm upper layer called the *epilimnion*, and a colder deep layer called the *hypolimnion*. These two strata are separated by a layer characterized by a thermal gradient that is called the *metalimnion*, which also contains the *thermocline*, defined as the zone where the temperature decrease is greatest with respect to depth. As the water in the epilimnion begins to cool in the fall and winter, the water becomes more dense and sinks toward the bottom until eventually the temperatures reach uniformity, or *isothermal*. This period is often described as the fall overturn, and the water will circulate freely until summer when daytime heating starts the process over again.

A secondary effect of stratification to highly productive, or *eutrophic*, waters is the partial or complete loss of oxygen, or *anoxia*, to the hypolimnion resulting from a high rate of oxygen consumption from bacterial respiration and decomposition of sedimenting organic matter. Following the development of anoxia, a whole set of organisms that thrive in anoxic conditions, most notably the sulfate reducing bacteria whose byproduct of metabolism is hydrogen sulfide (H_2S), increase rapidly. The H_2S will often continue to accumulate throughout the period of stratification and persist until the fall overturn when it is circulated up into the oxygenated epilimnetic waters, oxidized, and precipitated out as sulfate (SO_4). Ordinarily this is not a problem to reservoirs whose hypolimnetic waters remain isolated, but in some instances, such as a hydroelectric power plant where hypolimnetic water is released to generate electric power, the subsequent release of H_2S can have an impact on both downstream water quality, and local air quality.

The trophic status of Elephant Butte Reservoir has been described as both oligotrophic and eutrophic. Oligotrophy is the most accurate description of the general trophic status of the reservoir, but a change in trophic status to eutrophic may occur during late summer drawdown (Kidd et al. 1974). However, in recent years, despite reservoir levels near capacity, eutrophic conditions have also been observed to coincide with mid-summer stratification resulting in the development of anoxia and a buildup of hydrogen sulfide (H_2S) in the hypolimnion (Canavan 1998). The H_2S is then withdrawn from the hypolimnion through the power turbines facilitating

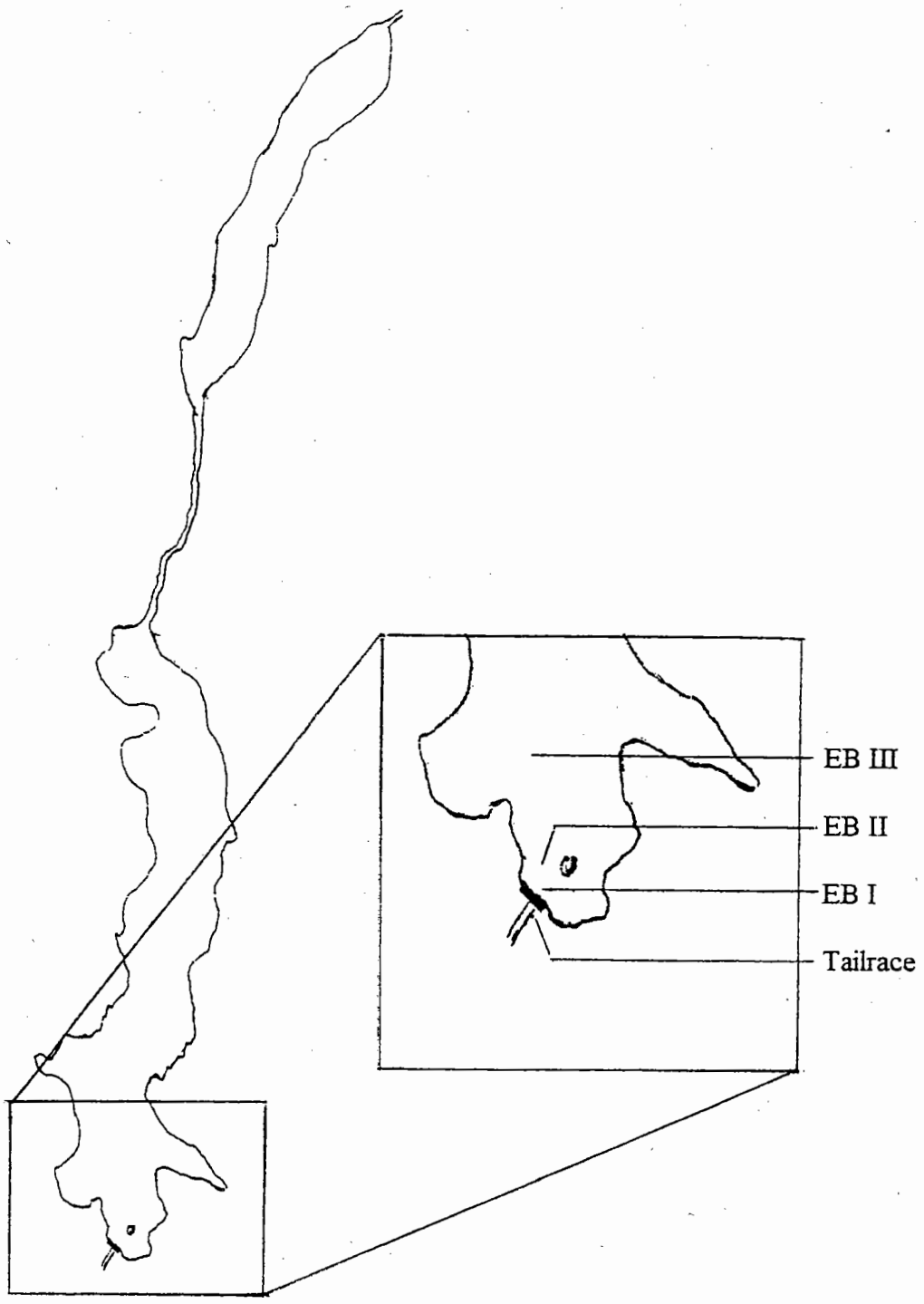

Figure 1. Elephant Butte Reservoir and location of the four study sites.

its release into the Rio Grande and the atmosphere below the reservoir.

Although anecdotal evidence suggests there has been a sporadic problem with generation of H_2S in the vicinity of Elephant Butte Dam in the past, atmospheric levels of H_2S became high enough in the fall of 1997 that local residents downstream complained of the odor. Employees of the USBR in both the power plant and the field division office at Elephant Butte Dam have also complained of the smell and have reported health problems with symptoms including headaches, nausea, and difficulty in breathing. In addition, water quality downstream in the Rio Grande appears to have deteriorated in recent years. A fish survey conducted in September 1998 encountered virtually no fish in the Rio Grande for 22 miles below the reservoir (Jaquez 1998). The release of H_2S enriched hypolimnetic waters has also been known to have a detrimental effect on the biota in waters below the dam in other systems (Petts 1984). In addition, it is not known what effect this will have on the life expectancy of the equipment at the power plant. As a result, a study was conducted to characterize the environmental conditions favorable to the buildup of H_2S in the hypolimnion and its subsequent release through Elephant Butte Dam.

Materials and Methods

Samples were collected monthly from April to December 1998 at four sites in the vicinity of Elephant Butte Dam (Figure 1). One site was located in the tailrace just below the dam (Tailrace), while three sites were located in the reservoir (EB I, EB II, and EB III). On site water quality data (temperature, pH, dissolved oxygen, conductivity, and oxidation-reduction potential) was collected with a multi parameter water quality monitoring probe (Hydrolab Surveyor II™) at one meter intervals from 0.5 m below the surface to 1.0 m above the bottom at all reservoir sites. Light penetration was measured with a Secchi disc. A second multi parameter water quality monitoring probe (Hydrolab DataSonde III™) was installed in the tailrace 1.0 m below the surface and programmed to collect data daily at two hour intervals for the entire study period. Following development of anoxia in the hypolimnion, H_2S concentration was determined by colorimetric technique (Hach Model HS-WR™) in the hypolimnion at EB I and the tailwater at Tailrace. In addition, water samples were collected at the EB I and Tailrace sites and analyzed for alkalinity, hardness, and sulfate. Water samples for laboratory analysis at EB I were collected at depths of 7.0 m, and 1.0 m above the bottom, to insure collection from both the epilimnion and hypolimnion, while samples at the Tailrace site were collected at 0.5 m below the surface.

Results and Discussion

Temperature and dissolved oxygen profiles for the EB I site are presented in Figure 2. The EB I site is the deepest site (45 m) of the three reservoir sites studied and therefore represents the most extensive reservoir profile determined. With the exception of depth, the data are also representative of the data collected for the EB II and EB III sites for a given sampling event. The reservoir was moving toward thermal stratification in April, and was clearly stratified for both dissolved oxygen and temperature by August with an anoxic hypolimnion from 32 m depth to the bottom at 45 m. The maximum thickness of the hypolimnion occurred in September. The breakdown of stratification was evident in October, while complete destratification and

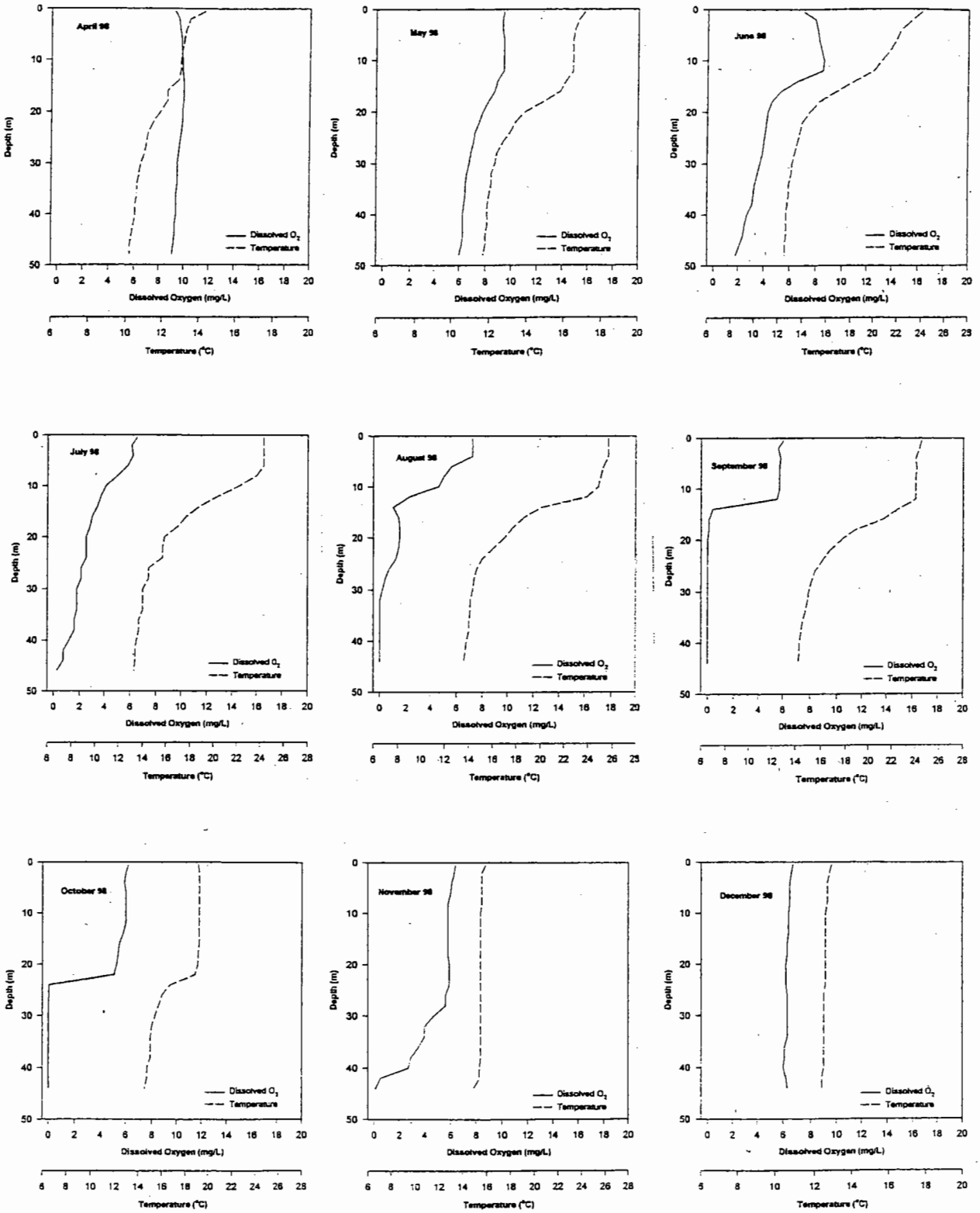

Figure 2. Temperature and dissolved oxygen profiles at EB I from April-December 1998.

subsequent mixis was underway by December. Although there are some minor differences, the data generally concur with data collected at the same site in 1996 and 1997 (Canavan 1998).

Alkalinity and hardness both exhibited increasing concentration with depth shortly following the onset of stratification, and maintained these conditions until complete overturn and subsequent mixis in December (Table 1). Alkalinity ranged from 110-129 mg/L in the epilimnion, and 124-139 mg/L in the hypolimnion, while hardness ranged from 144-169 mg/L in the epilimnion, and 150-206 mg/L in the hypolimnion. Calcium also exhibited increasing concentration with depth following the onset of stratification that persisted until December. Calcium ranged from 40.2-48.2 mg/L in the epilimnion, and 43.1-58.3 mg/L in the hypolimnion. Alkalinity and hardness reached peak concentration in October, while calcium concentration peaked in September.

An algal bloom that was observed across the reservoir and in the tailwater beginning the week of June 8-12 is believed to have been the impetus for the subsequent water quality changes observed in both the reservoir and tailwater. Light penetration had decreased from 6.5 m on April 21 to 3.8 m by June 29, and the water was light green in color, although there was no apparent phytoplankton floating on the reservoir surface. By August 21, light penetration had decreased further to 2.6 m and there was a noticeable amount of unidentified phytoplankton floating on the reservoir surface. On September 22, the bloom had subsided and light penetration was 3.7 m, and by October 19, all visible signs of the bloom were absent and light penetration was 4.4 m. Once the reservoir became thermally stratified in May, the changes in water quality as a result of the algal bloom would have had a profound impact on the biogeochemistry of the hypolimnion providing the environment for the generation of H_2S as well as other products of reduction processes (ie. Fe^{++}, Mn^{++}, PO_4^{-3}).

The initial impact the algal bloom had on the water chemistry is evident in the changes in alkalinity in the epilimnion. Between May 27 and June 29, shortly after the bloom appeared, the alkalinity dropped from 129 mg/L to 119 mg/L, and by August 21, the alkalinity had dropped further to 111 mg/L. This was undoubtedly a direct result of photosynthetic removal of CO_2 which induced the precipitation $CaCO_3$, and lowered the alkalinity. The precipitating $CaCO_3$ entering the hypolimnion would eventually undergo dissolution increasing the concentration of bicarbonate and alkalinity in the hypolimnion. From September to October the alkalinity in the hypolimnion increased from 127 mg/L to 139 mg/L and the HCO_3^- increased from 155 mg/L to 170 mg/L (data not shown).

While the gradient in alkalinity was primarily a result of decreasing concentrations in the epilimnion, the gradient in hardness was primarily a result of increasing concentrations in the hypolimnion, and was also related to the effects of the algal bloom. Following the development of the thermocline in May, the dissolved oxygen concentration of the isolated hypolimnetic waters decreased as a result of aerobic microbial respiration, and desiccating algae settling into the hypolimnion would have expedited this process. As a result of both respiration and decomposition processes there would have been a buildup of CO_2, followed by a decrease in pH, and an eventual shift from aerobic to anaerobic processes. Under the reducing conditions of the hypolimnion cations representative of hardness (Ca^{++}, Mg^{++}) would be released into solution causing an overall increase in hardness. The Ca^{++} (probably from both the bottom sediments and $CaCO_3$ precipitating from the epilimnion) concentration peaked at 58.3 mg/L in September, while

Table 1. Alkalinity, Hardness, Ca, Mg, and Sulfate for Tailrace and EB I. (E) epilimnion, (H) hypolimnion.

Site	Date	Depth (m)	Alkalinity (mg/L $CaCO_3$)	Hardness (mg/L $CaCO_3$)	Calcium (mg/L)	Magnesium (mg/L)	Sulfate (mg/L)
EB I (E)	5/27/98	7	129	152	45.4	9.4	115
EB I (H)	5/27/98	44	127	150	44.6	9.3	115
Tailrace	5/27/98	1	Sample not collected				
EB I (E)	6/29/98	7	119	154	44	10.8	109
EB I (H)	6/29/98	44	130	183	53.9	11.8	109
Tailrace	6/29/98	1	129	174	50.5	11.6	109
EB I (E)	7/24/98	7	111	150	41.9	11.0	113
EB I (H)	7/24/98	44	129	164	47.6	10.9	113
Tailrace	7/24/98	1	132	170	48.6	11.7	114
EB I (E)	8/21/98	7	111	168	46.5	12.6	108
EB I (H)	8/21/98	44	129	182	52.7	12.2	108
Tailrace	8/21/98	1	130	180	51.6	12.4	108
EB I (E)	9/22/98	7	110	169	48.2	11.9	108
EB I (H)	9/22/98	44	127	195	58.3	12.1	101
Tailrace	9/22/98	1	133	183	53.5	12.0	101
EB I (E)	10/19/98	7	119	157	43	12.2	115
EB I (H)	10/19/98	44	139	206	47.5	21.2	131
Tailrace	10/19/98	1	160	172	48.8	12.2	115
EB I (E)	11/16/98	7	121	144	40.2	10.7	116
EB I (H)	11/16/98	44	131	155	44.2	10.8	114
Tailrace	11/16/98	1	117	147	41.8	10.3	118
EB I (E)	12/14/98	7	122	152	42.8	11.0	110
EB I (H)	12/14/98	44	124	153	43.1	10.9	111
Tailrace	12/14/98	1	129	162	46.1	11.3	119

the concentration of Mg^{++} almost doubled from September to October from 12.1 mg/L to 21.2 mg/L. This subsequently led to the increase in hardness in the hypolimnion which by October had increased to 206 mg/L from pre-stratification levels of 150 mg/L. With an increase in hardness an increase in conductivity would also be expected. Although there was an increase in conductivity with depth it does not correspond clearly with the increase in hardness. However, laboratory measurements for total dissolved solids show a significant increase from 378 mg/L in August to 582 mg/L in October which does correspond with the increase in hardness (data not shown).

Sulfate exhibited no clear spatial or temporal trends but ranged from 101-131 mg/L with a mean concentration of 111 mg/L, and std. dev. = 4.8. However, in September the sulfate dropped from 108 mg/L in the epilimnion to 101 mg/L in the hypolimnion, and may be the result of conversion to H_2S. In October the reverse situation was observed when the sulfate ranged from 115 mg/L in the epilimnion to 131 mg/L in the hypolimnion possibly as a result of dissolution of sulfate from the bottom sediments in response to both low pH and oxidation-reduction potential (ORP).

Water quality determined on site for Tailrace and EB I is presented in Table 2. As stratification progressed the pH decreased, and although it dropped in both the epilimnion and hypolimnion, there was a concentration gradient from the surface to the bottom for all months except April and December when the reservoir was mixed. In both October and November the pH in the hypolimnion was essentially neutral. In addition, once anoxia developed in the hypolimnion, the ORP dropped precipitously until November when it reached -227 mV. Following the development of the highly reducing environment in the hypolimnion, the H_2S began to accumulate reaching 9.5 mg/L by November. The strong reducing conditions which were present in the hypolimnion by August would have provided the proper environment for sulfate reduction to take place. Prior to that time, there would be little or no accumulation of H_2S even under anoxic conditions given the neutral or basic pH values observed during the study. However, under anaerobic conditions combined with a declining ORP below 100 mV the reduction of sulfate to H_2S can result in an accumulation of H_2S in the hypolimnion of eutrophic systems as summer stratification progresses. Much of the H_2S formed would be expected to react with Fe^{++} forming insoluble FeS and precipitating out. High levels of H_2S would only be expected to develop after much of the Fe^{++} had been removed from the hypolimnion as precipitating FeS, and with H_2S reaching 9.5 mg/L by November, this appears to have been the case. These conditions would also favor the accumulation of H_2S from an external source such as a spring.

Although H_2S concentrations were not quantitatively measured in the atmosphere, atmospheric H_2S was detected by USBR employees at the power generating facility by August. The odor persisted until shortly after October 13 at which time power generation was suspended and controlled releases were terminated for the year until January 11, 1999 when power generation resumed. This is in contrast to the fall of 1997 (Canavan 1998), when the odor of H_2S was not detected until September and persisted until the reservoir underwent mixis in December, long after controlled releases were terminated on September 24. Even though the progression of stratification and subsequent turnover of the reservoir was similar between the two years, the development and persistence of H_2S was markedly different.

Table 2. Water quality determined on site at Tailrace and EB I. (E) epilimnion, (H) hypolimnion.

Site	Date	Depth (m)	Temp (°C)	pH	DO (mg/L)	Conductivity (μmhos/cm)	ORP (mV)	H_2S mg/L
EB I (E)	4/21/98	7	13.1	8.8	9.8	597	127	-
EB I (H)	4/21/98	44	10.3	8.6	9.3	600	135	-
Tailrace	4/21/98	1	11.0	8.6	9.4	595	152	-
EB I (E)	5/27/98	7	16.5	8.8	9.4	550	132	-
EB I (H)	5/27/98	44	11.8	8.1	6.3	550	149	-
Tailrace	5/27/98	1	11.8	8.2	6.3	546	170	-
EB I (E)	6/29/98	7	21.8	8.5	8.1	576	136	-
EB I (H)	6/29/98	44	12.7	7.7	2.4	583	156	-
Tailrace	6/29/98	1	15.8	8.2	4.8	568	103	-
EB I (E)	7/24/98	7	24.2	8.3	5.8	590	114	-
EB I (H)	7/24/98	44	13.2	7.5	0.5	604	133	-
Tailrace	7/24/98	1	13.5	7.6	3.1	626	120	-
EB I (E)	8/21/98	7	25.1	8.1	5.5	585	128	-
EB I (H)	8/21/98	44	13.6	7.4	0.0	606	-200	0.7
Tailrace	8/21/98	1	13.8	7.5	2.1	639	145	0.7
EB I (E)	9/22/98	7	24.0	8.1	5.8	572	137	-
EB I (H)	9/22/98	44	14.2	7.3	0.0	592	-200	1.9
Tailrace	9/22/98	1	14.2	7.5	2.2	545	-129	0.4
EB I (E)	10/19/98	7	19.2	7.8	5.9	593	130	-
EB I (H)	10/19/98	44	14.5	7.1	0.0	607	-220	9.1
Tailrace	10/19/98	1	14.6	7.4	4.2	697	-0.07	below detection limit
EB I (E)	11/16/98	7	15.6	7.6	5.9	603	134	-
EB I (H)	11/16/98	44	14.9	7.1	0.1	615	-227	9.5
Tailrace	11/16/98	1	16.1	7.6	8.7	500	0.062	below detection limit
EB I (E)	12/14/98	7	12.6	7.6	6.5	604	142	-
EB I (H)	12/14/98	44	12.4	7.7	6.3	602	151	below detection limit
Tailrace	12/14/98	1	11.6	7.9	7.8	665	151	below detection limit

Conclusions

The source of the H_2S has been speculated to be either from an underground spring entering the reservoir below the hypolimnion, or from production in the hypolimnion as a result of reduction processes. Up to 25% of geothermal springs are known to contain elevated levels of H_2S (Revelle and Revelle 1988), but even though there are numerous geothermal springs in the area, none are presently reported to be discharging noticeable levels of H_2S. The most import variables for the accumulation of H_2S in the hypolimnion derived from either source would be thermal stratification, anoxia and low ORP. However, at this time the most plausible source of the H_2S is internal production from decomposition and microbial processes as a direct result of the effects of the reducing conditions present in the hypolimnion following stratification. The combined results for all water quality parameters measured during 1998 at Elephant Butte Reservoir are consistent with those found in hypereutrophic systems and tend to support this theory. The differences between the 1997 and 1998 study years suggest that there are also other dynamic variables driving this phenomenon, and that facility management may be playing an important role in both the extent and persistence of the problem.

Recommendations

An expanded study should be designed to further examine the environmental conditions favorable to the buildup of H_2S in the hypolimnion and its subsequent release through Elephant Butte Dam, and should contain the following objectives:

1) Determine whether the source of the of the H_2S is from an underground spring entering the hypolimnion, or the result of reduction of SO_4 in the hypolimnion.

2) Determine the critical environmental variables associated with the buildup of H_2S in the hypolimnion.

3) If it is an underground spring, determine either the general or specific location of the spring.

4) Determine the extent H_2S and other products of reduction processes are being transported downstream of the dam, and their effect on water quality in the Rio Grande below the dam.

Samples should be collected from sites located longitudinally (north to south) across the study area at a minimum of eight sites. This should include one site in the Rio Grande at San Marcial to provide background data on water entering the reservoir. Four sites should be located in the reservoir; with one site in the flood plain above the Narrows, a second site below the Narrows, a third site mid-way between the Narrows and the dam, and a fourth site located at the buoy line at the dam (EB I from the 1998 study year). Three sites should be located in the Rio Grande below the reservoir; and include retaining the site in the tailrace, a second at the highway bridge crossing

the river just below the power station, and a third site just below the outfall of Cuchillo Negro Creek. All sites should be located as close to the thalweg as possible. This is extremely critical in the upper end of the reservoir, as water entering the reservoir may flow along the bottom for long distances during certain times of the year with little exchange of minerals, nutrients, or other constituents with the surrounding waters.

Sampling should be conducted on a monthly schedule beginning in March or April 1999 and continuing for a period of twelve months. In-field water chemistry data should be collected at all sites, and should include temperature, pH, dissolved oxygen, conductivity, and oxidation-reduction potential. To obtain depth profiles of all parameters data should be collected at one meter intervals from the surface to one meter above the bottom at all reservoir sites. The presence of hydrogen sulfide in the hypolimnetic water should be determined in the field utilizing one of the colorimetric techniques. Any positive results for H_2S should be further confirmed and quantified with an ion selective electrode.

Water samples should be collected and analyzed for alkalinity, hardness, nitrate, nitrite, total nitrogen, total phosphorous, orthophosphate, sulfate, organic carbon, iron and manganese. Samples should be collected from the surface (0.5 m) at all river sites, and collected at a depth of 5 m and from one meter above the bottom at each of the reservoir sites. In the event of an algal bloom, additional samples should also be collected for chlorophyll and phytoplankton analysis. Inflow and discharge volumes indicating where the discharge water is coming from, ie. upper or lower penstocks, spillway, balance valves etc., reservoir levels, and weather conditions should be obtained from the Bureau of Reclamation field office records and added to the database of the study as deemed appropriate.

The ultimate goal(s) of further research should be to determine conditions favorable to the buildup of H_2S in the hypolimnion of Elephant Butte Reservoir and its subsequent release through Elephant Butte Dam. This information could then be used to formulate a predictive model to monitor the potential occurrence and severity for a buildup of H_2S during a given year, and would lead to the determination of whether or not the problem is preventable. In the event the problem is unpreventable, the information could be used to develop a remediation plan to minimize or prevent the release of H_2S into the Rio Grande and atmosphere below Elephant Butte Dam.

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NMSU Scientist Studies Mercury Problem in N.M. Reservoirs

Date: April 28, 1995
Contact: Colleen Caldwell, (505) 646-8126
Editor: Natalie Johnson, (505) 646-5714

LAS CRUCES - Elevated levels of mercury make some fish like wall-eye and bass caught in New Mexico's reservoirs dangerous to eat, according to the New Mexico Fish Consumption Advisory. New Mexico State University fish biologist is trying to find out where the toxic metal is coming from and how it's affecting the ecosystem.

"There is no reason why we should have mercury in our diet, because it is toxic at high levels and non-essential," said Colleen Caldwell, an adjunct professor with NMSU's fishery and wildlife sciences department. "The main t7oute that humans get mercury in their systems is by eating fish."

Mercury becomes a problem because it "biomagnifies" through the food chain. "That means plants that accumulate mercury are eaten by small fish, then bigger fish eat the smaller fish," Caldwell explained. "The mercury concentration increases up through the food chain and eventually gets into humans.,,

At high concentrations, mercury can cause nerve tissue degeneration and birth defects. According to the Fish Consumption Advisory, mercury levels are high enough that pregnant and nursing women should avoid eating piscivorous fish (fish-eating fish) caught in New Mexico's Caballo and Elephant Butte reservoirs. Some levels are so high that grown men are advised to eat no more than one fish a year, Caldwell added.

The advisory is published by New Mexico's health, environment, and game and fish departments. Although scientists have known about the high mercury levels since the 1970s, they still aren't sure where the metal is coming from. "We can't pinpoint the entry of mercury into our reservoirs, but we do have theories about where it might be coming from." Caldwell said.

One possibility is that the mercury was left behind when an amalgamation process was used to extract gold from ancient mines. Since then, the mercury may have washed into the reservoirs, Caldwell said. Or, mercury from coal plants in north-central and western New Mexico may be moving through the atmosphere and depositing on vegetation and the soil, eventually ending up in the reservoirs.

"When we get a big rainfall in New Mexico, we get a scouring across our landscape in which all of the rain gets diverted to the arroyos, eventually making its way to the reservoir," Caldwell explained.

Since joining NMSU last September, she has worked to get her mercury research program up and running. In one project, Caldwell is directing a doctoral candidate who is looking at what environmental factors are influencing mercury in the water and sediments at Caballo. "We're looking at the dynamics of how mercury, transformed into an organic form, accumulates in the sediment and then in the animals."

In a second study, Caldwell and another graduate student will consider how the mercury gets transferred up the food chain and its biological effects on double-crested cormorants living at Caballo and Elephant Butte reservoirs.

"We've collected cormorant eggs and are going to analyze the mercury levels the eggs received from the mother birds," Caldwell said. "When the chicks hatch, we'll go back and take blood and feather samples to study mercury levels."

Once Caldwell gets an idea about how mercury is currently affecting aquatic ecosystems in New Mexico, she said she'll use that information to decide how best to monitor the mercury problem.