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AQUEOUS STUDIES OF HYDROGEN SULFIDE RELEASES FROM A HEAVY WATER EXTRACTION FACILITY

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AQUEOUS STUDIES OF HYDROGEN SULFIDE RELEASES FROM A HEAVY WATER EXTRACTION FACILITY

by

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Approved by

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ABSTRACT

Upsets in the operation of the wastewater strippers in the 400 Area of the Savannah River Plant have released hydrogen sulfide in quantities as large as 1800 kg to the effluent stream. Fish kills in the swamp area of Beaver Dam Creek have occurred following the large releases.

A literature survey revealed volatilization and oxidation as the major loss mechanisms of H_2S. Laboratory investigations supported the literature survey. The computer code for pollutant transport in a stream, LODIPS, has an option to account for sink-source effects in a stream. Volatilization and oxidation rate constants were developed for the sink option from two H_2S releases (18 kg and 118 kg) and results were predicted with LODIPS. Based on the predicted concentration-time profiles for various hypothetical cases, releases as small as 568 kg if discharged over a 30-minute period or releases as large as 1818 kg if discharged over a 360-minute period or less are lethal to swamp fish.

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AQUEOUS STUDIES OF HYDROGEN SULFIDE RELEASES FROM A HEAVY WATER EXTRACTION FACILITY

INTRODUCTION

Upsets in the operation of the wastewater strippers in the Heavy Water Extraction Facility in the 400 Area of Savannah River Plant (SRP) have released significant amounts (>1800 kg) of hydrogen sulfide into Beaver Dam Creek causing fish kills[1] in the swamp area. Using the computer code LODIPS,[2] a Beaver Dam Creek model of pollutant transport, developed from studies using a dye tracer, predicted downstream concentrations for selected release amounts and durations. Based on the concentration-time profiles of the model, lethal conditions for fish could be expected at the mouth of the creek at the Savannah River for a release of H_2S as small as 227 kg. Since previous releases of this magnitude did not result in fish kills, a study was initiated to evaluate H_2S behavior in the Beaver Dam Creek Area.

LITERATURE SURVEY

H_2S Aqueous Chemistry

H_2S behaves as a weak dibasic acid in aqueous solution. H_2S dissociates into hydrosulfide and sulfide ions depending on the pH of the solution (Figure 1):

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^= \qquad (1)$$

H_2S is lost from aqueous solutions by volatilization and oxidation. Maximum volatilization occurs at acidic pHs (infinitesimally dissociated) and ceases at basic pHs (infinitesimally undissociated). Figure 1 shows the relationship between pH and H_2S dissociation. Chen[3,4] has extensively investigated the oxidation of aqueous sulfide for freshwater systems. His data show oxidation occurs in the presence of the hydrosulfide ion only. Elemental sulfur was found to be the primary product of the oxidation reaction. The sulfur is slowly oxidized to sulfate by bacteria in an aerobic aqueous environment. The oxidation process will reverse (reduction) in an anaerobic aqueous environment.

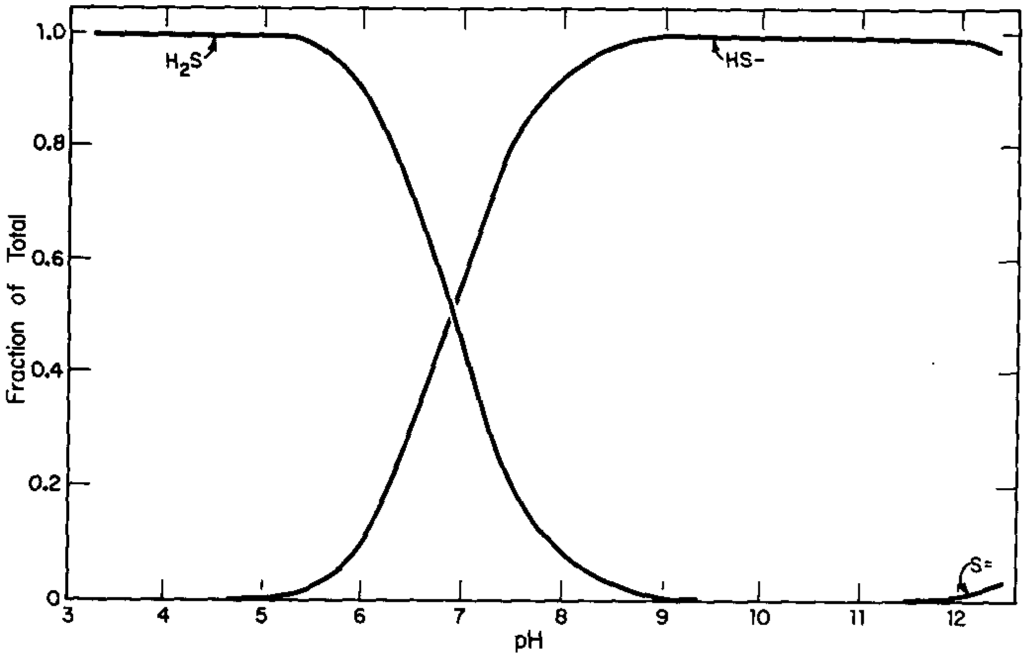

FIGURE 1. H_2S Dissociation in Aqueous Solution at 25°C

H_2S Toxicity to Fish

Information on H_2S toxicity to fish inhabiting the SRP swamp is scarce. Bonn and Follis[5] studied the H_2S susceptibility of channel catfish in relation to such factors as size and pH. A pH 7.0, death occurred to fingerlings at a concentration of 2.3 mg/L for 20 minutes and to advanced fingerlings at a concentration of 3.0 mg/L for 30-45 minutes. At pH 7.0, 3.2 mg/L was lethal to adults in about 30-45 minutes. Lethal conditions for fry channel catfish varied from 1.8 mg/L at pH 6.8, to 6.8 mg/L at pH 7.8 for a 3 hour exposure and a water temperature of 25-30°C. Minnows[6] and carp[7] were killed within 24 hours by H_2S concentrations in the range 5-7 mg/L. Two species of families common to the Savannah River Swamp are Spotfin shiners, which survived an H_2S concentration of 1.0 mg/L for 120 hours at 18°C before dying[8], and Orangespotted sunfish, which died at H_2S concentrations of 4.9-5.3 mg/L in about 10 minutes.[9]

LABORATORY INVESTIGATIONS

Aqueous Sulfide Methods to Detect Low-Level Concentrations

Aqueous sulfide solutions require analysis three minutes after sampling because of the volatilization and oxidation behavior.[10] The Hach Chemical Company manufactures two test kits. The Model HS-6 Test Kit makes use of the standard methylene blue procedure[10] to give purple color development proportional to the amount of sulfide present in the sample. Hach indicated the kit had a range of 0.01-3.0 mg/L H_2S, but our evaluation shows the effective range to be 0.1-1.0 mg/L. An attempt to replace the color comparator disc technique with a Bausch and Lomb Mini Spec 20 spectrophotometer to quantify the color change proved unsuccessful. A second method, the Model HS-7 Test Kit, also produced by Hach, uses an *Alka-Seltzer*® tablet to effervesce the H_2S from the water sample up through a paper disc in the top of the sample vial. The paper disc is treated with lead acetate and changes color (white-brown-black) in proportion to the amount of sulfide present. Hach indicated the kit had a range of 0.1-5.0 mg/L H_2S, but our evaluation shows the effective range to be 1.0-5.0 mg/L.

Pretreatment[10] was necessary to preserve a sample longer than three minutes. The analyses techniques required an acid-soluble sulfide.[10] Zinc sulfate (1 mL of 1N) was added to the sample container (500 mL) prior to collecting the sample. Sodium hydroxide (1 mL of 1N) was then added to precipitate the zinc sulfide. The zinc sulfide oxidizes slowly; hence, the sample cannot be preserved longer than a day.

Volatilization

Volatilization experiments were performed in a hood using sodium sulfide ($Na_2S \cdot 9\ H_2O$ - A.S.C. grade) as the stand-in for H_2S. The pH of the solution was adjusted to 4.8 by buffering with acetic acid-sodium acetate. In the first series of volatilization experiments, the solution was placed in a glass tray (volume - 28.94 cm × 17.15 cm × 1.91 cm) which was mounted on a magnetic stirrer for liquid agitation. The solution temperature was not controlled, but measured 20 ±1°C, and air flow above the liquid was adjusted to 30.5 linear m/min. Liquid concentrations were analyzed by the Hach Model HS-7 Test Kit, diluting the sample as necessary. A plot of the log of the concentration versus time gave the expected straight line (Figure 2). Regression analysis of the data yielded a correlation coefficient of 0.99 and a volatilization rate constant of 0.08 min^{-1}.

To evaluate the effect of solution depth on volatilization rate, the solution container was changed to a 1.0 L beaker (12.75 cm deep). Regression analysis of the concentration-time data yielded a correlation coefficient of 0.96 and a volatilization rate constant of 0.0095 min^{-1}. The volatilization rate increased about proportionately to the inverse of the depth in comparing the different containers. The rate was not directly proportional to the inverse of the depth because of container edge effects on air flow.

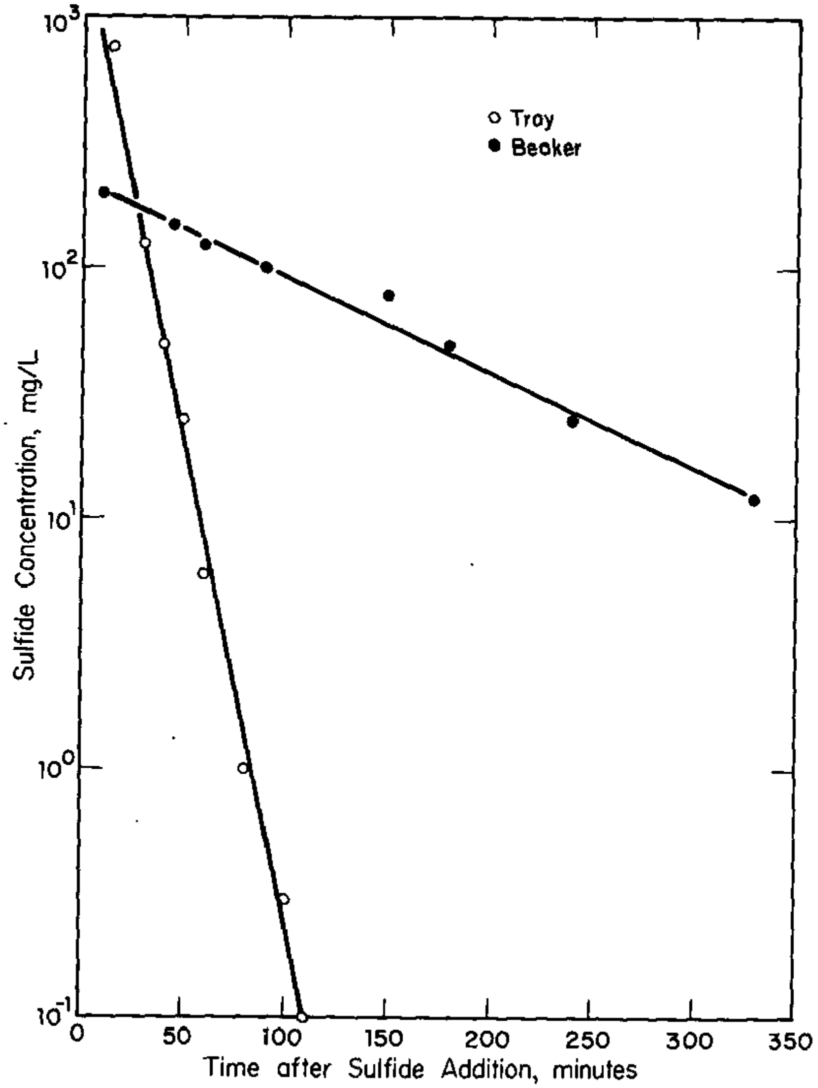

FIGURE 2. Volatilization of Sulfide in Distilled Water (pH 4.8 and Air Flow 30.5 mpm)

To evaluate its effect, the air flow was decreased to 15.2 linear m/min. The volatilization rate was found to vary proportionally with the square root of the air velocity as predicted from theory.

Oxidation

Oxidation experiments were performed with sodium sulfide as the stand-in for H_2S. The pH of the solution was adjusted to near neutral by buffering with sodium phosphate monobasic-sodium phosphate dibasic. Water for the solution was collected from Beaver Dam Creek and brought to room temperature (25 ±1°C) before proceeding. Using a magnetic stirrer for liquid agitation, sulfide was introduced into the water from a standardized sodium sulfide solution. Dissolved oxygen was measured with a portable Weston-Stack meter. Figure 3 shows some of the concentration-time profiles obtained. The solution at pH 11.3 was not buffered, and the pH remained constant during the experiment. The pH effect on oxygen depletion was the same as that observed by Chen.[4] However, comparison of oxygen depletion rates with those by Chen for the same experimental conditions (temperature, concentration, and pH) revealed a 30-fold increase in ours. This shows that the oxidizing rate is influenced by the creek water. A fine white precipitate (attributed to sulfur) was observed after oxidation of solutions with initial sulfide concentrations of 200 mg/L or greater.

FIELD EXPERIMENTS

Area of Study

Cooling water and waste water from the Heavy Water Extraction Facility combine in the 400 Area to form a channel known as the Girdler Sulfide (GS) Process Effluent. The water travels between the 400 Area and an outfall, noted as Location 1, in an underground pipe for about 760 m (Figure 4). Two-thirds of the discharge pipe is submerged at Location 1. The submergence is regulated by a pair of successive weirs, which expand the channel about 4-fold beyond normal for about 50 m. The GS Process Effluent and the Power Operation Effluent from the 400 Area combine approximately 600 m below the GS Process Effluent discharge pipe. On the GS Process Effluent, normal flow and temperature range from 45,000 Lpm and 38°C, in winter, to about 60,000 Lpm and 43°C, in summer. For the Power Operation Effluent, the temperature is nearly ambient (25 ±5°C) with flow ranging from 75,000 Lpm, in winter, to 115,000 Lpm, in summer. The effluents follow man-made channels prior to the swamp, and rocks placed in the channel for erosion control create several cascades

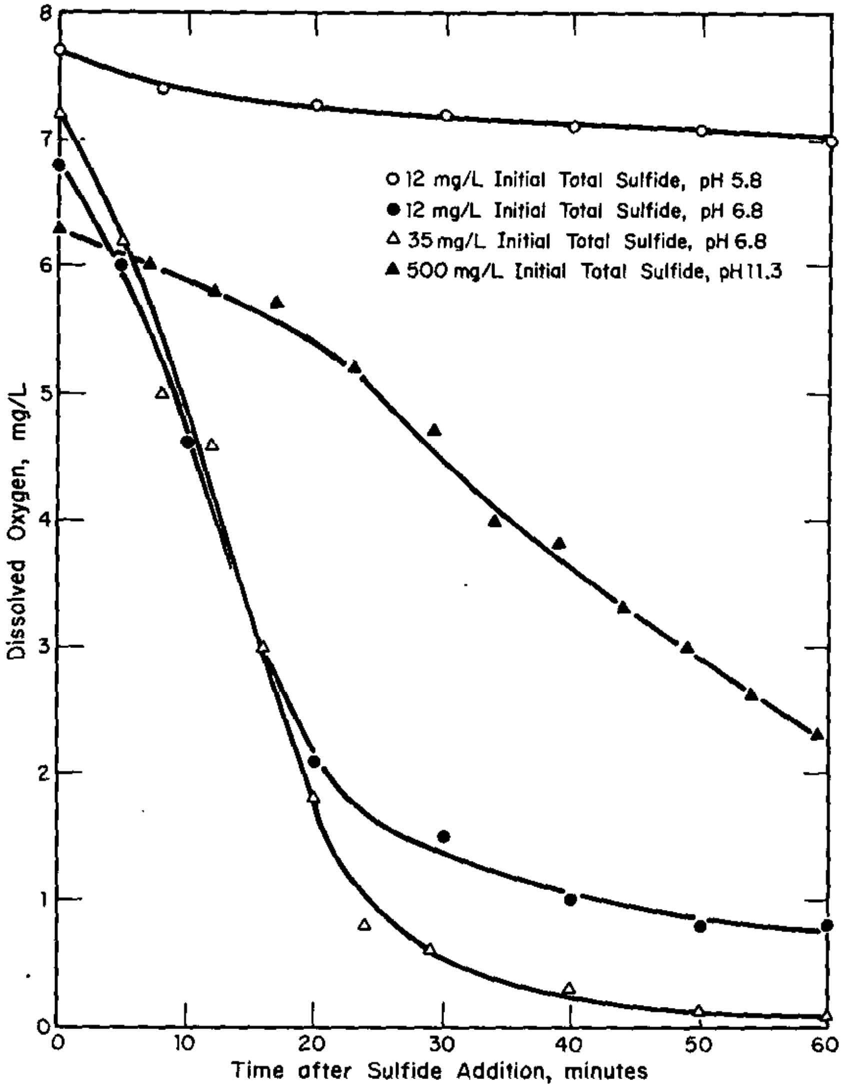

FIGURE 3. Oxidation of Beaver Dam Creek Water With Sodium Sulfide

on the GS Process Effluent. A relatively dense forest canopy grows from about 50 m below Location 1 to the mouth of the creek at the Savannah River, with the exception of the area around the delta.

Stream measurements for H_2S release No. 1 were made at Location 1 and Location 3 (Figure 4). Measurements were made at Locations 1, 2, and 3 during the second release. 400 Area personnel sampled in their area during both releases.

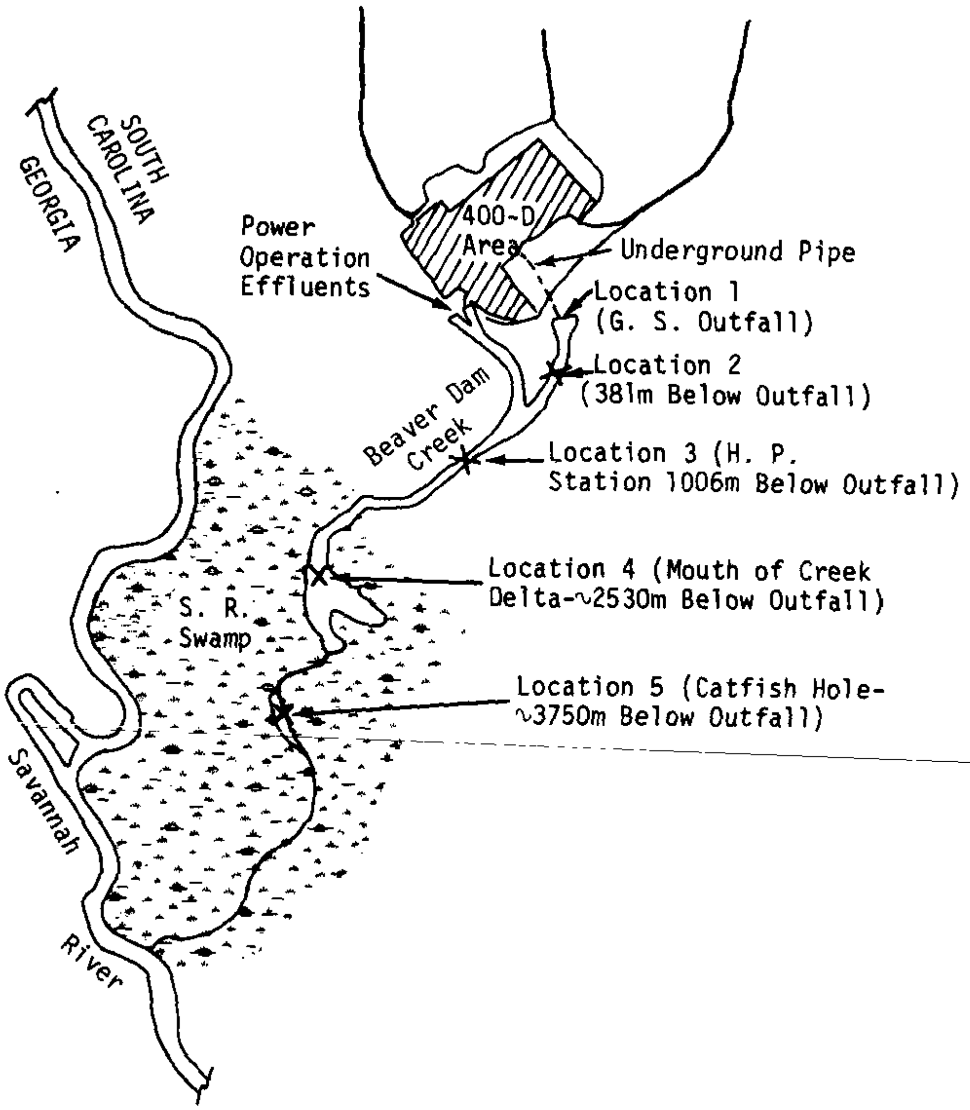

FIGURE 4. The Beaver Dam Creek Region Below the 400 Area at SRP

Safety Considerations

H_2S gas is very toxic to humans. According to the SRP Industrial Hygiene manual,[11] a person loses his ability to smell H_2S gas when he has been exposed to a concentration above 100 ppm from 2-15 minutes. Unconsciousness will result from an exposure of 500 ppm for two minutes or less, and death will result if exposure continues for thirty minutes or more. Death is spontaneous at concentrations in excess of 1000 ppm.

Each person participating in this test was equipped with a Scott "Air Pak" and a 3 minute bottle of air for escape. SRP Health Physics personnel used Dräger tubes to survey the H_2S concentrations in the air during the releases. Lead acetate paper was also used to indicate the presence of significant air concentrations of H_2S. The white paper turns brown at >1 ppm of H_2S concentration. The "Air Pak" was used briefly by the person sampling the liquid at Location 1 near the peak of the releases.

Two-way radio communication was maintained between each location and the Heavy Water Extraction Facility during the test.

Release No. 1

On July 15, 1977, 118 kg of H_2S was released into the GS Process Effluent in the 400 Area by steam reductions to a wastewater stripper in the Heavy Water Extraction Facility.

At Location 1, liquid samples were analyzed for H_2S concentration using the Hach Test Kits. A portion of the samples was preserved and the analyses confirmed in the laboratory after the experiment. A recording Hydrolab was used to monitor temperature, pH, dissolved oxygen (D.O.), and oxidation-reduction potential (ORP). Wind speed and direction were monitored at Location 1 about 5.5 m above the surface of GS Process Effluent. Health Physics Environmental Monitoring performed the liquid sampling and analysis at Location 3.

Figure 5 shows the measured H_2S concentrations in the stream at Locations 1 and 3 and in the air near the wall of the outfall at Location 1. The average wind speed was 4.4 km/hr at a wind direction of 150° during the release at Location 1. The wind direction was about 180° to the direction of stream flow (i.e., the air sampling near the wall was downwind from the stream).

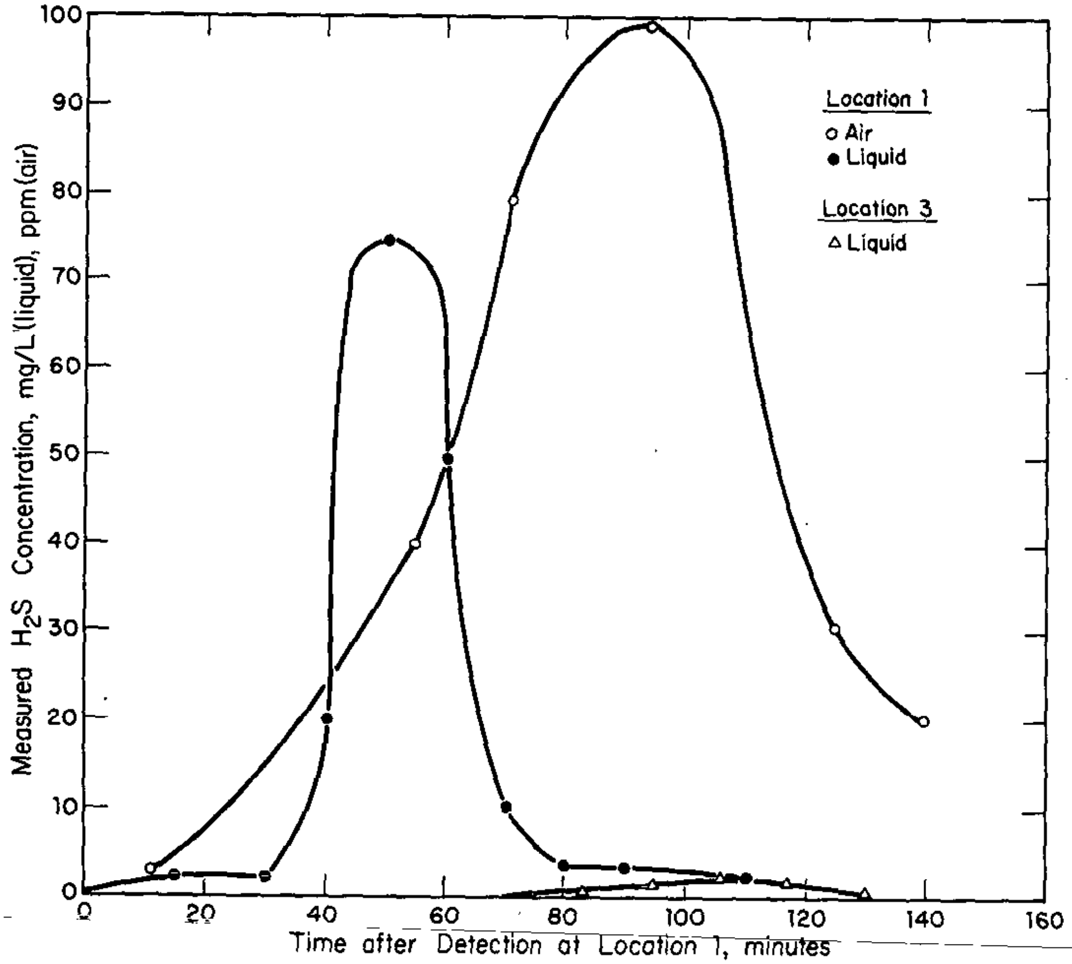

FIGURE 5. 118 kg H_2S Release Concentration-Time Profiles on the GS Process Effluent and Beaver Dam Creek

Figure 6 shows the variation in the values of the Hydrolab parameters (pH, D.O., and ORP) with the measured H_2S concentration at Location 1. Figure 7 is a photograph of the stream at the GS Process Effluent at Location 1 before the release. Figure 8 shows the same location near the peak of the release, revealing the milky appearance of the water after oxidation of the H_2S. The color of the water was the same as that observed in the laboratory studies with sulfide concentrations above 200 mg/L. Figure 9 shows the variation in the values of the Hydrolab parameters (pH and D.O.) with the measured H_2S concentration at Location 3. The major pH shifts at Location 3 are associated with caustic and acid regenerations of resins used in the water treatment process by the power operation of the 400 Area. The water temperature at Location 1 during the release was 43 ±0.5°C and at Location 3, it was 35.5 ±0.5°C.

Release No. 2

On August 30, 1977, 18 kg of H_2S was released into the GS Process Effluent. At Location 1, sampling was the same as in the previous release. The sampling at Location 2 was also similar except meteorological conditions were not measured at this location. Health Physics Environmental Monitoring performed the liquid sampling and analysis at Location 3.

Figure 10 shows the measured H_2S concentrations in the stream at Locations 1 and 3. No H_2S was detectable at Location 3 on this release. Air samples taken near the wall of the outfall at Location 1 were very erratic in H_2S concentration. The average wind speed at Location 1 was 3.2 km/hr with the direction varying from 90° to 240°. The air temperature was ∿30°C compared to 40°C on the first release. The maximum H_2S concentration at Location 2 was 1 ppm, 0.5 m above the water surface at the edge of the stream. This is the minimum detection level of the Dräger technique. Figures 11 and 12 show the variation in the pH, D.O., and ORP with H_2S concentration at Location 1 and Location 2, respectively. Water temperatures measured during the release were 41.5 ±0.5°C at Location 1, 41.0 ±0.5°C at Location 2, and 34.5 ±0.5°C at Location 3.

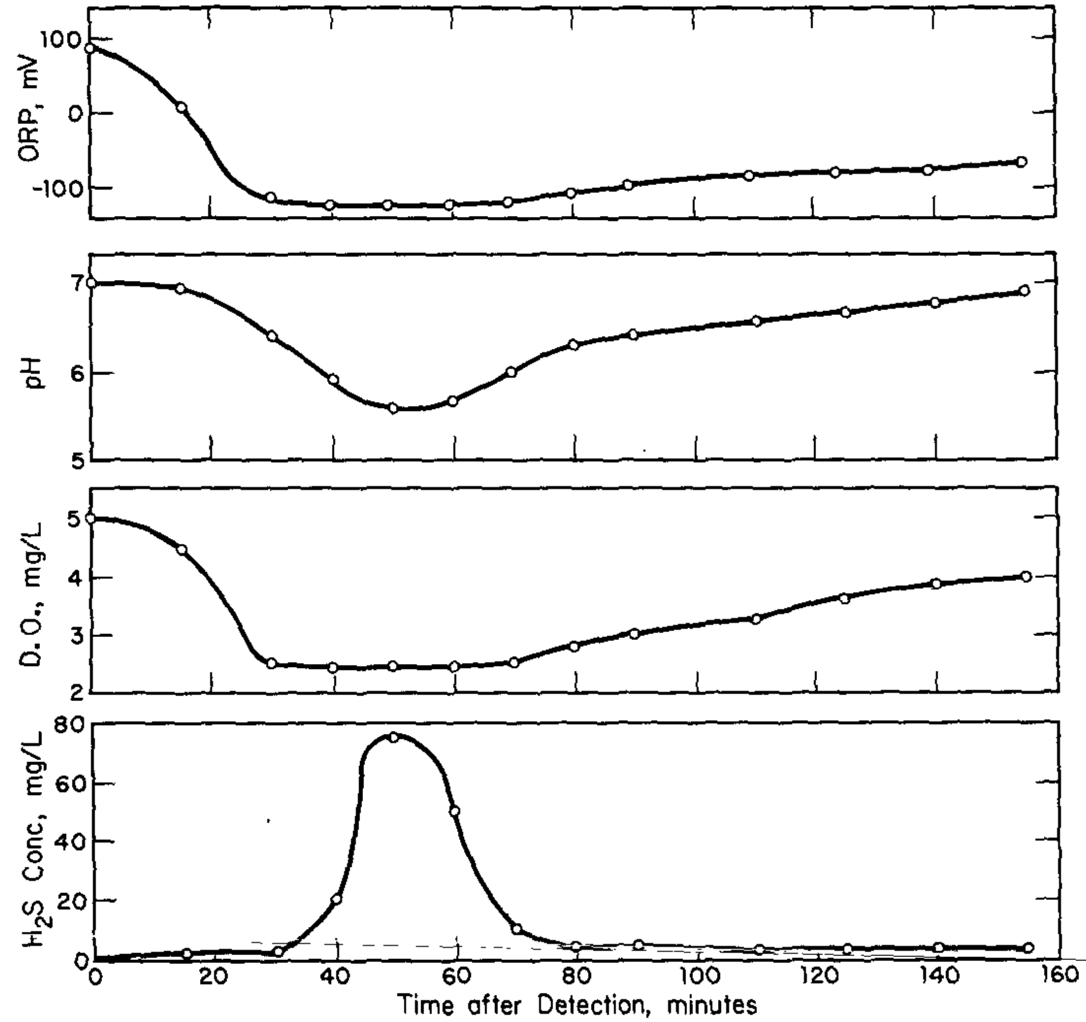

FIGURE 6. Aqueous Properties at Location 1 on GS Process Effluent for 118 kg H_2S Release

FIGURE 7. GS Process Effluent at Location 1 Prior to the H_2S Release

FIGURE 8. GS Process Effluent at Location 1 Near the Peak of the H_2S Release

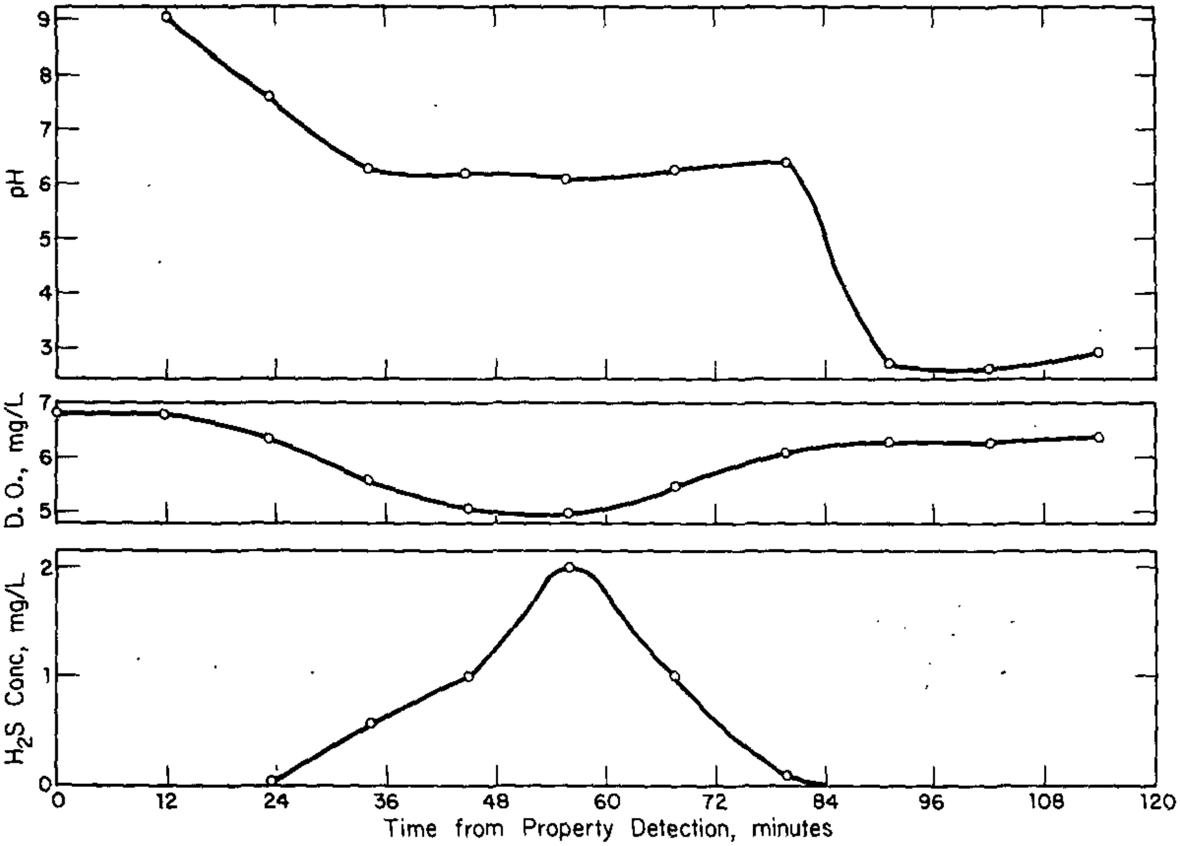

FIGURE 9. Aqueous Properties at Location 3 on Beaver Dam Creek for 118 H_2S Release

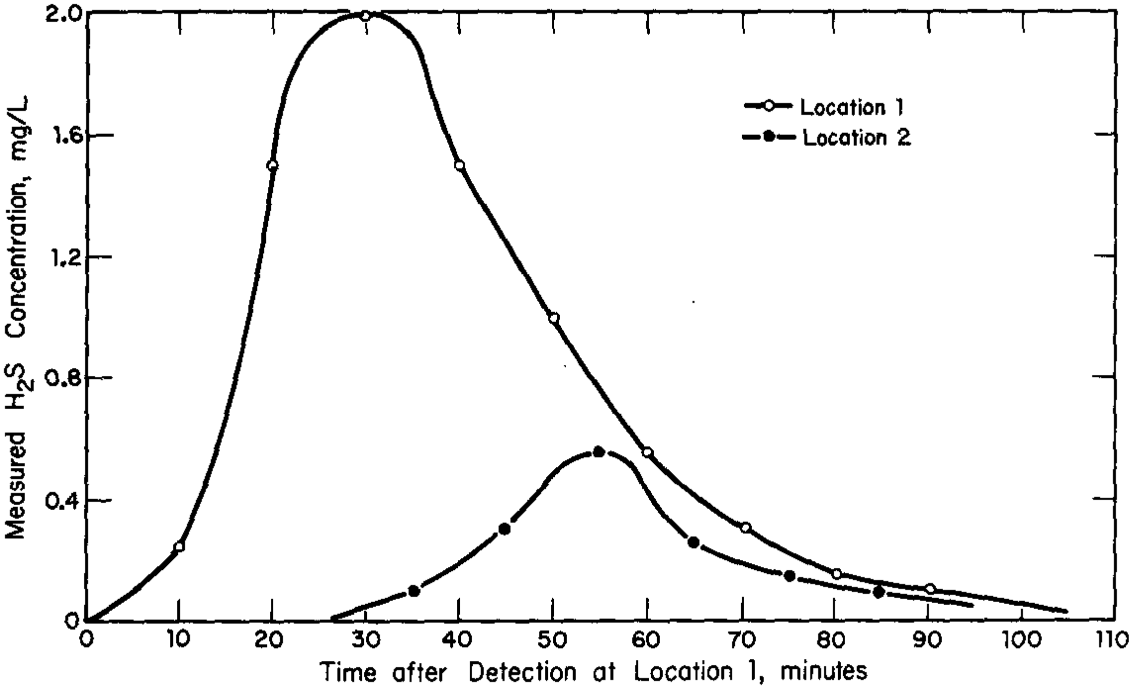

FIGURE 10. 18 kg H_2S Release Concentration-Time Profiles on the GS Process Effluent

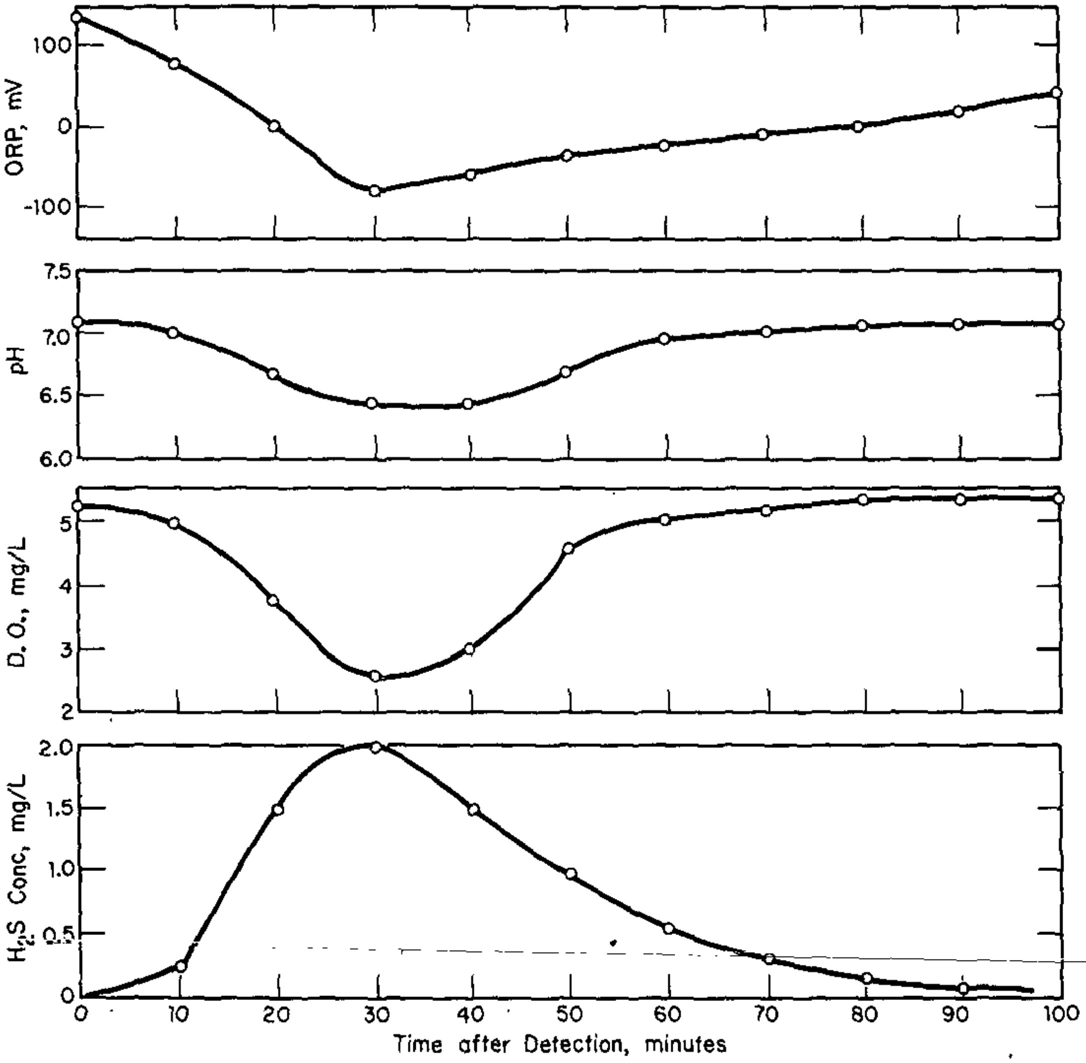

FIGURE 11. Aqueous Properties at Location 1 on GS Process Effluent for 18 kg H_2S Release

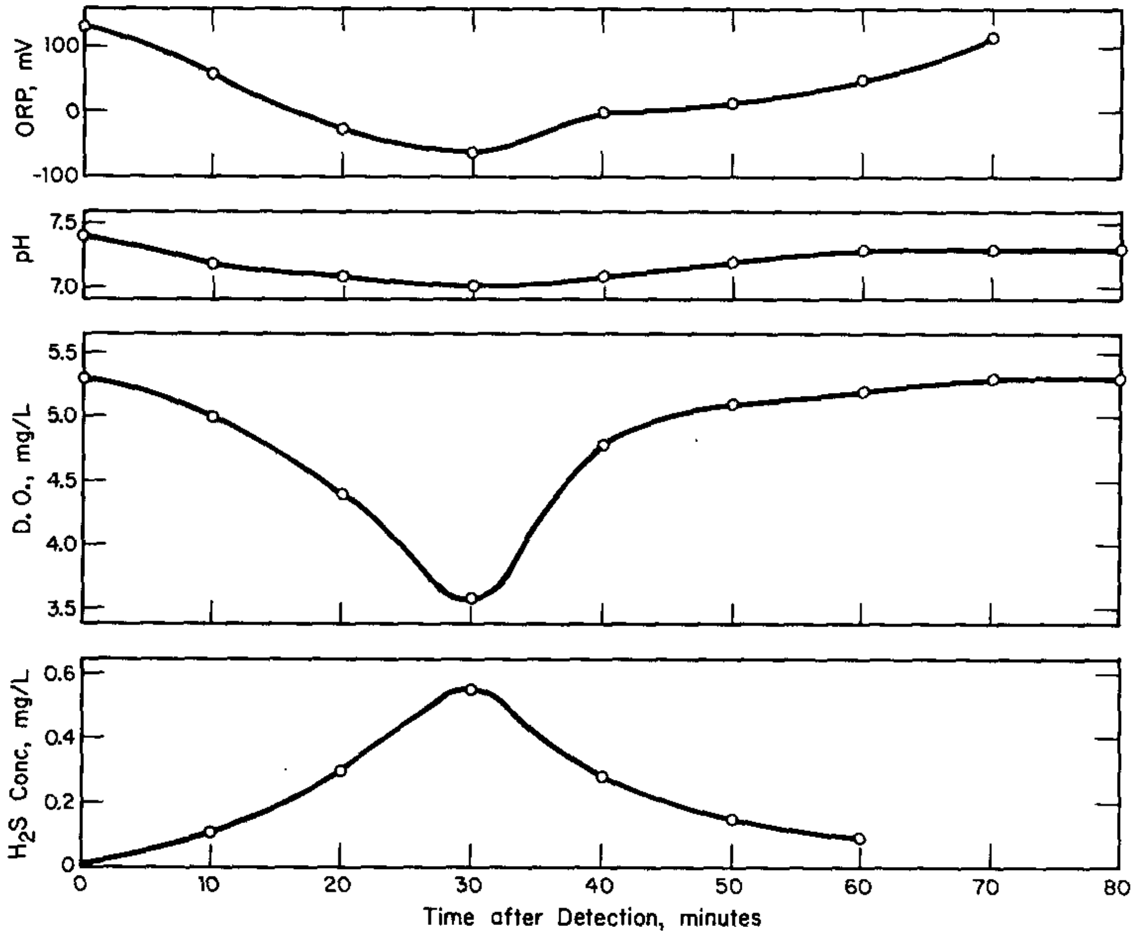

FIGURE 12. Aqueous Properties at Location 2 on GS Process Effluent for 18 kg H_2S Release

Data Discussion

The pH becomes most acidic at the maximum H_2S concentration on both releases, while the dissolved oxygen was least at the maximum H_2S concentration on the 18 kg release only (Figures 11 and 12). The dissolved oxygen reaching a minimum prior to the maximum H_2S concentration on the 118 kg release (Figure 6) is attributed to the pH decreasing below 6. Below pH 6, the hydrosulfide ion (HS^-) is insignificant (Figure 1). The laboratory experiment on oxidation at pH 5.8 (Figure 3) showed limited dissolved oxygen reduction. The ORP in Figure 6 shows the same profile as the dissolved oxygen. Hence, the flatness of the dissolved oxygen curve near the maximum H_2S concentration is not due to a desensitized oxygen probe.

Table 1 lists the amount of H_2S calculated at each sampling station from the time-integrated H_2S concentration and the volumetric flow rate of the stream. Table 1 also lists the H_2S that was calculated to be lost due to oxidation. The loss was derived from the dissolved oxygen deficit. The technique used is discussed in the section (LODIPS Model Development." H_2S loss due to oxidation for Release No. 1 calculates as 43% of the total loss (Location 1 to Location 3) and for Release No. 2 calculates as 56% of the total loss (Location 1 to Location 2). The percentages differ because as the amount of released H_2S increases, pH decreases and therefore so does oxidation. The H_2S loss not due to oxidation is attributed to volatilization, as the volatilization cannot be determined directly from the data.

MODELING H_2S TRANSPORT IN BEAVER DAM CREEK

LODIPS Model Development

LODIPS uses a one-dimensional equation to describe the tracer-pollutant transport in a stream:

$$\overset{\text{I}}{\overline{\frac{\partial C_{(x,t)}}{\partial t}}} = \overset{\text{II}}{\overline{D_{(r)}\frac{\partial^2 C_{(x,t)}}{\partial x^2}}} \quad \overset{\text{III}}{\overline{-\bar{U}_{(r)}\frac{\partial C_{(x,t)}}{\partial x}}} + \overset{\text{IV}}{\overline{\sum_{j=1}^{J} S_j}} \qquad (2)$$

where $C_{(x,t)}$ = concentration of tracer-pollutant in the stream at a point x and time t

$D_{(r)}$ = dispersion coefficient for reach r

$\overline{U}_{(r)}$ = mean transport velocity for reach r

S_j = uptake or release of tracer-pollutant by a dead zone* (j = 1) or interactive phase** (j > 1) within the stream

J = total number of sink/source effects

The terms in Equation 2 represent, respectively:

I temporal change in concentration

II longitudinal dispersion

III longitudinal convective mass transfer

IV sink/source effect within the stream

TABLE 1

Hydrogen Sulfide Amount at Sampling Stations and Loss Due to Oxidation Between Stations

Release No. 1

Location:	*400 Area*		*Location 1*		*Location 3*
H_2S Amount Present in Stream (kg)	118.2		102.3		10.0
H_2S Oxidized (kg)		15.0		39.4	

Release No. 2

Location:	*400 Area*		*Location 1*		*Location 2*
H_2S Amount Present in Stream (kg)	18.2		4.1		0.9
H_2S Oxidized (kg)		5.2		1.8	

---

* A relatively inactive area in a stream.

** Nonconservative processes such as ion exchange, sorption/desorption, volatilization, etc.

The fourth term represents the departure of a tracer-pollutant from bulk dispersion behavior. The model requires site specific characterization of the dispersion (D_r), the mean velocity ($\overline{U}_r$), and a dilution factor for each reach between sampling stations. Table 2 lists the calculated values for D_r, $\overline{U}_r$, and the dilution factors for the Beaver Dam Creek model from a Rhodamine WT dye study conducted prior to the H_2S releases. Rhodamine WT is a conservative tracer (no significant interaction with the stream or its environment). Only bulk dispersion is considered since no significant dead zone behavior occurred in the dye study.

Sink-source effects require first order rate processes. The sign convention is negative for sinks and positive for sources. Equation (1) in the Appendix describes the volatilization and oxidation removal of H_2S. Rate constants of total H_2S loss (K') were determined from the measured H_2S concentrations using the parameter estimate mode[2] of LODIPS. These were 0.0380/min for the first release (reach: Location 1 - Location 3) and 0.0589/min for the second release (reach: Location 1 - Location 2).

A rate constant of H_2S loss due to oxidation was calculated for each release by two methods. Both methods require that the H_2S concentration-time curves approach a normal distribution.

TABLE 2.

LODIPS Coefficients for the Predictive Calculations of H_2S Releases to Beaver Dam Creek

Reach (See Figure 4)	*Distance From Location 1 (M)*	*Mean Velocity (m/min)*	*Dispersion (m^2/min)*	*Stream Dilution Factor*	*Oxidation* (min^{-1})*	*Volatilization (min^{-1})*
L-1 to L-2	381	14.87	9.07	1.00	.0034	.0364
L-2 to L-3	1006	23.16	55.28	0.23	.0034	.0206
L-3 to L-4	2530	25.79	55.28	1.00	.0034	.0206
L-4 to L-5	3750	7.74	306.58	1.00	.0034	.0206

---

* 454 kg H_2S release only

The first method is based on the dissolved oxygen deficit at Location 1, but does not involve the reach modeled. Assumptions for the calculation are:

- Oxidation commenced with the mixing of the cooling water with the combined waste water (should be oxygen free) in the 400 Area,
- Fifteen-minute mean travel time to Location 1 after cooling water combines with the combined waste water from all units,
- One mole of oxygen reacted with one mole of sulfide,*
- Insignificant re-aeration of the water in the underground conveying system,
- Oxidation rate remained constant during the transport period (tested by calculating the rate constant by the second method).

The H_2S loss due to oxidation from the 400 Area to Location 1 is calculated by:

$$P_1\left(\frac{\text{millimole}}{32\text{ mg }O_2}\right)\left(\frac{34\text{ mg }H_2S}{\text{millimole}}\right) = A_1 \qquad (3)$$

where

P_1 = Time-integrated O_2 deficit at Location 1

A_1 = H_2S loss due to oxidation at Location 1

The oxidation rate from the 400 Area to Location 1 is:

$$K_o = \frac{1}{\bar{t}} \ln \frac{T_{400} - A_1}{T_{400}} \qquad (4)$$

where

K_o = Oxidation rate constant

$\bar{t}$ = Mean travel time between locations

T_{400} = Time-integrated H_2S concentration at 400 Area

---

* Chen[4] found this to be the ultimate stoichiometry in his studies of the auto-oxidation.

The time-integrated H_2S concentration in the 400 Area is:

$$(H_{400})/E_f = T_{400} \tag{5}$$

where

H_{400} = H_2S present in the 400 Area

E_f = Calculated flow rate for GS Process Effluent

The second method uses Equation (7) of the Appendix and requires the calculation of total H_2S loss rate constant (K') and a re-aeration rate constant (K_R) for the reach modeled. Accounting for the oxygen depleted, the re-aeration rate is:

$$K_R = \frac{1}{-\bar{t}} \ln \frac{P_{3,2}}{P_1 + O_{1-3,2}} \tag{6}$$

where

K_R = Re-aeration rate constant

$P_{3,2}$ = Time-integrated O_2 deficit at Location 3 (Release No. 1) and at Location 2 (Release No. 2)

$O_{1-3,2}$ = O_2 removed due to oxidation [(Location 1 to 3) - Release No. 1] [(Location 1 to 2) - Release No. 2]

The O_2 removed due to oxidation, Release No. 1 from Location 1 to Location 3 and Release No. 2 from Location 1 to Location 2, is:

$$H_{1-3,2}\left(\frac{\text{millimole}}{34 \text{ mg } H_2S}\right)\left(\frac{32 \text{ mg } O_2}{\text{millimole}}\right) = O_{1-3,2} \tag{7}$$

where

$H_{1-3,2}$ = H_2S loss due to oxidation from Location 1 to 3 (Release No. 1) and from Location 1 to Location 2 (Release No. 2)

The H_2S loss due to oxidation from Location 1 to Location 3 (Release No. 1) and Location 1 to Location 2 (Release No. 2) is solved for as follows:

$$\frac{T_1 - H_{1-3,2}}{T_1} = e^{-(K_o)(\bar{t})} \tag{8}$$

where

T_1 = Time-integrated H_2S concentration at Location 1

K_o = Oxidation rate constant from Equation (4)

The rate constant of total H_2S loss in Release No. 1 from Location 1 to Location 3 and Release No. 2 from Location 1 to Location 2 is:

$$K' = \frac{-1}{\bar{t}} \ln \frac{T_{3,2}}{T_1} \tag{9}$$

where

$T_{3,2}$ = Time-integrated H_2S concentration at Location 3 (Release No. 1) and at Location 2 (Release No. 2)

From the Appendix, Equation 7 is:

$$K_o = \frac{(K_R - K')(P_{3,2} - P_1 e^{-K_R\bar{t}})}{T_1 (e^{-K'\bar{t}} - e^{-K_R\bar{t}})} \tag{10}$$

For the first method, the oxidation rate constant from the 400 Area to Location 1 is calculated as 9.66×10^{-3}/min for Release No. 1 and 2.26×10^{-2}/min for Release No. 2. Using the second method for Release No. 1, the oxidation rate constant from Location 1 to Location 3 is 1.04×10^{-2}/min based on a calculated re-aeration rate constant of 2.32×10^{-2}/min and a calculated total H_2S loss rate constant of 3.84×10^{-2}/min for the same reach. Using the second method for Release No. 2, the oxidation rate constant from Location 1 to Location 2 is 2.09×10^{-2}/min based on a calculated re-aeration rate constant of 4.04×10^{-2}/min and a calculated total H_2S loss rate constant of 6.06×10^{-2}/min for the same reach.

With the oxidation rates known, the volatilization rates were determined from the LODIPS H_2S loss rate constants. For Release No. 1, the value determined for the reach Location 1 to Location 3 is 2.83×10^{-2}/min. For Release No. 2, the value determined for the distance from Location 1 to Location 2 is 3.64×10^{-2}/min. Using the mean travel times of Release No. 1 and Release No. 2, the value determined for the reach Location 2 to Location 3 is 2.06×10^{-2}/min. The equation is:

$$(K_V\bar{t})_{1,2} + (K_V\bar{t})_{2,3} = (K_V\bar{t})_{1,3} \tag{11}$$

where

K_V = Volatilization rate constant

LODIPS Calculations

LODIPS was used to predict downstream H_2S concentrations for selected release cases. The release location in the model is Location 1. The concentration-time profiles of the actual test releases at Location 1 (Figures 5 and 10) resemble the normal distribution curve, so the release concentration-time profiles for the calculations were specified as a normal distribution curve (Figure 13).

The oxidation rate constant varied with the amount of H_2S released; hence, the oxidation rate constants were established for the selected amounts of H_2S hypothetically released. To do this, a relationship was developed between H_2S concentration and the dissolved oxygen deficit. The pH was correlated with the measured H_2S concentration at Location 1 for the 118 kg and 18 kg H_2S releases. Analysis of regression yielded the following equation with a correlation coefficient of 0.99:

$$H^+ = 5.44 \times 10^{-5} \sqrt{H_2S_m} - 5.52 \times 10^{-8} \tag{12}$$

The pH was then plotted with dissolved oxygen deficit at Location 1 (Figure 14). A dissolved oxygen deficit versus time curve was created for each hypothetical release amount from the H_2S concentration-time curve at Location 1. The oxidation rate constant was then calculated by the first method used in "LODIPS Model Development." Table 3 lists the oxidation rate constants calculated for different hypothetical release amounts. Downstream concentration-time profiles calculated using LODIPS for an example release of 454 kg are shown in Figure 15. The rate constants used in the calculation are given in Table 2. Table 4 lists the maximum concentration at the selected locations for different release amounts and durations.

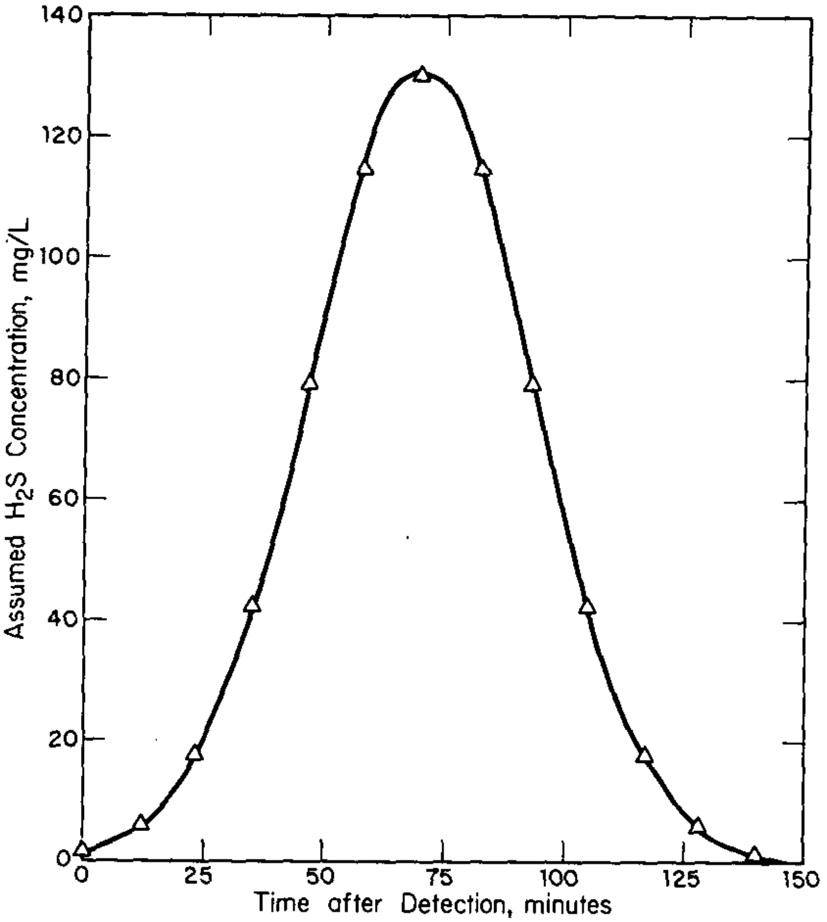

FIGURE 13. Assumed Concentration-Time Release Profile at Location 1 for 454 kg H_2S Release

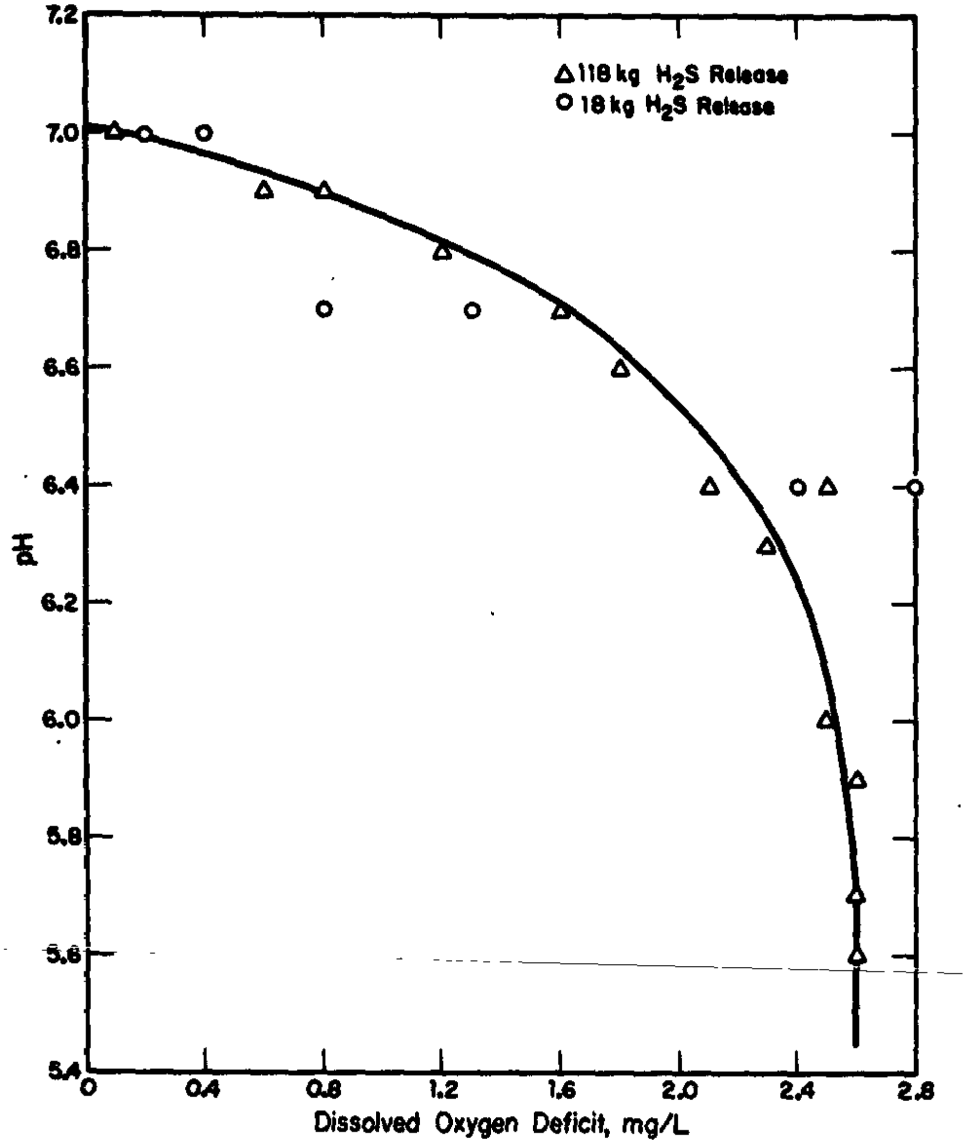

FIGURE 14. pH versus Dissolved Oxygen Deficit from Data Collected at Location 1

Modeling Discussion

Comparisons of the oxidation rate constants for the reach from the 400 Area to Location 1 to reaches modeled in each release show good agreement.

Release No. 1 (118 kg)

Reach 400 Area to Location 1: 9.66×10^{-3}/min

Reach Location 1 to Location 3: 1.04×10^{-2}/min

Release No. 2 (18 kg)

Reach 400 Area to Location 1: 2.26×10^{-2}/min

Reach Location 1 to Location 2: 2.07×10^{-2}/min

Also, the total H_2S loss rate constant calculated by Equation (1) in the Appendix for each release agrees well with those determined by LODIPS.

Release No. 1 (118 kg)

Calculated by equation: 3.84×10^{-2}/min

LODIPS parameter estimate: 3.80×10^{-2}/min

Release No. 2 (18 kg)

Calculated by equation: 6.06×10^{-2}/min

LODIPS parameter estimate: 5.89×10^{-2}/min

TABLE 3

Oxidation Coefficients for Predictive Calculations by LODIPS

H_2S Release Amount in 400 Area (kg)	*Oxidation (min^{-1})*
227	.0057
454	.0034
568	.0028
682	.0024
909	.0018
1363	.0012
1818	.0009

TABLE 4

Predicted Maximum H_2S Concentrations at Selected Locations for Selected Release Amounts and Durations

Release Amount (400 Area), kg	*Release Duration (400 Area), min*	*Maximum Concentrations, mg/1*				
		Location 1 (G. S. Outfall)	*Location 2 (381 m below Outfall)*	*Location 3 (H.P. Station 1006 m below Outfall)*	*Location 4 (Creek Delta Mouth ~ 2530m below outfall)*	*Location 5 (Catfish Hole ~ 3750 m below outfall)*
227	60	110.0	35.8	3.9	0.8	--
227	120	62.8	21.4	2.4	0.5	--
454	30	363.4	120.3	13.7	3.0	.036
454	60	227.2	80.5	9.6	2.2	.034
454	120	129.8	46.8	5.6	1.3	.029
568	30	459.8	154.5	17.9	4.1	.052
682	60	345.6	125.7	15.3	3.8	.066
682	120	197.5	73.0	9.0	2.3	.056
909	60	466.3	172.1	21.3	5.4	.10
909	120	265.8	99.7	12.5	3.3	.087
1363	120	402.5	152.3	19.4	5.2	.14
1363	180	281.7	107.3	13.7	3.8	.12
1363	240	216.8	83.4	10.7	3.0	.11
1818	120	539.8	207.3	26.7	7.4	.22
1818	240	290.5	112.6	14.6	4.1	.16
1818	360	198.7	78.7	10.3	2.9	.12

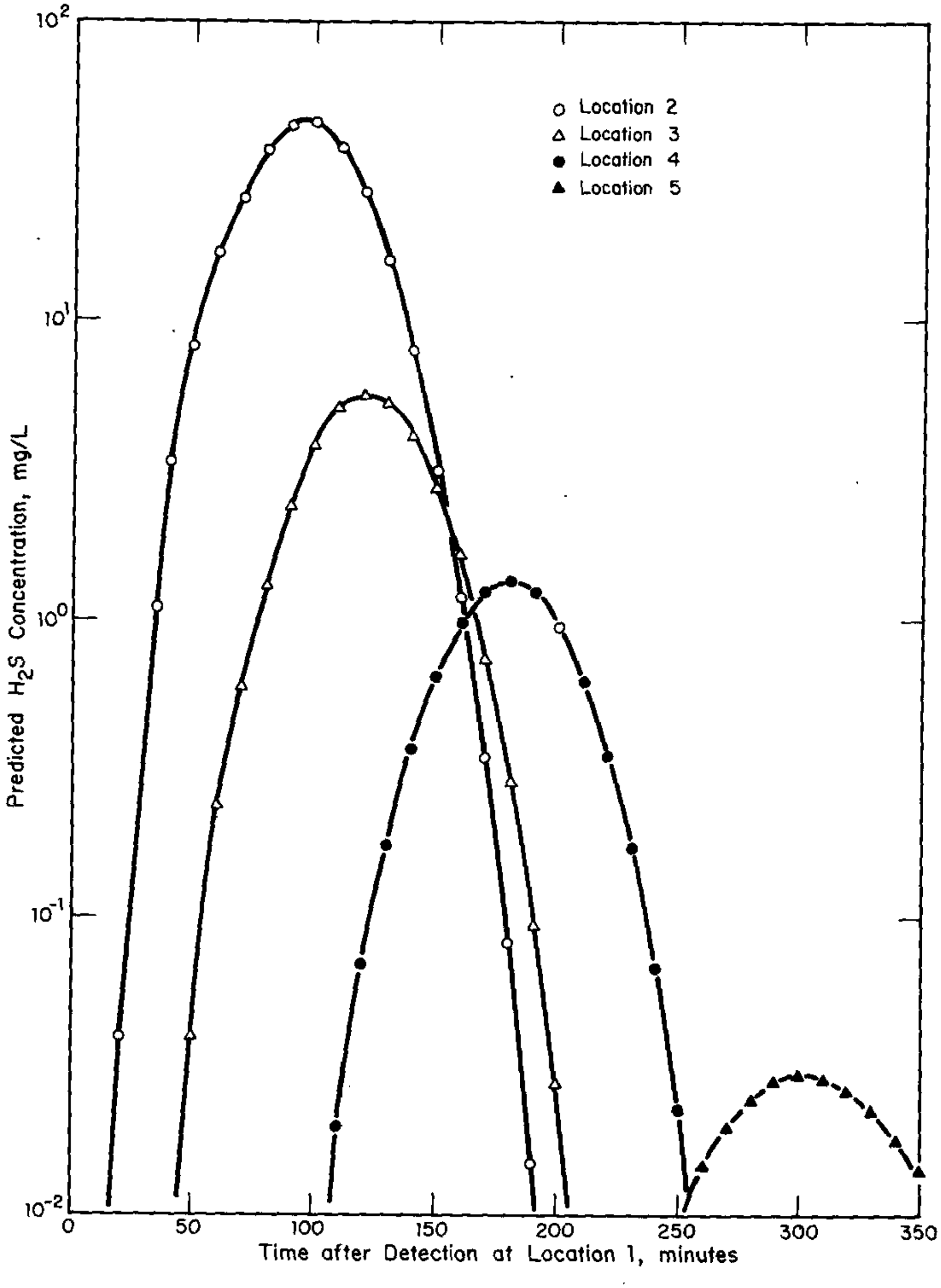

FIGURE 15. Downstream Concentration-Time Profiles for 454 kg H_2S Release in 400 Area.

Figures 16 and 17 illustrate the departure of the measured H_2S transport from that calculated by the LODIPS model without H_2S loss by oxidation and volatilization. The comparisons demonstrate the significant nonconservative nature of the H_2S behavior.

The influence of decreasing velocity and increasing dispersion (Reach Location 4 to Location 5 compared to Reach Location 3 to Location 4; Table 2) on hydrogen sulfide loss is shown in Figure 15 (Location 5 compared to Location 4).

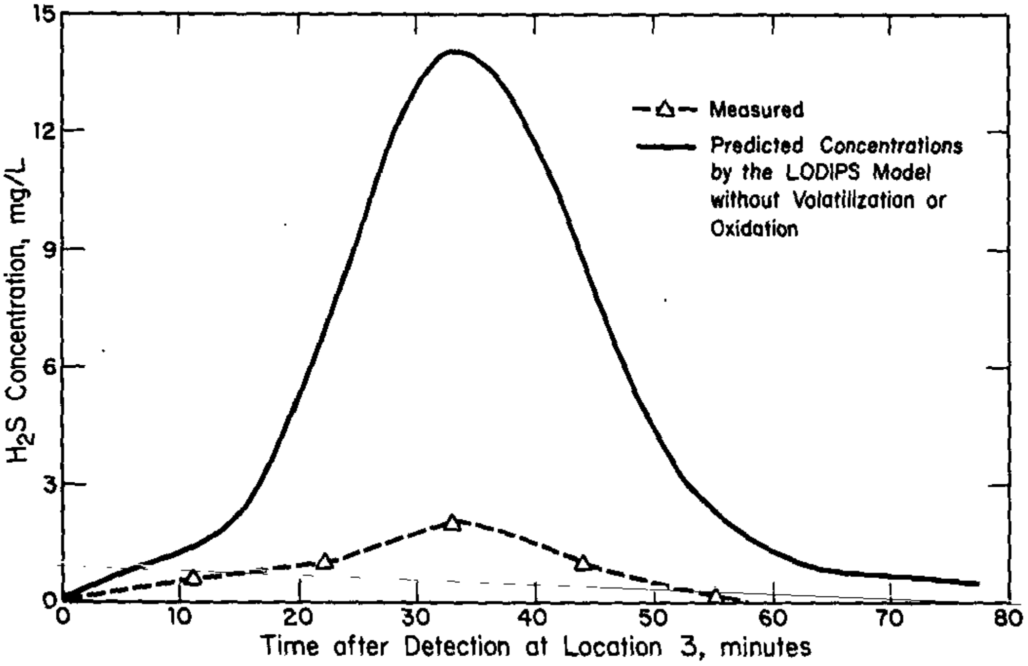

FIGURE 16. 118 kg Release Concentration-Time Profile at Location 3 on Beaver Dam Creek

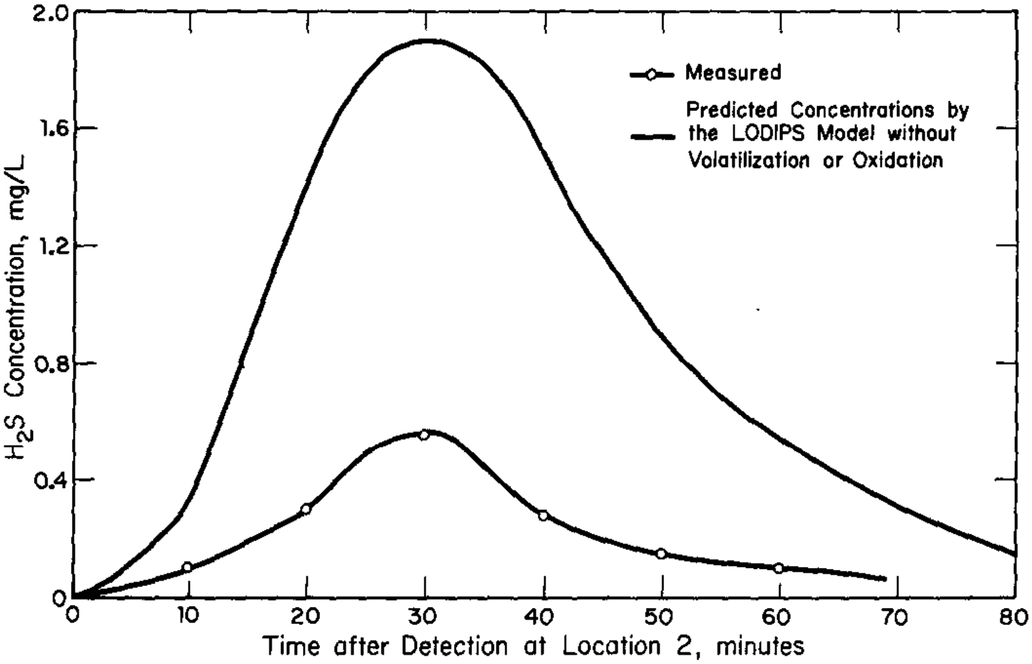

FIGURE 17. 18 kg Release Concentration-Time Profile at Location 2 on the GS Process Effluent

RELEASE AMOUNT-DURATION FOR LETHAL DOSE TO SWAMP FISH

Information on H_2S toxicity of fish has been limited to the literature survey. The sources do not include a study of the effect of higher temperature (∿ 30°C), pH (< 6.5), and reduced dissolved oxygen (3 mg/L) on the lethal dose as expected to be encountered in the swamp area following a large release.

A plot of the time-integrated lethal concentrations for fish versus exposure concentration is shown in Figure 18. The lethal time-integrated concentrations from the curve of Figure 18 were applied to Location 4 (mouth of the creek delta - Figure 4) to determine when lethal conditions existed for swamp fish. Swamp fish are known to frequent the creek as far up as the creek delta. Figure 19 shows the profile obtained based on the cases examined (Table 4) with the LODIPS model.

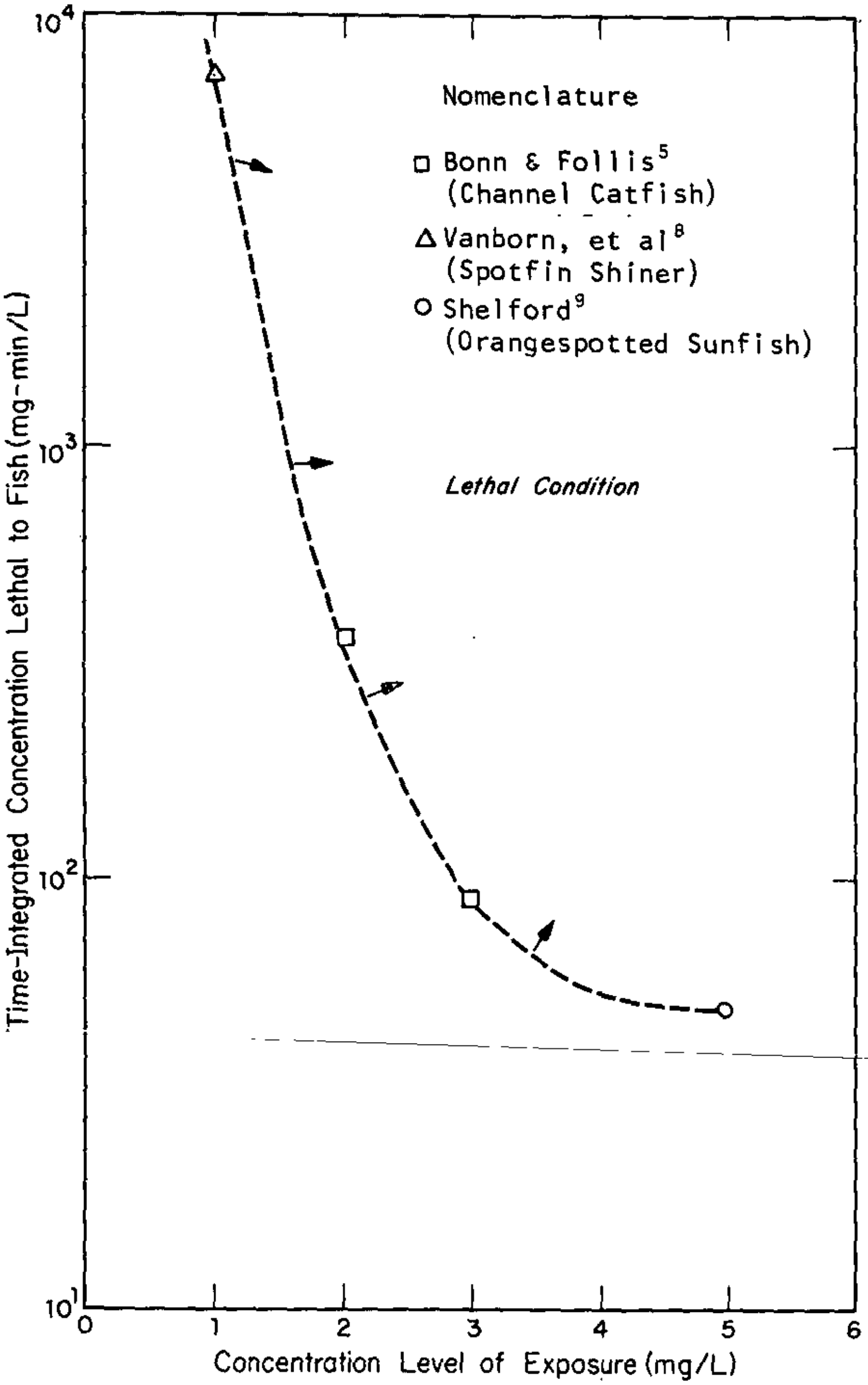

FIGURE 18. Relationship Between Concentration in Solution, Time-Integrated Concentration, and Lethality to Fish Indigenous to Savannah River Swamp

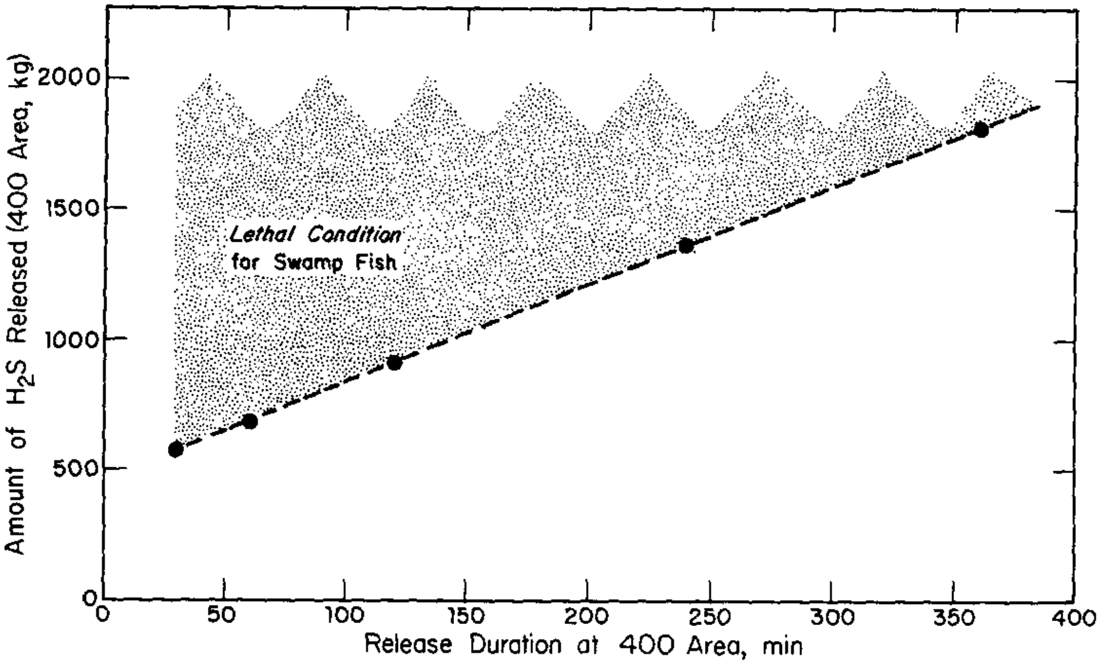

FIGURE 19. Predicted Release Conditions (Amount Released and Duration of Release) That Would Result in Fish Kills in Beaver Dam Creek

CONCLUSIONS

Both volatilization and oxidation contributed significantly as sources of H_2S loss in the test releases. H_2S loss due to oxidation for Release No. 1 (118 kg) was calculated as 43% of the total loss in the reach Location 1 to Location 3 and for Release No. 2 (18 kg) was calculated as 56% of the total loss in the reach Location 1 to Location 2.

Reliable predictions of H_2S concentrations downstream are anticipated with the use of the sink option of LODIPS accounting for volatilization and oxidation.

Lethal conditions to swamp fish are expected for releases as small as 568 kg discharged over a 30-minute period or releases as large as 1818 kg if discharged over a 360-minute period or less.

APPENDIX

OXIDATION THEORY

The rate of change for H_2S in an aqueous system is given by:

$$\frac{dT}{dt} = -(K_o + K_v)T = -K'T \qquad (1)$$

where:

T = H_2S Concentration

K_o = Oxidation Rate Constant (min^{-1})

K' = Total H_2S Loss Rate Constant

K_v = Volatilization Rate Constant

The oxidation rate is assumed to be first order in the stream with respect to H_2S. Since the H_2S concentration in an aqueous system is not dependent on the dissolved oxygen concentration, an oxygen term in the above equation is unnecessary.

The rate of change of oxygen in a stream is given by the Streeter-Phelps equation:[12]

$$\frac{dP}{dt} = K_oT - K_RP \qquad (2)$$

where:

P = Concentration of Dissolved Oxygen Deficit

K_R = Re-aeration Rate Constant

Using equation (1) and separating terms:

$$\int_{T_i}^{T_n} \frac{dT}{T} = -K' \int_{o}^{\bar{t}} dt \qquad (3)$$

where:

T = Time-Integrated Concentration of H_2S

$\bar{t}$ = Mean Travel Time Between Locations

Using equation (2) and separating terms:

$$\int_{P_i}^{P_n} \frac{dP}{K_o T - K_R P} = \int_{o}^{\bar{t}} dt \qquad (4)$$

where:

P = Time-Integrated Concentration of Oxygen Deficit

Substituting integrated equation (3) into equation (4):

$$\int_{P_i}^{P_n} \frac{dP}{K_o T_i e^{-K't} - K_R P} = \int_{o}^{\bar{t}} dt \qquad (5)$$

Integrating equation (5) and separating terms gives:

$$P_n = \frac{K_o T_i}{K_R - K'} (e^{-K_R \bar{t}}) + P_i e^{-K_R \bar{t}} \qquad (6)$$

Solving equation (6) for the oxidation rate constant:

$$K_o = \frac{(K_R - K')(P_n - P_i e^{-K_R \bar{t}})}{T_i (e^{-K' \bar{t}} - e^{-K_R \bar{t}})} \qquad (7)$$

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