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STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY

MEMORANDUM
June 10, 1981

To: John Bernhardt

From: Joseph Joy

Subject: Sulfide Concentrations in Vicinity of LOTT STP Bypass Outfall, Budd Inlet

As part of the Budd Inlet fish kill investigation, a limited sulfide/D.O. concentration survey was undertaken. The survey was accomplished on June 5, 1981 during a -2.5 foot low tide. The survey encompassed four sites in the vicinity of the LOTT STP bypass outfall (Figure 1). This was where approximately 50,000 recent hatchery-released juvenile chinook salmon were found dead on June 2, 1981.

METHODS

At each site a surface and near-benthic water sample was taken. Each sample was analyzed for total sulfides using a LaMotte-Pomeroy^R field kit, dissolved oxygen by Winkler's azide modification method, pH using a field meter, and temperature by mercury thermometer. Depth samples were retrieved by a Kemmerer sampler. All sampling occurred between 1400 and 1605 hrs.; no change in tide level was evident over the course of the survey.

RESULTS AND DISCUSSION

Results of these analyses are presented in Table 1. Included are calculated undissociated H_2S values based on temperature, total sulfide concentrations, and pH concentrations (APHA, 1976; Broderius and Smith, 1976). The calculated H_2S values may be higher than true undissociated H_2S concentrations because total dissolved sulfides were not measured. Metal complexes in the samples could contain sulfide compounds and thereby increase the total sulfide values. Also, reported dissolved oxygen levels may be lower than actual levels because sulfides interfere with the Winkler method. Slight delays in fixing samples after collection also may have contributed to this problem.

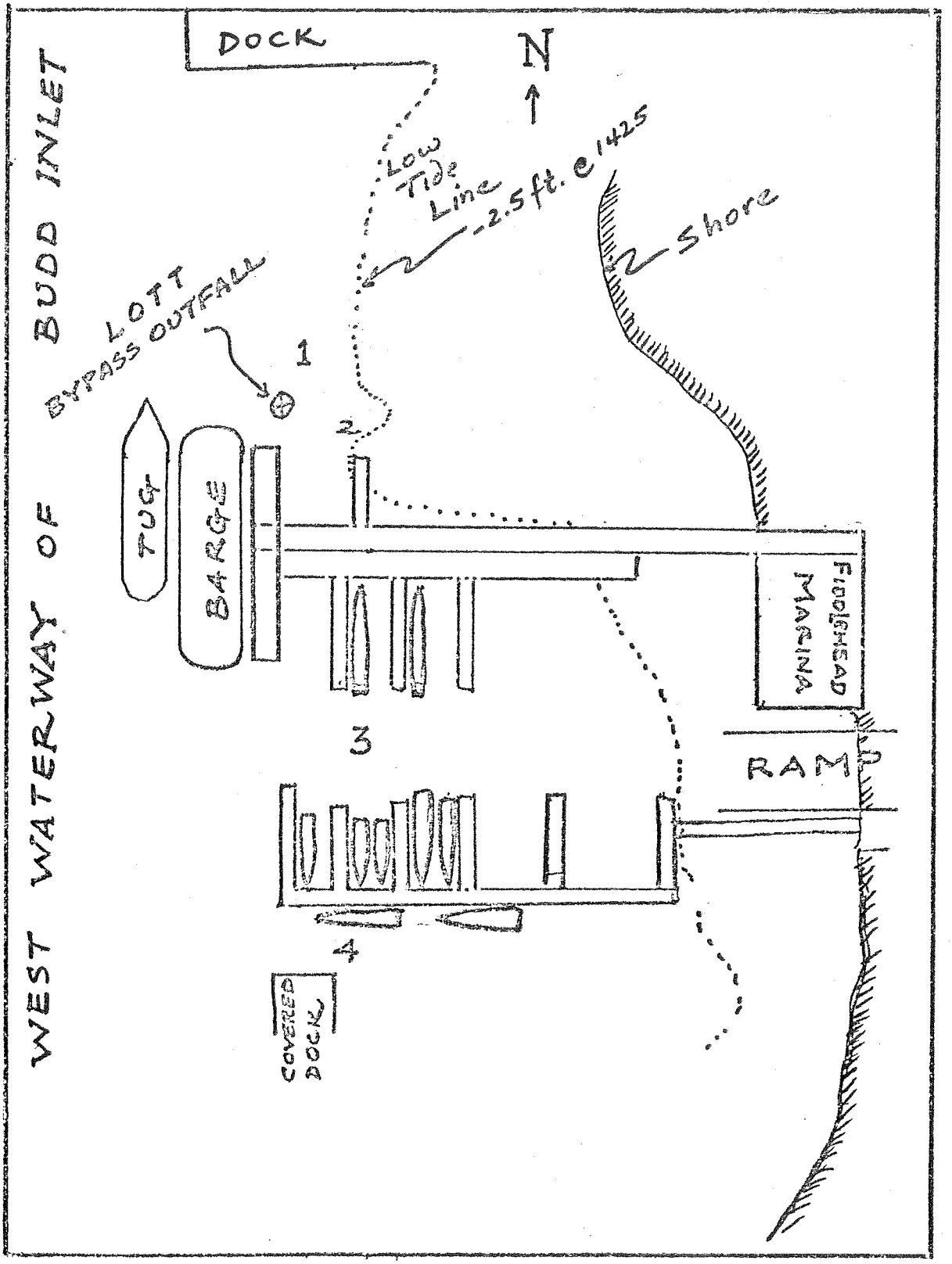

Fig. 1. Station locations for H_2S/D.O. survey on Budd Inlet, June 5, 1981.

Table 1. Results of Water Sample Analyses Near LOTT Outfall Bypass, Budd Inlet, on Jun

Station	Time	Depth (feet)	Dissolved Oxygen (mg/L)	Total Sulfide (mg/L)	H_2S[1/] (mg/L)	Temp
1	1410	0	4.55	0.20	0.14	
	1425	6	4.70	0.30	0.16 (0.15)[2/]	
2	1440	0	3.65	0.35	0.26 (0.25)	
	1500	1.5	3.40	0.80	0.51 (0.50)	
3	1520	0	9.10	N.D.	N.D.	
	1540	6	4.10	0.40	0.17	
	1615	7.5	6.00	--	--	
4	1555	0	8.35	<0.10	<0.05	
	1605	9	5.75	0.25	0.16	

[1/] Calculated from Table 9, pg. 70 Broderius, S., and L. Smith, Jr. (1976).

[2/] Calculated from Standard Methods (APHA, 1976) using conductivity at 33,000 umhos/cm f

N.D. = None Detected.

STP effluent could be seen breaking the surface at a vigorous rate from the outfall during the survey. Exposed benthic sediments along the shore near the outfall looked rich with organic detritus of outfall origin. Gas bubbles were seen rising in the vicinity of Sites 1 and 2. This phenomenon is common to areas where benthic organic decomposition is taking place. Grey strands of sewage fungus were seen attached to the finger piers below the waterline.

Highest H_2S and lowest D.O. concentrations were found at Site 2. This site was the shallowest of the four sites and probably the most protected against currents and surface water movements. Low pHs also were found at Site 2 and also contributed to a higher percentage of calculated H_2S being present in the sample.

Station 1, although near the outfall, did not have as high sulfide concentrations. Water movement in the area was swift and could have played a part in reducing sulfide concentrations.

Depth samples at Sites 3 and 4 contained some sulfides and lower D.O. concentrations than their respective surface samples.

The EPA criterion for all water is set at 2 ug/L (.002 mg/L) undissociated H_2S (U.S. EPA, 1979). Undissociated H_2S is dependent upon the total dissolved sulfide concentration, the pH, and temperature of the water. The dissolved oxygen concentration and ionic strength of the solution also are involved. Basically, as the pH falls below 7.0, the percentage of H_2S increases while the percentage of HS^- decreases. The EPA standard refers to the H_2S fraction of total dissolved sulfides.

There has been some criticism of this standard especially as it relates to marine waters (Thurston, Russo, Fetterolf, et al., 1979). Critics point out that bottom fish and other species inhabit estuarine areas of natural sulfide production as well as areas around outfalls where the 2 ug/L H_2S standard often is exceeded by two or three orders of magnitude.

Still, there are some studies that suggest that juvenile salmonoids are affected by H_2S at concentrations found during this study. It was found that 30 percent and 90 percent mortalities had occurred with juvenile chinook salmon kept for 72 hours at total dissolved sulfide concentrations of 1.00 and 1.78 mg/L, respectively (Holland, et al., 1960). Using the tables and nomograph mentioned earlier, these concentrations exhibited undissociated H_2S concentrations of .21 ppm and 0.38 ppm in water of the following characteristics (Table 2):

Table 2. Physical and Chemical Characteristics of Water Used in H_2S Toxicity Tests (Holland, et al., 1960).

pH = 7.7	Temperature = 9.4°C
D.O. = 8.7	Specific Gravity = 1.0235
Chlorinity = 17.8 o/oo	Total Alkalinity = 100 ppm

A 96-hour LC_{50} for juvenile rainbow trout in freshwater was found to be 0.0181 mg/L H_2S at a pH of 7.7 and at 12.3°C (Smith, et al., 1976). The lethal threshold concentration after 17 days' exposure was found to be 0.0121 mg/L H_2S in the same study.

A positive correlation between a total sulfide concentration greater than 0.3 mg/L and pink and chum juvenile salmon mortalities was seen at Port Angeles Harbor pulp mill outfalls (Ziebell, et al., 1970). Exposure to 0.5 mg/L total sulfides caused immediate distress in these fish near these outfalls. Eleven years later, mortalities occurred although pulp discharge had been diverted or ceased (DOE, 1976). Organic decomposition in sludge beds and evolving sulfides were considered to cause the mortalities observed.

There are some questions concerning the mode of toxic action of H_2S upon fish. Listed symptoms are: irrigation and frenzied rushing; then respiratory paralysis, stupor, loss of equilibrium and edema in the gill areas which causes suffocation (Tsai, 1975). Whether molecular level respiration interferences and enzyme inhibition also contributes to death is unknown (Broderius and Smith, 1976).

Department of Fisheries livebox investigations in the outfall vicinity indicated that the cause of fish death was other than suffocation alone (Clark, 1981). Fish were said to have internal organ damage and hemorrhages. Studies on effects of 1:3.1 to 1:8.5 dilutions of synthesized kraft waste effluent in sea water produced fish with discolored livers, internal hemorrhages, and opaque pupils (Holland, et al., 1960). Calculated total dissolved H_2S concentrations in these experiments ranged from 0.53 mg/L to 0.20 mg/L, respectively.

CONCLUSIONS

Whether oxygen starvation and H_2S poisoning were the primary causes of the fish kill in Budd Inlet is unknown. All data are not in, but it is possible that the fish were exposed to similar levels of H_2S and low dissolved oxygen on June 2. During this study, it was observed that a low tide cycle would probably force fish toward the marinas and outfall if they were in the west channel of the inlet. The mud flats west of the apparent river channel were fully exposed directly across from the survey area.

If further investigations are made on sulfide and D.O. concentrations, dissolved sulfide should be measured and D.O. analyses should be made using a technique without sulfide interferences.

JJ:cp

Attachments

cc: Jim Krull
Larry Peck, WDF

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