

## F.E. Walter Reservoir Hydrogen Sulfide Investigation

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### Introduction

Personnel located at the F.E. Walter Dam and Lake in east-central Pennsylvania reported the occurrence of a noxious, hydrogen sulfide odor in early August. Ongoing water quality studies indicated that the lake was thermally stratified and anoxic conditions existed throughout the deeper waters of the lake. In response to a request for technical assistance through the Water Operations Technical Support (WOTS) Program, a supplemental water quality study was conducted to evaluate the observations of hydrogen sulfide odors at the project. Water quality constituents related to the occurrence of hydrogen sulfide odors (temperature, dissolved oxygen concentration, pH, hydrogen sulfide, reduced (ferrous) iron, and soluble manganese) were measured on August 13 and 14, 2002. Mr. Greg Wacik, Mr. David Williams (CENAP), and Mr. Ken Kulp (CENAB) participated in the study and Mr. George Sauls (CENAP) attended sampling efforts in the tailwater.

### Background

The formation of hydrogen sulfide comes from the reduction of sulfate (via a bacterial reaction) to various forms of sulfide species (depending upon the pH). Sulfur is present in surface and groundwater and comes from a variety of sources (soils, minerals, plant and animal tissues, and the atmosphere). In lakes and reservoirs that maintain dissolved oxygen concentrations above detection limits (e.g. are aerobic), sulfur is typically in the oxidized (sulfate) form and hydrogen sulfide is only formed when the intensity of the anaerobic (low or no dissolved oxygen) environment (e.g., water column or sediment) is conducive for microbial reduction. The production of hydrogen sulfide (via sulfate reduction) is preceded by biological utilization of dissolved oxygen, nitrate, oxidized manganese, and oxidized iron in waters that have been isolated from dissolved oxygen producing biota (e.g. algae). This sequence in the utilization (reduction of oxidized species) results in the sequential increase in concentrations of reduced forms of nitrogen (e.g., ammonia), manganese (e.g.  $Mn^{2+}$ ), iron ( $Fe^{2+}$ ), sulfur (e.g.,  $HS^-$ , and  $H_2S$ , depending on pH), and eventually carbon ( $CH_4$  or methane) in the bottom waters until the lake mixes and aerobic conditions redevelop. For bottom-level release projects, increased concentrations of reduced constituents are often observed in the discharge and downstream tailwater region. The removal or oxidation of reduced constituents is specific for each element and varies with discharge and site characteristics but water quality improves with increased distance from the dam. Typically, hydrogen sulfide degasses in the vicinity of the dam discharge and noxious odors are most notable.

Hydrogen sulfide is toxic to most organisms and produces a detectable odor at relatively low concentrations. Additional information on the production of hydrogen

sulfide in reservoirs and safety issues related to the formation of hydrogen sulfide can be found in the hydrogen sulfide folder at

<ftp://erdc-ftp.wes.army.mil/pub/outgoing/ellab/ashby>.

## Methods

Measurements of temperature, dissolved oxygen concentration, percent saturation, pH, and conductivity were conducted at 1-meter depths to 0.5 m from the bottom to define the vertical structure at three established in-lake stations (Bear Creek arm, Lehigh River arm, and the intake tower). Measurements were collected with a Hydrolab multiparameter probe, which was calibrated prior to use. Discrete samples were collected near the bottom and at a mid-level depth at each station using a Van Dorn type water-sampling device for measurements of hydrogen sulfide, ferrous iron, and soluble manganese (primarily reduced). A surface sample was also collected for chemical analysis in the vicinity of the intake tower. Samples were held in the dark until lakeside analyses could be conducted. Samples were collected in the tailwater at 5 locations, immediately below the stilling basin in a deep pool, the first riffle zone downstream from the pool and at the Lehigh River gauge, the PA Turnpike bridge, and the Tannery bridge crossing (the latter 3 samples were collected and analyzed on August 14, 2002 by Mr. Greg Wacik). Analysis for hydrogen sulfide, ferrous iron, and soluble manganese were conducted using a HACH DR2000 Spectrophotometer within 10 minutes of sample collection for the tailwater samples and approximately 1-2 hours after sample collection for the lake samples. Methods for analysis are described in HACH 1992.

## Results and Discussion

### Reservoir Water Quality

In-lake profiles (Figures 1-3) defined the extent of thermal stratification and anoxic conditions. In general, the lake was well-stratified with the thermocline at a elevation near 1370 feet National Geodetic Vertical Datum (NGVD) (or a depth of about 7 feet) and generally anoxic conditions below the thermocline. The anoxic region was well established throughout the deeper portions of the lake.

Concentrations of hydrogen sulfide ranged from 0.014 to 0.49 mg/l and were generally greater near the bottom of the lake. The higher concentration observed at mid-depth at the Lehigh Creek arm station is somewhat anomalous but is supported the detection of a sulfide odor in the sample at the time of collection and in the lab at the time of analysis.

Concentrations of ferrous (reduced  $\text{Fe}^{2+}$ ) iron ranged from 0.02 to 1.51 mg/l with greater concentrations in the bottom waters at the intake tower station. Manganese was only measured in the bottom water at the intake tower station and was 0.726 mg/l. Given the dissolved oxygen concentration (near 0 mg/l) and pH (6.2 standard units) the manganese was most likely to be in the reduced ( $\text{Mn}^{2+}$ ) and therefore, soluble form.

### Tailwater Quality

Operation records indicated a discharge of near 250 cubic feet per sec (cfs) on August 11, 492 cfs on August 12, 246 cfs on August 13, and 340 cfs on August 14.

Temperature and dissolved oxygen values of 20.2 °C and 8.72 mg/l (97% saturation) were observed in the tailwater at the time of sample collection on August 13. Hydrogen sulfide concentrations ranged from 0.003 mg/l at the most downstream sampling site to 0.047 mg/l at the PA Turnpike Bridge (the next site upstream). Lower concentrations near the stilling basin resulted in a peak in concentrations in the downstream region of the tailwater (Figure 4). The mechanism for the greater concentrations of hydrogen sulfide in the tailwater downstream from the dam was not readily apparent but could be related to sample collection on different dates with changes in discharge (e.g., increased discharge on August 14 could have resulted in increased release of deeper water that would have resulted in increased hydrogen sulfide concentrations. Soluble iron (measured as ferrous ( $\text{Fe}^{2+}$ ) and ferrous plus ferric ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) responded as would be expected with concentrations decreasing with time (e.g., distance) from 0.66 to 0.18 mg/l for ferrous and from 0.88 mg/l to 0.58 mg/l for ferrous plus ferric iron (Figure 4). Rapid changes in concentrations of reduced iron (e.g., minutes due to rapid oxidation to particulate ferric forms) would be expected to overshadow impacts of changes in discharge as was observed for hydrogen sulfide concentrations. Response to changes in discharge (e.g., peak concentrations in the downstream region of the tailwater) has been observed for total iron and turbidity (Ashby et al. 1999). Manganese concentrations ranged from 0.01 mg/l to 0.88 mg/l with the maximum concentration observed at the first riffle immediately downstream from the pool below the stilling basin. This value was higher than the concentration observed in the pool below the stilling basin (0.44 mg/l), possibly due to an increased residence time at the sample collection point, which was at the bank and well out of the discharge flow field. Increased residence time would allow for increased oxidation and mixing with release waters of different concentrations associated with changes in discharge.

### Summary and Conclusions

Conditions conducive for the formation of hydrogen sulfide in the bottom waters were observed at the three in-lake stations at F.E. Walter Reservoir and the formation of hydrogen sulfide was confirmed with actual measurements. Concentrations of hydrogen sulfide in the discharge were within the range that would, and did, produce a detectable smell. Although measurable concentrations of hydrogen sulfide were observed in the discharge and downstream, adverse impacts to the fisheries were not observed.

Increased concentrations of ferrous iron in the discharge resulted in the “coating” of rocks with a rust-like (iron oxide) “coating” in the vicinity of the tailwater near the dam. This type of coating can negatively impact the community structure of aquatic systems (McKnight and Feder 1984, coat bacteria (Ghiorse 1984) and macroinvertebrates (Gerhardt and Westermann 1995) reduce food resources (Wellnitz et al. 1994), and have toxic effects on respiratory organs of biota (Koryak et al 1972). While no immediate adverse impacts to the aquatic community were observed, sampling of the benthic invertebrate community should occur to evaluate potential impacts. Increased concentrations of reduced manganese can increase treatment costs at water treatment facilities but observed concentrations should not be a concern since there are no water supply intakes in the region of the affected tailwater.

The development of anoxic conditions resulting in the production of hydrogen sulfide and reduced iron and manganese, previously unobserved in the release water at

the project, may be attributed to increased material loading and associated with increased runoff. Higher loads of organic material and soils likely increased the availability of sulfur, iron, and manganese, coupled with warmer bottom water (increasing the rate of microbial processes), resulted in an increase in the intensity of anoxic conditions and mobilization of reduced constituents. The potential for a re-occurrence of similar conditions in subsequent years exists (if there was a significant material load retained in the lake) and monitoring should be continued next summer using a strategy similar to that used this year.

The major adverse impact was the potential health threat to project personnel associated with the degassing of hydrogen sulfide. Health and safety information referenced above was provided to project personnel. Degradation of concrete and steel structures exposed to hydrogen sulfide is also a common phenomenon and an inspection of appropriate sites at the project should be considered and conducted after the lake has mixed and prior to stratification next year.

## References

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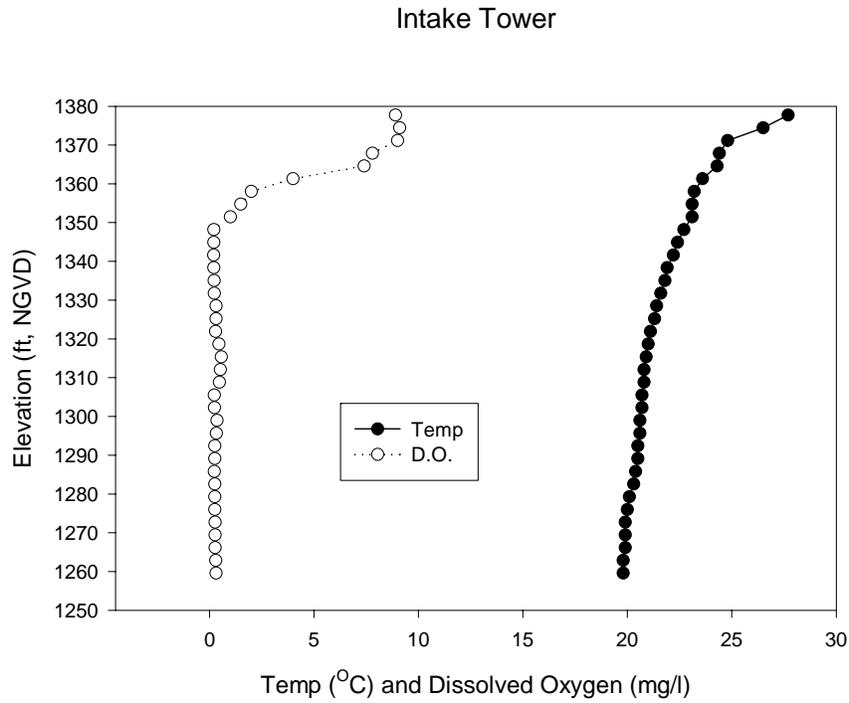


Figure 1. Temperature and dissolved oxygen concentrations at the intake tower.

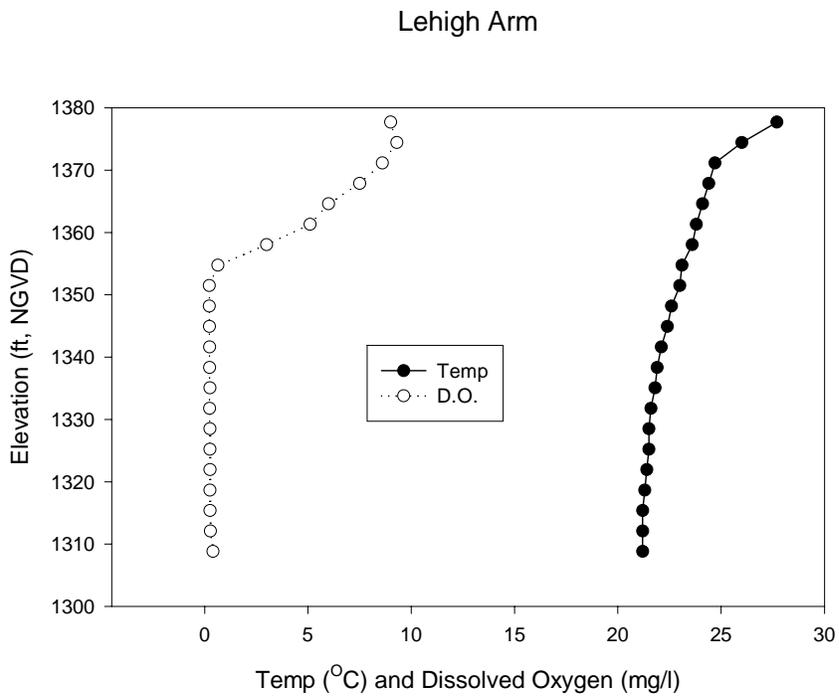


Figure 2. Temperature and dissolved oxygen concentrations in the Lehigh River arm.

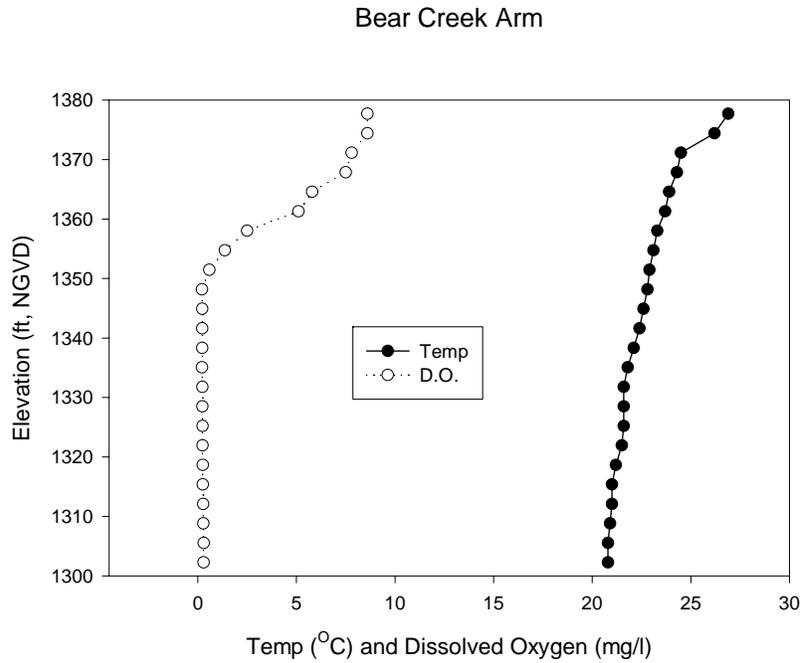


Figure 3. Temperature and dissolved oxygen concentrations in the Bear Creek arm.

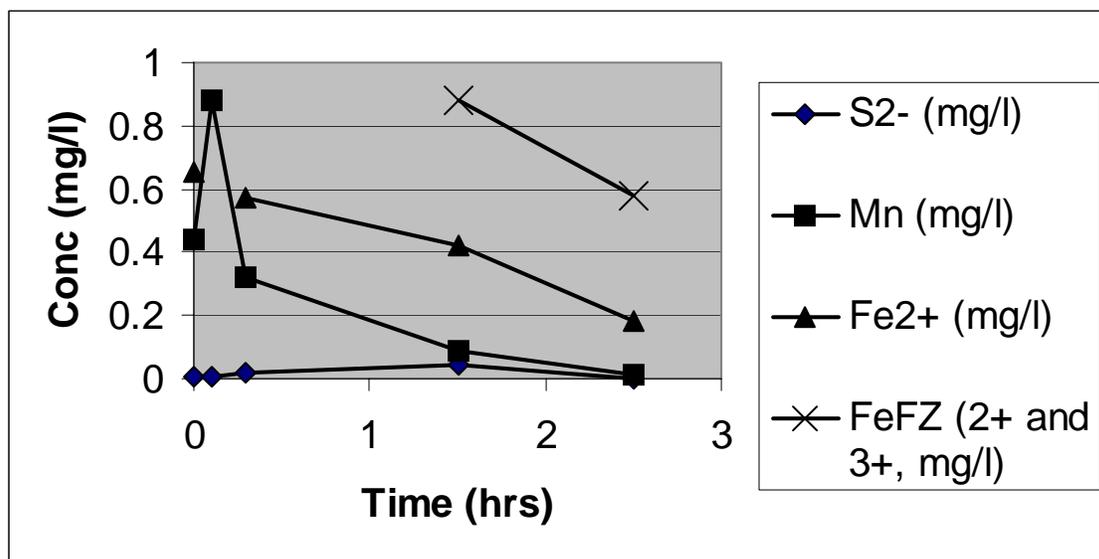


Figure 4. Concentrations of sulfide (S<sup>2-</sup>), manganese (Mn), and iron (as ferrous Fe<sup>2+</sup> and ferrous and ferric (Fe<sup>3+</sup>)) in the tailwater as a function of estimated travel time.