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Waters of various salinities were secured from the Umpqua estuary, the Umpqua River, and the open ocean near the mouth of the estuary. The rate of oxidation of sulfides in these various waters was investigated to assess the potential longevity of free sulfides in estuarine waters.

The rate of disappearance of sulfides showed no simple relationship with salinity. Estuarine water exhibited the fastest rate of oxidation with decreasing rates observed in river water and open ocean water.

The effects of aged water samples on the oxidation rate of sulfides were investigated. The results indicated that fresher samples exhibit a faster oxidation rate than aged samples in estuarine, open ocean, and river water.

A Study on the Oxidation of Sulfides in Estuarine Waters

by

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INTRODUCTION

The estuarine environment is an important ecological area for a large number and variety of plants and animals. It is a zone of many complex biological, chemical, and physical interactions. Disruption of the natural ecosystem of the estuary can be detrimental not only to the estuarine environment, but also to the offshore environment since many oceanic species will reside within the estuary for parts of their life stages.

Under certain conditions free sulfides may be formed in the bottom deposits of an estuary through microbial action. The release of these free sulfides from the deposits into the overlying water can occur naturally or can be induced by the disruption of the bottom sediments. The release of free sulfides into the overlying water can affect the water quality and alter the ecosystem in two ways. First, free sulfides can be toxic to plants and animals, and second, the oxidation of the sulfides can cause a reduction in the dissolved oxygen content of the waters. Both of these effects can result in detrimental alterations to the estuarine ecosystem.

This study was conducted to investigate the longevity of free sulfides in the water column overlying estuarine benthal deposits prior

to their oxidation to less toxic or non-toxic forms. The primary purpose of the study was to determine whether salinity could be correlated to the rate of oxidation of the sulfides. Subsequent investigations were also made to determine the effects of fresh and aged water samples on the oxidation rate.

THE ESTUARINE BENTHIC SYSTEM

The estuarine system is an area of great complexity. It is inhabited by a variety of different plants and animals. It also serves as a feeding, spawning, and breeding area for many oceanic species.

Estuaries are influenced by two distinct water masses, freshwater input from the river and seawater input from the ocean due to tidal excursions. Thus, salinities will range from nearly 0 °/oo in the upper reaches of the estuary to 30 °/oo or above near the mouth of the estuary. Both the ocean and the river supply the estuary with a wide variety of organic and inorganic materials. Man can also provide the estuary with organic and inorganic materials through the disposal of wastes into the estuarine waters.

The estuary can be divided into two distinct yet interrelated areas, the pelagic and the benthic. The pelagic refers to the water column overlying the bottom sediments. The benthic refers to the bottom sediments or deposits. These deposits can be divided into an aerobic and an anaerobic zone. The depth of the aerobic layer in the deposits is dependent on particle size, permeability, deposition of organic matter, vertical mixing, and the action of burrowing animals (16).

Figure 1 shows a simplified model of a benthic system (6). This figure does not include larger animals which would feed on the plants

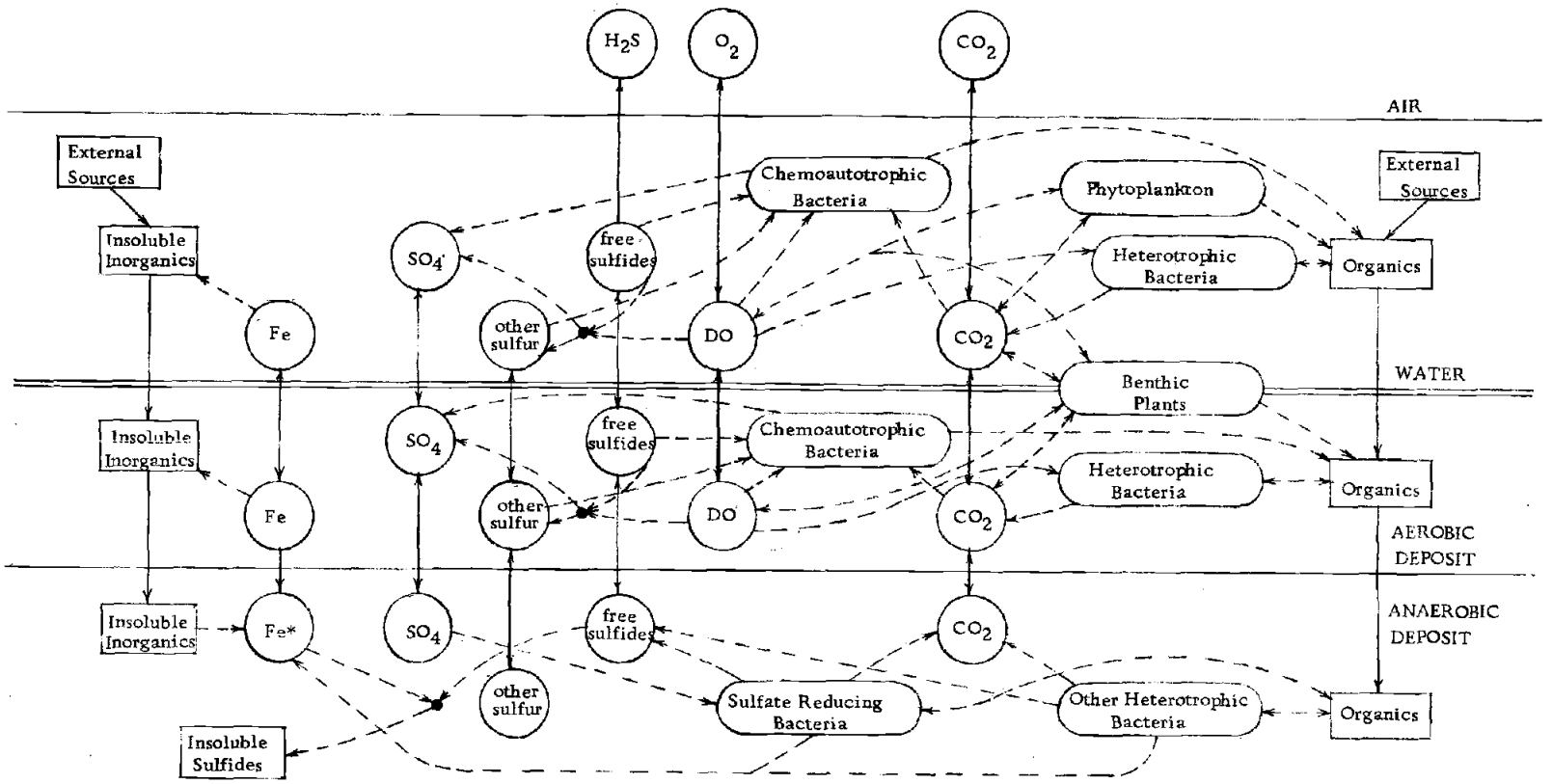

Figure 1. Conceptual model of benthic system (6).

and organic matter present in the area. These animals range from zooplankton and protozoa to larger fish and crustaceans.

Plants in the pelagic and benthic environments synthesize organic matter from carbon dioxide (CO_2) by photosynthesis using light as an energy source. They release oxygen to the system in the presence of light and utilize oxygen in the absence of light. Chemoautotrophic bacteria can also synthesize organic matter from CO_2. These bacteria obtain energy by the oxidation of inorganic compounds such as sulfides, ammonia, ferrous iron, or hydrogen gas. This organic matter produced by the plants and chemoautotrophic bacteria can be utilized as a source of energy by higher life forms.

Heterotrophic bacteria also use organic matter as a source of energy. These bacteria oxidize organic material to more stable organic forms and/or inorganic materials such as CO_2.

In aerobic environments molecular oxygen is used as a hydrogen acceptor during the oxidation of organic and inorganic material by bacteria. However, under anaerobic conditions other hydrogen acceptors must be utilized. These hydrogen acceptors may be organic or inorganic compounds. Thus, the oxidation of organic materials under anaerobic conditions may result in the reduction of organic or inorganic compounds. Inorganic compounds which may serve as hydrogen acceptors include sulfates and nitrates. These reduced compounds, both organic and inorganic, may still be used as

a source of energy by chemoautotrophic or heterotrophic organisms in the presence of molecular oxygen. Photoautotrophs can also utilize these reduced compounds as hydrogen donors for the reduction of CO_2 to organic matter using light as an energy source. These organisms do not require aerobic conditions. An important example of photoautotrophs are the anaerobic purple and green sulfur bacteria (4, 16, 34).

SULFUR IN THE ESTUARINE ENVIRONMENT

Sulfur compounds occur in a number of different forms and valence states throughout the environment. The most common forms found in the aqueous medium include sulfates, sulfides, sulfites, elemental sulfur, and polythionates. Sulfur is also a component of some amino acids, and hence, is also present in some organic matter.

As illustrated in Figure 1, sulfur is an important component in the estuarine benthic system. Under certain conditions free sulfides may be formed in the anaerobic layers of the bottom deposits. Free sulfides in this thesis will refer to all three sulfur components of the following pH dependent equilibrium:

$$H_2S \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{2-} + 2H^+$$

The concentration of each of the above equilibrium components can be determined from the pH of the medium, the concentration of one of the components, and the dissociation constants of H_2S and HS^- (1).

Free sulfides are produced in the benthic environment by the anaerobic decomposition of organic matter or by the reduction of sulfates under anaerobic conditions. In seawater, sulfate reduction probably accounts for the major portion of the production of sulfides (16). Sulfate reducing bacteria are strict anaerobes. Two types of bacteria are thought to be capable of sulfate reduction. The first type oxidize organic matter and reduce sulfates to hydrogen sulfide (H_2S),

and the second type oxidize hydrogen gas while reducing sulfates (34). The hydrogen gas may be formed during anaerobic fermentation processes. Thus, sulfate reduction is dependent upon anaerobic conditions, the presence of sulfates, and the presence of decomposable organic matter (9, 17, 19, 27, 29).

Once formed, sulfides may be present within the deposits as H_2S, HS^-, or S^{2-} depending on the pH. These free sulfides react with the reduced forms of many metallic ions to form insoluble metallic sulfides. Especially prevelant in estuarine muds is ferrous sulfide (FeS) which causes the black layers of anaerobic deposits (3, 8, 9, 34). Ferrous sulfide can further react to yield pyrite (FeS_2) in older sediments. Several mechanisms for the conversion of FeS to FeS_2 have been postulated (3, 8, 34). Thus, free sulfides formed in the anaerobic layers of estuarine bottom deposits tend to form metallic sulfide complexes, especially with iron, since it is usually the most abundant metallic cation present.

If sufficient iron or other metallic cations are present within the deposit, free sulfide levels will remain low. However, should the available iron or other metallic cations be sufficiently depleted, free sulfides may build up within the sediments. These free sulfides may then be released into the aerobic zones of the deposits or the overlying water (6). Free sulfides may also be released to the overlying water by disruption of the bottom sediments. In some instances the oxidation

of FeS may also result in the release of H_2S into the water (3, 29).

Some of the free sulfides produced in the anaerobic layers may be oxidized by purple or green photoautotrophic bacteria if light is able to penetrate to the anaerobic zones of the deposits (4, 16, 34). Part of these free sulfides may also be oxidized, chemically or biologically, in the aerobic zones of the sediments. However, significant quantities of free sulfides may still escape to the water column where they may be either chemically or biologically oxidized in the presence of dissolved oxygen (5, 16, 34).

The release of free sulfides into the overlying waters presents two problems. First, the oxidation of these sulfides will exert an oxygen demand and result in the depletion of the dissolved oxygen content of the water. Second, free sulfides, especially H_2S and HS^-, may be lethal to many fish, crustaceans, and other estuarine organisms. Lethal concentrations of free sulfides have been found to range from 0.7 mg/l to 1.0 mg/l (15, 18, 23, 25, 28, 30, 31). Studies also indicate that early life stages of some fish are more susceptible to sulfide toxicity, and that the depletion of dissolved oxygen due to the presence of sulfides lowers the tolerance of these fish to the toxic effects (25). Concentrations of free sulfides as low as 0.3 mg/l have been noted to cause distress in certain fish (23).

Recent investigations in some tidal flat areas of Oregon estuaries have noted free sulfide levels of about 1 mg/l in waters containing more

than 4 mg/l of dissolved oxygen (7). These findings would indicate that lethal levels of free sulfides may exist for substantial periods of time in the water, even in the presence of excess dissolved oxygen. These facts suggest a need for investigations on the longevity of free sulfides in estuarine waters.

THE OXIDATION OF SULFIDES

Several investigations have been conducted on the oxidation of sulfides in both distilled and saline water. Studies in distilled water have provided insight on the pathway and kinetics of the reaction (2, 12, 13). These studies indicated that the oxidation of free sulfides in water may yield sulfur, thiosulfate, sulfite, sulfate, or a mixture of these four sulfur species. The products of oxidation were found to be dependent on the initial oxygen to sulfide ratio and the length of time the reaction was allowed to proceed. Stoichiometrically, the oxidation of sulfide will require 0.5 moles, 1.0 moles, 1.5 moles, or 2.0 moles of oxygen for oxidation to sulfur, thiosulfate, sulfite, and sulfate, respectively.

Investigations in distilled water in the pH range from 11 to 14 indicated that the oxidation proceeded through the HS^- species, and that the various intermediate products of oxidation could react with each other (2). Recent investigations confirmed the complexity of the reaction due to the interaction of the various intermediate products of oxidation (12, 13).

These recent studies also showed that the reaction was sensitive to pH changes (12, 13). The findings led to the conclusion that H_2S and S^{2-} are not as reactive as the HS^- species, and hence, in acid or very alkaline solutions the rate of oxidation is decreased. The results

also noted the presence of a polysulfide species in the mildly acid to mildly basic pH range (6.5-8.5) which caused a sharp increase in the oxidation rate in this pH range. The presence of a polysulfide species which enhances the rate of oxidation in this pH range agrees with earlier findings on the reactivity of this species (10). Investigations in distilled water also noted an increase in the rate of oxidation with increasing sulfide concentration and increasing oxygen to sulfide ratio (2, 12).

Other studies have been conducted in distilled water to investigate the effects of different catalysts and inhibitors on the oxidation rate (11). These studies showed that small concentrations of metal ions, especially those found in the transition series of metals, greatly accelerate the rate of oxidation. Even calcium and magnesium were found to have some catalytic effect. Organic compounds having a catalytic effect included formaldehyde, hydroquinone, nitrophenol, phenols, and urea. None of the organic compounds exhibited as great an accelerating effect as did the metal ions. Inhibitors of the oxidation included cyanide, EDTA, nitrilotriacetic acid, and peptone. The inhibitory effects were small compared to the catalytic effects.

The catalytic effects of metal ions are believed to account for the rapid oxidation of sulfides in seawater as compared to distilled water. Studies on the oxidation of sulfides in saline waters have been conducted under a variety of different reaction conditions. There has

also been a large range of reaction rates noted, partly due to the variable reaction conditions.

Due to the lack of correlation among the previous investigations, a detailed analysis of each study does not seem warranted. However, several pertinent observations can be noted.

Two investigations have shown that microbial action did not significantly affect the oxidation rate in seawater (24, 33).

Studies performed in the presence of excess oxygen and at essentially constant oxygen tensions generally resulted in small half-life values and typical first order reaction kinetics. Half-life values ranged from 20 minutes to 2.5 hours (22, 33). In other studies increases in the initial oxygen to sulfide ratio were found to increase the oxidation rate when both oxygen and sulfide levels changed constantly during the reaction (14, 24).

Investigations in which sulfides were introduced into the water as H_2S resulted in first order reaction kinetics at various initial sulfide and oxygen concentrations. Half-life values ranged from 12 hours to 70 hours (24). Other investigations indicated that the reaction was too complex to be defined by second order kinetics (14). These findings seem to indicate that the reaction may be influenced by factors besides initial sulfide and oxygen concentrations.

In studies conducted using estuarine waters taken from known sulfide producing areas, coagulation and filtration of the seawater

prior to the introduction of the sulfides decreased the rate of oxidation (33). In this same study the addition of bottom muds to the sample enhanced the rate of oxidation. These findings also seem to indicate the possibility that factors other than sulfide and dissolved oxygen concentrations may significantly affect the rate of oxidation.

In only one study was the salinity of the water medium noted, it being approximately 30 °/oo (14). Also, in only one study was the age of the water sample noted (22). In this study the water was denoted as fresh, but fresh was not defined quantitatively. This study yielded a half-life of approximately 20 minutes under conditions of excess dissolved oxygen.

LABORATORY INVESTIGATIONS

Scope

The investigations presented in this thesis were conducted to provide further insight on the oxidation of sulfides in estuarine waters. Because salinities may vary over a large range of values within the estuary, the effects of different salinities on the oxidation rate of sulfides were studied. The investigations were performed in waters of different salinities secured from the estuary and from sources outside of the estuary proper. The effects of the different salinities and the different water samples on the oxidation rate were studied by monitoring the change in sulfide concentration with time in the various samples.

Sampling

All water samples were obtained in 20 liter polyethylene jugs by immersing the jugs directly into the water being sampled. Estuarine samples were obtained from the Umpqua estuary near Reedsport, Oregon. Open ocean samples were taken off the South Jetty near the mouth of the Umpqua estuary approximately three miles south of Reedsport. River water was secured from the Umpqua River about 28 miles east of Reedsport. Figure 2 shows a map of the area and the sampling locations. Samples were taken during the months of July, August, and September 1972.

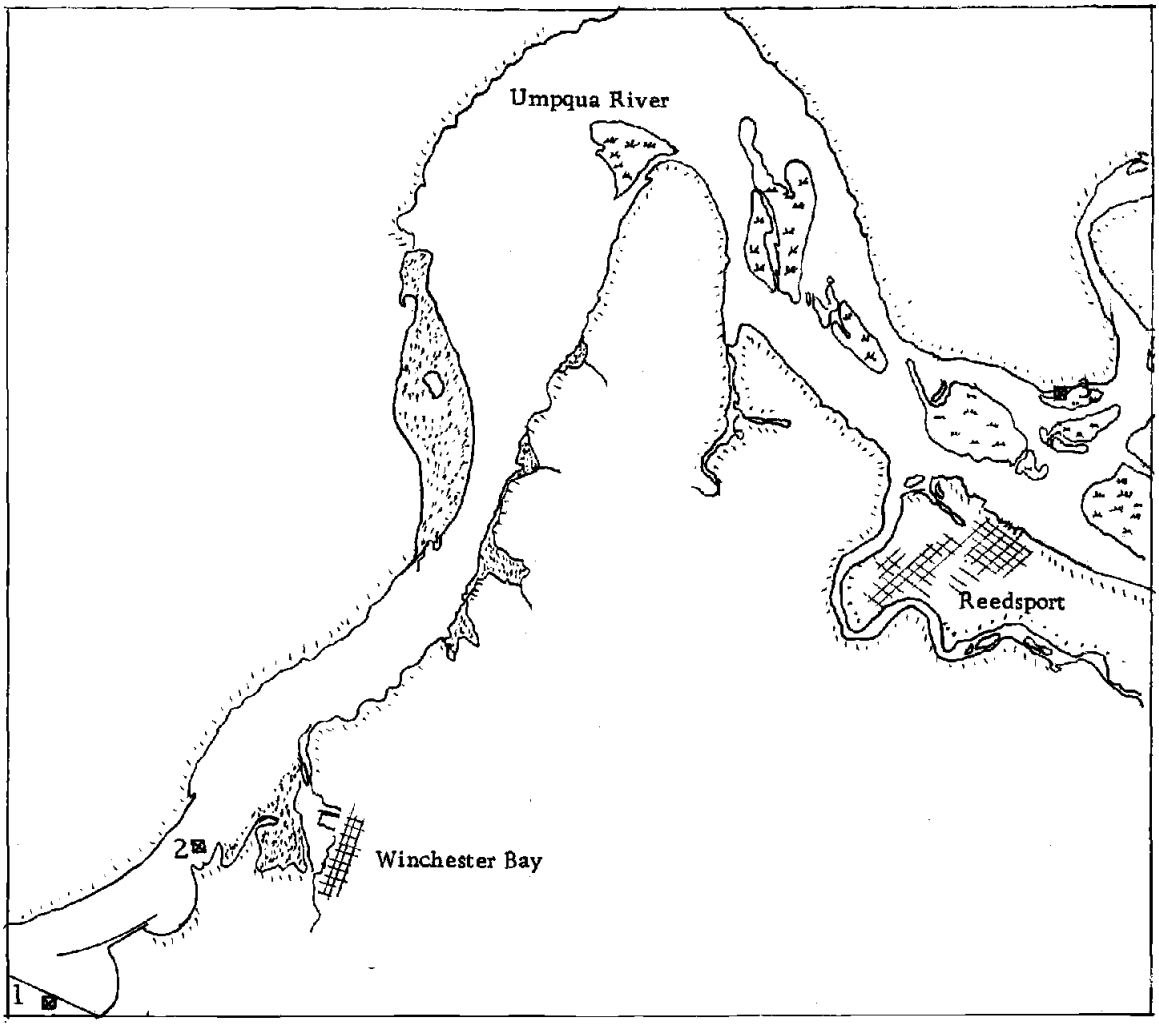

Figure 2. Map of Umpqua estuary near Reedsport, Oregon, denoting sampling locations 1, 2, and 3.

Analyses

Initial dissolved oxygen determinations were made using the Azide-Modification of the Winkler technique as outlined in Standard Methods (1).

Salinities were measured using a Bisset-Berman Model 6220 Laboratory Salinometer. The salinometer was standardized with substandard seawater of known salinity. Salinities were recorded to the nearest tenth.

A Beckman Zeromatic II pH meter was used for pH determinations.

Sulfide concentrations were measured using an Orion silver sulfide specific ion probe and an Orion Model 407 specific ion meter. The silver sulfide probe was used in conjunction with an Orion Model 90-02 double junction reference electrode. The exact procedure followed for the sulfide determinations is presented in the Appendix.

The buffer solution used in the experiments was prepared by diluting 500 milliliters (ml.) of 0.2 M boric acid and 2.5 ml. of 0.2 M sodium hydroxide to 1.0 liter (1). Approximately 59 ml/l of buffer was added to the water samples. The buffer solution was developed empirically with reference to Manual of Microbiological Techniques (26). A boric acid-borate buffer was chosen based on previous investigations conducted in the same pH range desired for this study (12).

Experimental Procedure

A number of experimental runs were conducted to insure good duplication of results and initial sulfide concentrations for each experiment to be run. After several weeks of trials and modifications, the procedures outlined below were chosen to be best suited for the study. Careful attention was used to insure that the same procedure was followed in each experimental run.

All glassware to be used for each experiment was cleaned with a 50% solution of hydrochloric acid (HCl) and thoroughly rinsed with tap water and distilled water.

Stock sulfide solutions were prepared in 250. 0 ml. of the same water to be used for a particular experiment. The water was first boiled and cooled and then transferred to a pyrex aspirator bottle. The aspirator bottle was tightly stoppered with a rubber cork which had two glass tubes inserted in it so that nitrogen gas could be bubbled through the water. These glass tubes had short pieces of tygon tubing on the exterior ends which could be clamped shut. The bottles were also equipped with a serum stopper for withdrawing portions of the stock solution with syringes. Purified nitrogen gas was bubbled through the water in the aspirator bottle for 30 to 45 minutes to drive off any remaining dissolved oxygen.

Sulfides were introduced into the deoxygenated water in the form of $Na_2S \cdot 9\ H_2O$ crystals. The crystals were first cleaned using

approximately 8 N HCl to remove oxidized surface layers. The cleaned crystals were weighed on a Mettler balance and added directly to the water in the aspirator bottle. Enough $Na_2S \cdot 9\ H_2O$ was added to yield a stock solution of approximately 150 mg/l as sulfide. After addition of the Na_2S crystals, the nitrogen flow to the aspirator bottle was shut off and the bottle was completely sealed by closing the clamps on the gas introduction and air relief tubes. The stock solution was then placed in a 20°C incubator until needed. Previous trials indicated that stock solutions prepared in this manner remained at a constant sulfide concentration for two days, and that stock solutions of nearly the same concentration could be consistently prepared. It should be noted that due to the instability of Na_2S, there is a possibility of the presence of some other more oxidized sulfur species in the stock solution. The cleaned Na_2S crystals were exposed to the atmosphere for a short period during weighing.

The water samples used in each experiment were transferred from the sampling containers to a 20 liter polyethylene jug for aeration. The length of aeration will be discussed for each particular experiment. This jug was thoroughly cleaned between each experiment in the same manner as the glassware. The jug was also kept in the same 20°C incubator.

For experiments 1 and 2 the water samples were not buffered. For all subsequent experiments the boric acid-borate buffer previously

described was used. The buffer was added directly to the aeration jug prior to filling the reaction bottles. Previous trials demonstrated that 59 ml/l of the buffer solution would yield a pH between 8.0 and 8.5 for all samples to be studied.

The reaction bottles used for the experiments were standard 300 ml. BOD bottles. The bottles were filled from a bottom port on the aeration jug and stoppered to exclude air bubbles. These bottles were also kept in the same 20°C incubator after filling.

The reaction bottles were inoculated with the stock sulfide solution using 10.0 ml. and 30.0 ml. plastic syringes. After withdrawing the stock solution from the aspirator bottle through the serum stopper, a piece of tygon tubing connected to a piece of glass tubing was slipped over the end of the hypodermic needle. The stoppers from the BOD bottles were removed, and 5.0 ml. of stock sulfide solution were added to the bottom of each bottle using the above syringes. The bottles were then re-stoppered and placed in the 20°C incubator. Previous trials using a tracer dye showed that none of the stock solution would be displaced from the bottle when it was re-stoppered.

Initial sulfide concentrations were determined by shaking the inoculated reaction bottle for one minute to disperse the sulfide solution and subsequently withdrawing 10.0 ml. of the sample into 10.0 ml. of Standard Anti-Oxidant Buffer (SAOB). (See the Appendix for details on the SAOB.) The samples were withdrawn using 20.0 and

30.0 ml. syringes equipped as previously described with tygon tubing and glass tubing. The samples were then analyzed for free sulfide concentration with the specific ion probe. Sulfide concentrations at various time intervals were measured in the same manner.

All experiments were run in duplicate; that is, two different reaction bottles were analyzed for each time interval. Two samples were also withdrawn from each duplicate bottle. Results of the sulfide determinations were usually within 0.10 mg/l on all samples analyzed.

Initial dissolved oxygen was determined on duplicate bottles which contained no sulfides. Attempts to follow the change in dissolved oxygen using the Azide-Modification of the Winkler technique failed to yield good results. The method failed due to interference from sulfides and the oxidation products of the sulfides.

The pH of the samples was determined initially and at various time intervals using approximately 30 ml. of sample. These samples were taken from the same bottles as the sulfide determination samples.

RESULTS AND DISCUSSION

In the discussion of the following experiments, the time required for the disappearance or oxidation of 50% of the initial sulfides will be used for comparative purposes. This value does not imply a half-life associated with first order reaction kinetics. No attempt was made to define the reaction order of the oxidation rate in these studies.

Experiment 1 was conducted in water obtained near the mouth of the estuary at sampling point 2 (see Figure 2). The salinity of this sample was 32.2 °/oo. The water was stored at 4°C for three days and then aerated for approximately 12 hours at 20°C before the experiment was started. The initial sulfide concentrations in duplicate bottles were 2.40 mg/l and 2.41 mg/l, and the initial oxygen to sulfide ratio (O_2:S^{2-}) by weight was approximately 3.1. The pH of this sample rose from 8.8 to 9.4 after the addition of the sulfide stock solution. Thereafter, the pH of the reaction medium did not change more than 0.2 of a pH unit during the course of the run.

Figure 3 shows a plot of the sulfides remaining vs. time for this experiment. Initially, the disappearance of sulfides was rapid followed by a gradual reduction in the rate as the concentration of sulfides and dissolved oxygen decreased. Fifty percent of the initial sulfides had disappeared in approximately nine hours. This value was somewhat higher than expected at this higher salinity. The plot indicates that

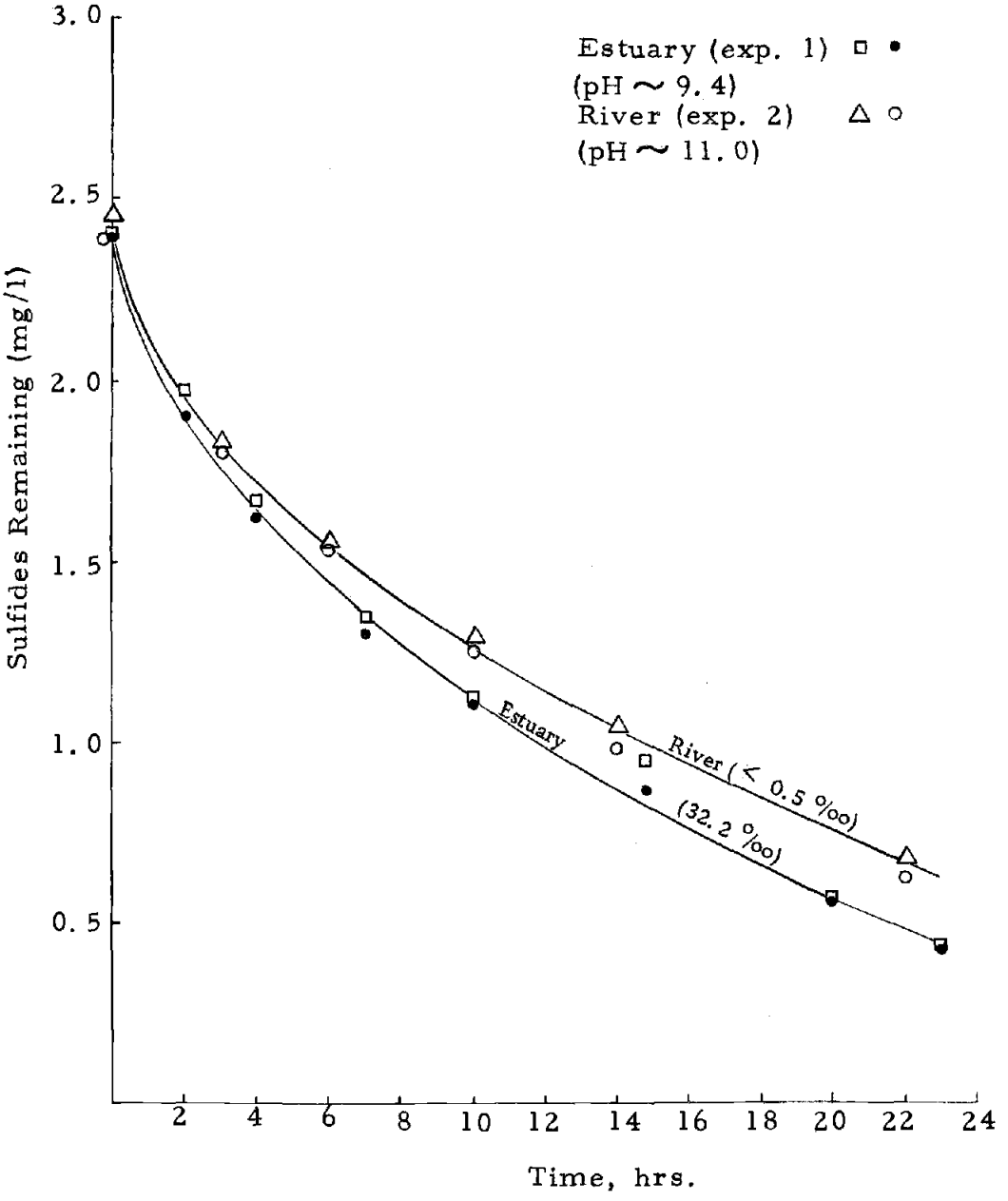

Figure 3. The disappearance of sulfides with time in estuarine water and river water.

good duplication of results was achieved with the technique used for the study.

For experiment 2 the opposite extreme in salinity was investigated. Water for this experiment was taken from the Umpqua River about 28 miles upstream from Reedsport. The river water had a salinity of less than 0.5 °/oo. This sample was stored at 4°C for six days and subsequently aerated for 12 hours at 20°C before the start of the experiment. Because the salinity of the samples will not change significantly with age, it was not expected that differences in storage time for the various samples would affect the oxidation rate at this time.

The initial sulfide concentrations in duplicate bottles were 2.46 mg/l and 2.39 mg/l for this run. The initial O_2:S^{2-} by weight was approximately 3.7. The differences in initial O_2:S^{2-} are a result of the higher dissolved oxygen saturation value for the lower salinity samples compared to samples of higher salinity. These small differences in O_2:S^{2-} should not result in significant differences in the rate of oxidation since in all cases there is an excess of dissolved oxygen available for the reaction.

The pH of the river water rose from 7.9 to 11.0 after the addition of the stock sulfide solution. During the course of the experiment, the pH did not change by more than 0.3 of a pH unit.

This large rise in pH indicated that the river water had very little capacity to buffer the addition of the Na_2S stock solution. Since previous studies (12) demonstrated that pH can significantly affect the oxidation rate, the need for a buffer system for future experiments became evident. However, this experiment was completed.

Figure 3 depicts the sulfides remaining vs. time for experiment 2. This curve was similar to the plot for experiment 1; however, the rate of disappearance of sulfides for the river water was slower. Fifty percent of the initial sulfides were oxidized in approximately 11 hours during this run. This slower rate was expected in the essentially zero salinity river water as compared to the higher salinity estuarine water of experiment 1. Furthermore, if previous studies (12) on the pH dependence of the oxidation rate in distilled water can be applied to estuarine and river water, then the estuarine water would exhibit a much slower rate at pH 9.4 than it would at pH 11.0. Thus, the differences in the oxidation rates in the two different waters could be substantially greater. However, catalytic effects, which could enhance the rate in both samples, could dampen the pH dependence of the reaction. Considering these effects, it becomes difficult to correlate the data from these two experiments.

These findings on the buffering capacity and pH changes in the water may be an important factor when considering the oxidation of sulfides in the natural environment. The addition of Na_2S tends to

increase the pH of the system while the addition of H_2S would tend to decrease the pH of the system. Since in a true estuarine system the majority of free sulfides would most likely be introduced into the water as H_2S, future studies might introduce free sulfides in the form of H_2S gas to determine if this factor might affect the oxidation.

For the remainder of the experiments a boric acid-borate buffer was used to maintain a pH close to 8.0 during the course of the reaction. This pH region was chosen since it is within the normal range of pH found in natural waters.

Experiment 3 utilized open ocean water as the medium. The water was obtained from outside the reaches of the estuary at sampling point 1 (see Figure 2). The salinity of this sample was 31.1 °/oo. This water was stored at 4°C for one day and then aerated for approximately 12 hours prior to the start of the experiment. The buffer solution was added directly to the aeration jug and mixed before the reaction bottles were filled. The initial pH of the reaction medium after the addition of the stock sulfide solution was 8.35, and the pH remained within 0.2 of a pH unit throughout the run. The initial sulfide concentration was 2.32 mg/l in both duplicate bottles, and the initial $O_2:S^{2-}$ by weight was 3.2.

The rate of disappearance of sulfides during this experiment was expected to be about the same as that found in the high salinity estuarine water used in experiment 1. However, as seen in Figure 4, the

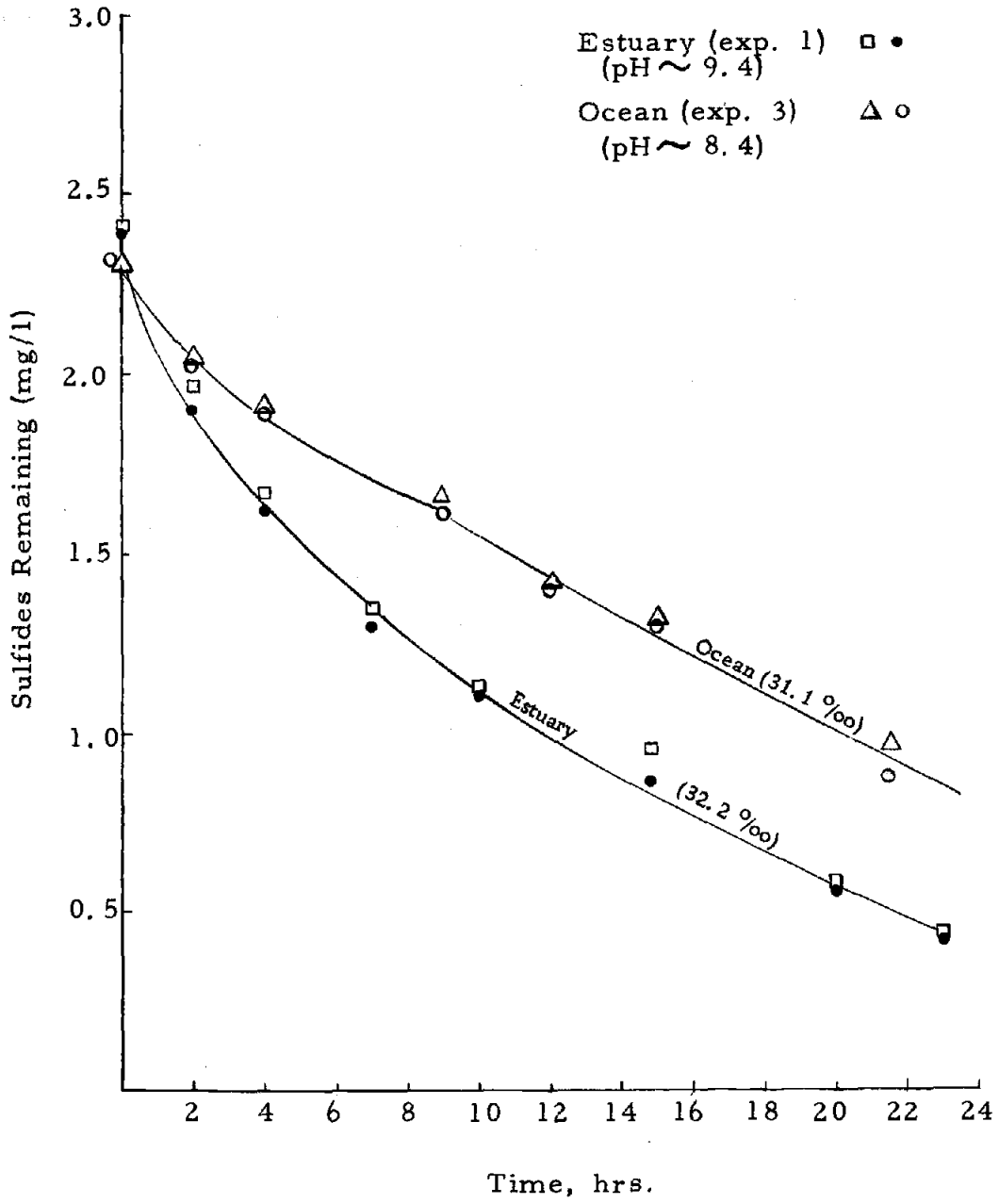

Figure 4. A comparison of the disappearance of sulfides with time in estuarine water and ocean water of approximately the same salinity.

rate for the open ocean water was much slower with 50% of the initial sulfides being oxidized in approximately 17 hours. Although the estuarine water of approximately the same salinity (32.2 °/oo) was run at a higher pH, it did not seem reasonable that a change of one pH unit would afford such a large difference in the rate of disappearance of sulfides. Rather, it appeared that some factor other than salinity was either enhancing the rate in the estuarine water or inhibiting the rate in the open ocean water. Future experiments were expected to provide further insight on these findings.

Experiment 4 was conducted in water secured from the mid-reaches of the estuary at sampling point 3 (see Figure 2). The salinity of this water was 13.7 °/oo. This sample was stored for five days at 4°C, and then aerated for 12 hours before the start of the experiment. The sample was buffered as in experiment 3. The initial pH of the reaction medium was 8.25, and it remained within 0.2 of a pH unit throughout the run. The initial sulfide concentrations in duplicate bottles were 2.22 mg/l and 2.20 mg/l, and the initial O_2:S^{2-} by weight was 3.7.

As seen in Figure 5, this sample exhibited the fastest rate of oxidation of any samples tested to this point. Fifty percent of the initial sulfides had disappeared after approximately 6.5 hours. The results of this experiment, coupled with the results of experiments 2 and 3, again seem to indicate the presence of some factor in the

estuarine water which enhances the rate of oxidation. Although experiment 2 using high salinity estuarine resulted in a slower rate than experiment 4, part of this difference could be the result of the different pH values at which the experiments were run. Also, the higher salinity estuarine water was sampled from a location which receives a substantial input of open ocean water, and hence, the influence of the open ocean water could dampen the apparent catalytic effects noted in both estuarine water samples.

Experiment 5 utilized river water taken from the Umpqua River about 28 miles upstream from Reedsport. The salinity of this sample was less than 0.5 °/oo. This water was stored at 4°C for nine days and then aerated for 12 hours prior to the experimental run. The sample was buffered in the same manner as previous experiments. The initial pH of the reaction medium was 8.35, and it remained within 0.2 of a pH unit throughout the experiment. The initial sulfide concentrations in duplicate bottles were 2.21 mg/l and 2.10 mg/l, and the initial O_2:S^{2-} by weight was 4.0.

Figure 5 shows the sulfides remaining vs. time plot for experiment 5. The results indicated that the oxidation rate was faster in the low saline river water than the open ocean water but slower than the rate in the estuarine water. Fifty percent of the initial sulfides were oxidized in approximately 12 hours in this experiment. These findings show that river water does exhibit a substantial catalytic effect on the

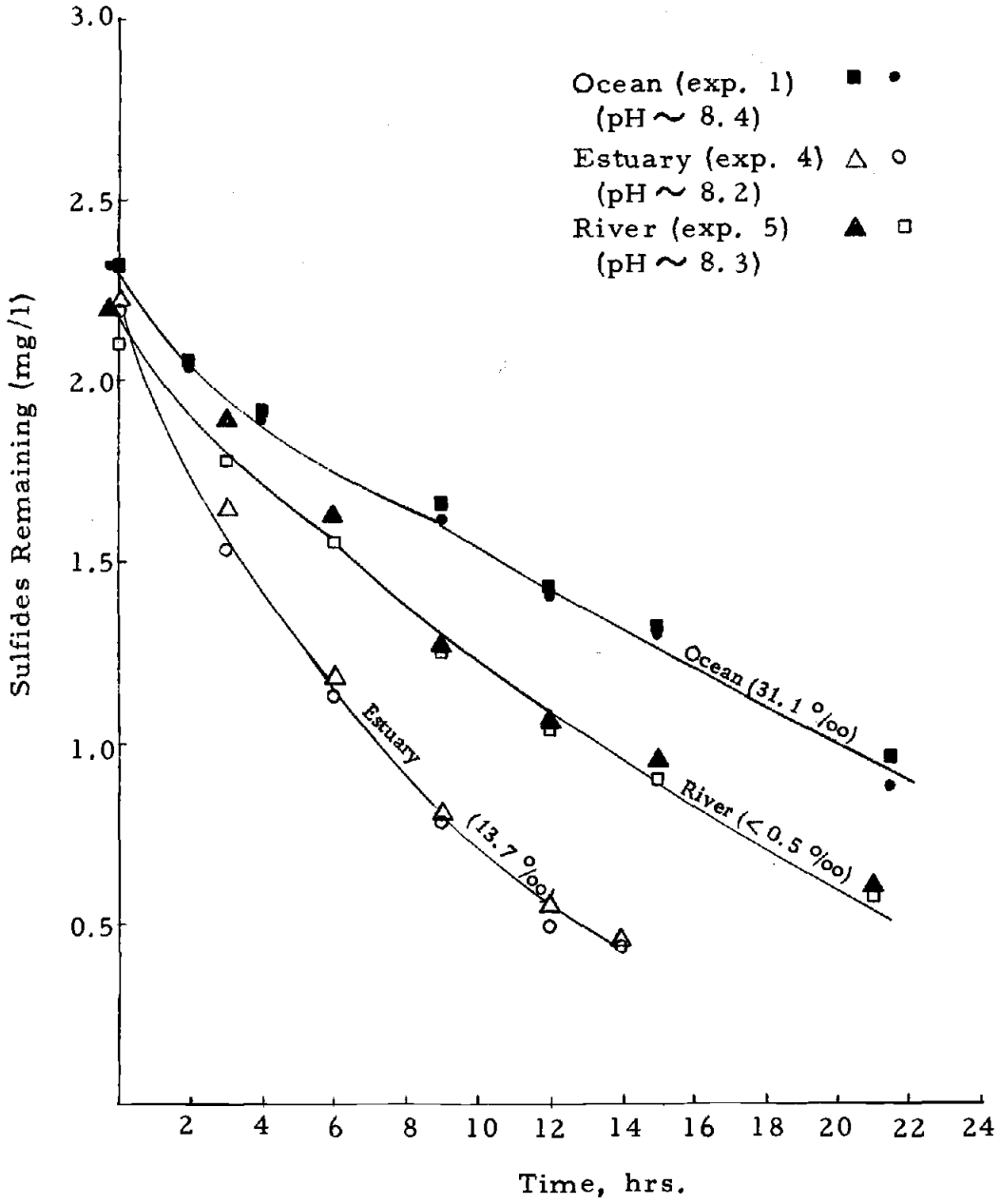

Figure 5. A comparison of the disappearance of sulfides with time in estuarine water, river water, and ocean water.

rate of oxidation. These results, coupled with the results of the two previous experiments, seem to nullify the hypothesis that the rate of oxidation is directly related to the salinity of the water. Rather, the combined data of experiments 1 through 5 suggests the presence of some catalytic factor within the estuary which is not apparent in the open ocean or river water. Another possibility is that the rate of oxidation is inhibited at higher salinities. However, the results of experiments 2 and 3 do not seem to be in accordance with the latter possibility.

Experiments 6 and 7 were conducted to test the hypothesis that the estuarine water possessed some catalytic factor which enhanced the rate of oxidation. If this hypothesis were correct, it seemed possible that the age of the sample might also affect the oxidation rate. Therefore, fresh samples were used for these next two experiments. Fresh implies a sample between three and six hours old, since this time period is required to sample and return to the lab to run the experiment.

For experiment 6 the water sample was taken from sampling site 3 (see Figure 2), and it was immediately returned to the lab. The experiment was started approximately four hours after sampling. The salinity of this sample was 13.9 $^{o}/_{oo}$. The water was aerated for approximately one hour before the run was started. It was buffered as in previous experiments. The initial pH of the reaction medium

was 8.3, and it remained within 0.2 of a pH unit during the experiment. The initial sulfide concentrations in duplicate bottles were 2.32 mg/l and 2.21 mg/l, and the initial O_2:S^{2-} by weight was 3.3.

The sulfides remaining vs. time plot for this run is shown in Figure 6. The results seemed to demonstrate that the age of the sample has a definite affect on the rate of oxidation. Figure 7 illustrates the differences in the oxidation rate between the fresh estuarine water of experiment 6 and the aged estuarine sample of experiment 4 on an expanded time scale. Both samples were taken from the same location and were nearly the same salinity. Fifty percent of the initial sulfides were oxidized in approximately three hours in experiment 6, while a 50% reduction of the initial sulfides took approximately 6.5 hours in experiment 4. These differences in oxidation rate appear to be associated with the age of the samples, the water in experiment 4 being five days old as compared to the four hour old sample of experiment 6. These results provide further evidence that the rate of oxidation cannot be correlated with salinity alone. Rather, the findings suggest the possible presence of some unstable catalytic factor which enhances the rate in the estuarine water.

For experiment 7 water was taken from the open ocean and the Umpqua River at the same locations sampled in experiments 3 and 5. These samples were immediately returned to the lab and mixed to yield a salinity close to that of the estuarine water of experiment 6.

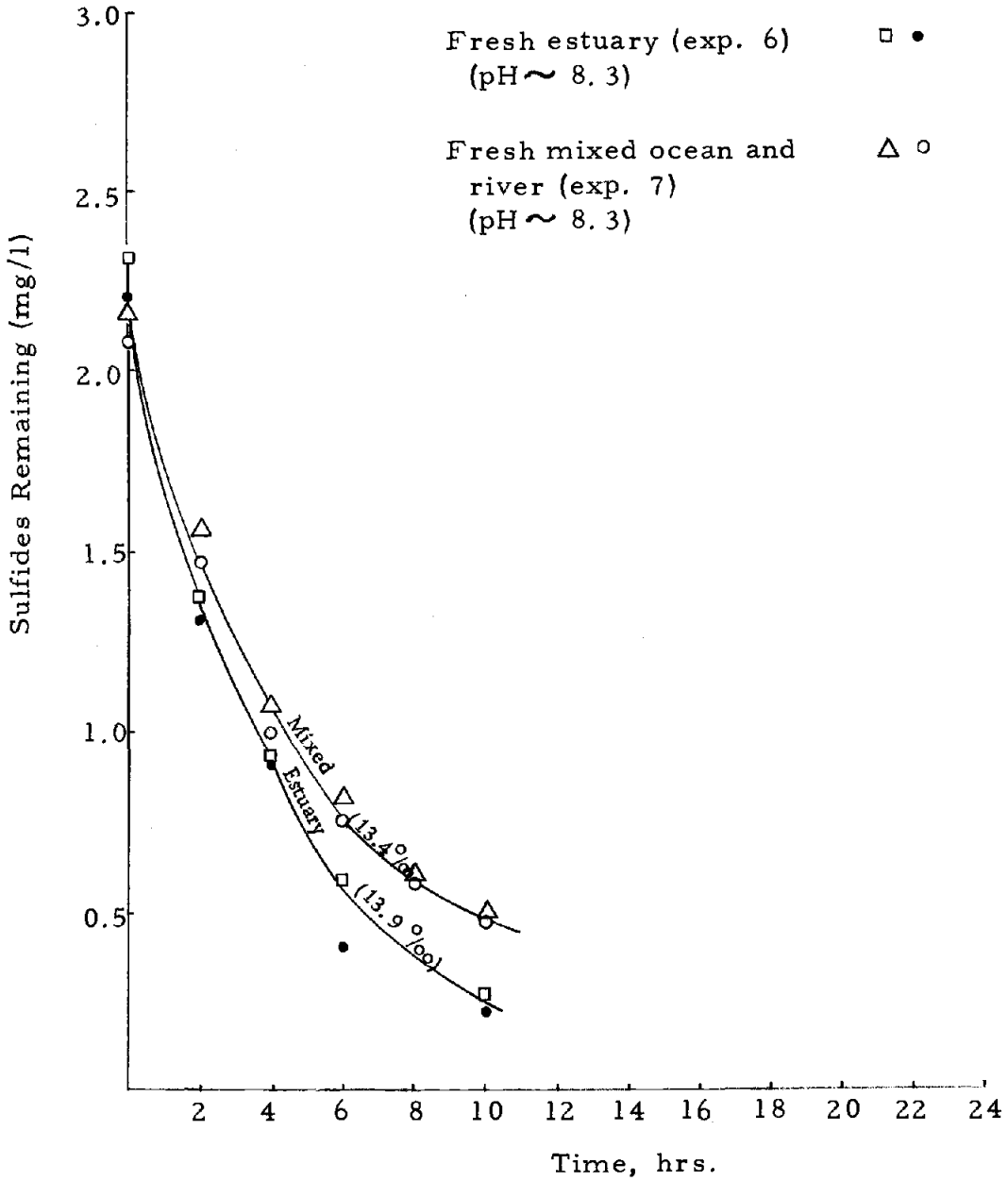

Figure 6. A comparison of the disappearance of sulfides with time in fresh estuarine water and fresh mixed ocean and river water of approximately the same salinity.

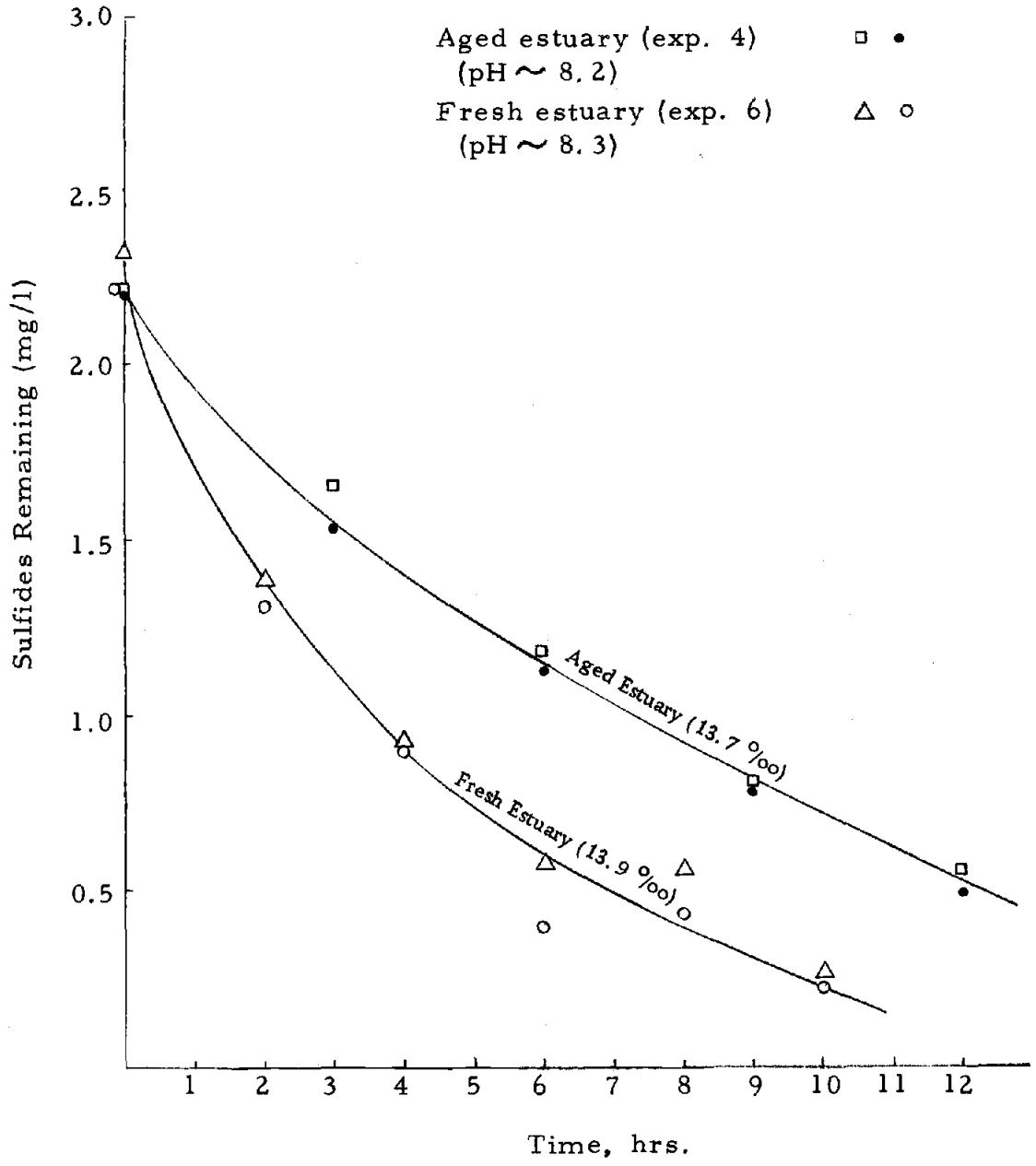

Figure 7. A comparison of the disappearance of sulfides with time in fresh estuarine water and aged estuarine water sampled from the same location.

The salinity of this mixed sample was 13.4 °/oo. This water was aerated for approximately one hour prior to the start of the experiment. It was buffered as in previous experiments. The initial pH of the reaction medium was 8.3, and it remained within 0.2 of a pH unit throughout the run. The initial sulfide concentrations in duplicate bottles were 2.17 mg/l and 2.08 mg/l, and the initial O_2:S^{2-} by weight was 3.7.

As can be seen in Figure 6, the rate of disappearance of sulfides was nearly the same as in experiment 6 for the first two hours. However, after approximately two hours, the rate in the mixed sample decreased faster than in the estuarine sample. Fifty percent of the initial sulfides were oxidized in approximately four hours in the mixed sample as compared to three hours in the estuarine sample. At the end of ten hours the mixed sample had decreased to approximately 0.50 mg/l free sulfide, while the estuarine sample had decreased to about 0.25 mg/l free sulfide. Figure 8 shows the results of these two experiments on an expanded time scale which more clearly depicts the differences in the oxidation rates.

The results of experiments 6 and 7 do seem to indicate that the age of the water sample has an effect on the rate of oxidation of sulfides. The findings also indicate that there is a difference in the oxidation rate in estuarine water and mixed open ocean and river water of approximately the same salinity.

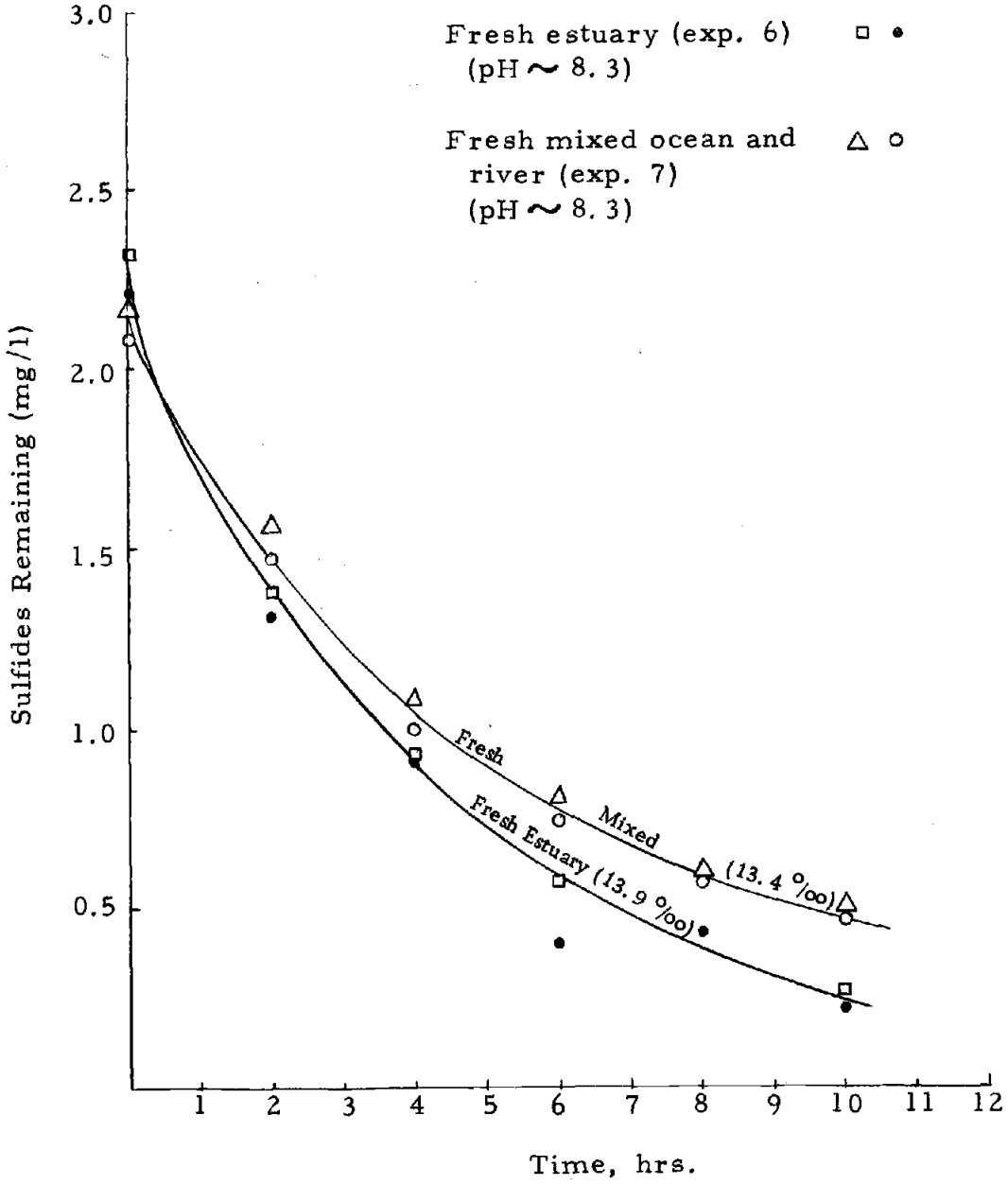

Figure 8. A comparison of the disappearance of sulfides with time in fresh estuarine and fresh mixed ocean and river water of approximately the same salinity on an expanded time scale.

The final phase of this study was designed to further investigate the effects of age of various water samples on the oxidation rate of sulfides. Samples of open ocean, estuarine, and river water were taken from the same locations as sampled in experiments 3, 5, and 6. These samples were returned to the lab immediately, and experiments were started within six to seven hours after sampling. Four experiments were conducted using open ocean, estuarine, river, and mixed ocean and river water. The salinities of the ocean, estuarine, river, and mixed samples were 32.9 °/oo, 12.3 °/oo, less than 0.5 °/oo, and 12.5 °/oo, respectively. All of the above samples were aerated for approximately 30 to 40 minutes, and all were buffered as in previous experiments. For these four experiments only the initial sulfide concentration and the sulfide concentration after eight hours were determined. Data from previous experiments indicated that differences in the amount of sulfides remaining could be contrasted fairly well after this time interval.

After these initial four experiments, the water samples were stored at room temperature, 20°C to 25°C, for five days. After this storage time, the same type of experiment as outlined above was run using the aged samples.

Table 1 shows the results of these eight experiments. The results indicated that the age of the water sample did affect the rate of oxidation. All of the samples, except the estuarine water, showed a

Table 1. The effects of age on the disappearance of sulfides in estuarine water, ocean water, river water, and mixed ocean and river water.

Sample (salinity)	Age	Initial pH	Initial $O_2:S^{2-}$	Initial [sulfides] (mg/l)	[Sulfides] after 8 hrs (mg/l)	Δ [Sulfides] (mg/l)	% Sulfides Remaining
Estuary (12.3 °/oo)	6-1/2 hrs	8.2	3.8	2.19	0.48	1.71	22
Mix (12.5 °/oo)	6 hrs	8.4	3.9	2.15	0.97	1.18	45
Ocean (32.9 °/oo)	6-1/2 hrs	8.5	3.6	2.16	1.29	0.87	60
River (< 0.5 °/oo)	6-1/2 hrs	8.3	3.8	2.23	0.63	1.60	28
Estuary (12.3 °/oo)	5 days	8.4	3.6	2.09	0.41	1.68	20
Mix (12.5 °/oo)	5 days	8.3	3.8	2.03	1.05	0.98	52
Ocean (32.9 °/oo)	5 days	8.4	3.4	2.07	1.43	0.64	69
River (< 0.5 °/oo)	5 days	8.4	3.9	2.06	0.90	1.16	43

decrease in the amount of sulfides oxidized after eight hours when the sample had been stored for five days. The sulfides remaining after eight hours increased from 45% to 52%, 60% to 69%, and 28% to 43% for the mixed, ocean, and river water samples, respectively, after five days storage. The estuarine water sample showed a slight decrease from 22% to 20% in the concentration of sulfides remaining after eight hours for the fresh and aged samples, respectively. However, a previous run, experiment 4, utilizing estuarine water of approximately the same salinity and sampled from the same location, showed a definite decrease in the sulfides remaining after eight hours when stored for five days.

Table 2 shows the results of the four studies made on fresh and aged estuarine waters obtained from the same sampling location, and also, the results of the three studies made on fresh and aged mixed ocean and river water samples. Table 3 shows the results of previous experiments run in fresh and aged open ocean and river water samples. A comparison of Tables 1, 2, and 3 provides evidence, although not entirely conclusive for the estuarine samples, that age does have an affect on the rate of oxidation of sulfides in the waters tested.

The data also indicate that the oxidation does proceed at a faster rate in the estuarine waters, a fact that seems to evince the presence of some catalytic factor within the estuarine water which enhances the rate. The effects of this catalytic action do not seem as

Table 2. The effects of age on the disappearance of sulfides in estuarine water and mixed ocean and river water of approximately the same salinity.

Sample (salinity)	Age	Initial pH	Initial $O_2:S^{2-}$	Initial [sulfides] (mg/l)	[Sulfides] after 8 hrs (mg/l)	Δ[Sulfides] (mg/l)	% Sulfides Remaining
Estuary (13.9 °/oo)	4 hrs	8.3	3.2	2.27	0.39	1.88	17
Mix (13.4 °/oo)	4-1/2 hrs	8.3	3.7	2.13	0.59	1.54	28
Estuary (12.3 °/oo)	6-1/2 hrs	8.2	3.8	2.19	0.48	1.71	22
Mix (12.5 °/oo)	6 hrs	8.4	3.9	2.15	0.97	1.18	45
Estuary (12.3 °/oo)	5 days	8.4	3.6	2.09	0.41	1.68	20
Mix (12.5 °/oo)	5 days	8.3	3.8	2.03	1.05	0.98	52
Estuary (13.7 °/oo)	5 days	8.2	3.8	2.21	0.93	1.28	42

Table 3. The effects of age on the disappearance of sulfides in ocean water and river water.

Sample (salinity)	Age	Initial pH	Initial $O_2:S^{2-}$	Initial [sulfides] (mg/l)	[Sulfides] after 8 hrs (mg/l)	Δ[Sulfides] (mg/l)	% Sulfides Remaining
Ocean (32.9 °/oo)	6-1/2 hrs	8.5	3.6	2.16	1.29	0.87	60
Ocean (31.1 °/oo)	1 day	8.4	3.2	2.32	1.55	0.77	67
Ocean (32.9 °/oo)	5 days	8.35	3.4	2.07	1.43	0.64	69
River (< 0.5 °/oo)	6-1/2 hrs	8.3	3.8	2.23	0.63	1.60	28
River (< 0.5 °/oo)	5 days	8.4	3.9	2.06	0.90	1.16	43
River (< 0.5 °/oo)	9 days	8.35	4.1	2.16	1.38	0.78	64

apparent in the open ocean, river, or mixed samples. The data also show that the river water exhibits a faster rate of oxidation than the open ocean or mixed waters when fresh samples were analyzed. These findings enforce the assumption that factors other than salinity appear to have a measurable affect on the rate of oxidation. The slow rate evidenced in the open ocean water could possibly be due to the lack of certain catalysts or to an inhibitive action.

RECOMMENDATIONS

A flow through system, in which free sulfides can be introduced into the water as H_2S gas rather than Na_2S crystals, would probably provide better simulation of actual field conditions. This type of laboratory method would provide a better evaluation of the effects that buffering capacity and pH changes may have on the oxidation rate.

Future studies might investigate the oxidation rate in the field using water immediately after sampling. These field studies could provide more knowledge on the effects aging of the water has on the rate.

Consideration might also be given to securing water samples from known sulfide producing locations to investigate what effects waters from different areas within the estuary may have on the oxidation rate.

SUMMARY AND CONCLUSIONS

The investigations conducted in this study have led to the following conclusions:

1. The time required for a 50% reduction of initial sulfide concentration ranged from 3 hours to 17 hours in estuarine, river, and open ocean waters. These values indicated the presence of catalysts in these waters which increased the rate of oxidation beyond those rates reported in the literature for distilled water.
2. Although there were differences in the disappearance of sulfides observed in estuarine, river, and open ocean waters, no simple relationship between salinity and the rate was apparent.
3. The rate of oxidation of sulfides in estuarine, river, and open ocean waters was affected by the age of the water. Fresher waters exhibited a faster rate of oxidation than aged waters.
4. Fresh estuarine water exhibited a faster rate of oxidation of sulfides than open ocean water, river water, or mixed open ocean and river water of the same salinity as the estuarine water. Therefore, there appeared to be some catalytic factor present in the estuarine water which had a measurable affect on the rate of oxidation.
5. Fresh river water, secured from locations not influenced by tidal excursions, displayed a faster rate of oxidation of sulfides

than open ocean water. A mixture of the open ocean water and river water exhibited a rate which was greater than the rate observed in open ocean water but less than the rate observed in the river water.

The results of this study might help to explain the variation in rates of oxidation noted in previous investigations, especially since age may affect the rate. The findings also indicate that the rate of oxidation of sulfides could vary in different areas of an estuary, as well as from one estuary to another, since factors other than salinity appear to exert a measurable effect on the rate. The investigations illustrate the complexity associated with the oxidation of sulfides in natural waters and the need for more detailed analysis to fully define the kinetics of the reactions.

BIBLIOGRAPHY

1. American Public Health Association. Standard methods for the examination of water and wastewater. 13th ed. New York, 1971. 874 p.

2. Avrahami, M. and R. M. Golding. The oxidation of the sulphide ion at very low concentrations in aqueous solutions. Journal of the Chemical Society (A), 1968, p. 647-651.

3. Bass-Becking, L. G. M. Biological processes in the estuarine environment. VI. The state of iron in the estuarine mud. Iron sulphides. Proceedings. Koninklijke Nederlanse Akademie van Wetenschappen Amsterdam, ser. B, 59:181-189. 1956.

4. Bass-Becking, L. G. M., I. R. Kaplan, and D. Moore. Limits of the natural environment in terms of pH and oxidation-reduction potentials. Journal of Geology 68(3):243-284. 1960.

5. Bass-Becking, L. G. M. and E. J. F. Wood. Biological processes in the estuarine environment. I. Ecology of the sulfur cycle. Proceedings. Koninklijke Nederlanse Akademie van Wetenschappen Amsterdam, ser. B, 58:160-181. 1955.

6. Bella, D. A. and J. E. McCauley. Environmental considerations for estuarine dredging operations. Presented at the World Dredging Conference IV, New Orleans, Louisiana, Dec. 1-3, 1971.

7. Bella, D. A., A. E. Ramm, and P. E. Peterson. Effects of tidal flats on estuarine water quality. Journal of the Water Pollution Control Federation 44(4):541-556. 1972.

8. Berner, R. Diagenesis of iron sulfide in recent marine sediments. In: Estuaries, ed. by G. H. Lauff, Washington, D. C., American Association for Advancement of Science. Publication 83. 1967. p. 268-272.

9. Bloomfield, C. Sulphate reduction in waterlogged soils. Journal of Soil Science 20(1):207-220. 1969.

10. Bowers, J. W., M.J.A. Fuller, and J. E. Packer. Autoxidation of aqueous sulphide solutions. Chemistry and Industry, Jan. 8, 1966, p. 65-66.

11. Chen, K. Y. and J. C. Morris. Oxidation of sulfide by O_2: catalysis and inhibition. Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers 98(SA1):215-227. Feb. 1972.

12. Chen, K. Y. and J. C. Morris. Oxidation of aqueous sulfide by O_2: I. General characteristics and catalytic influences. Presented at 5th International Water Pollution Research Conference, San Francisco, California, July, 1970. (In press)

13. Chen, K. Y. and J. C. Morris. Oxidation of aqueous sulfide by O_2: II. Kinetic presentation. Presented at 43rd Annual Conference of the Water Pollution Control Federation, Boston, Mass., Oct. 4-9, 1970.

14. Cline, J. D. and F. A. Richards. Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature, and pH. Environmental Science and Technology 3(9):838-843. 1969.

15. Federal Water Pollution Control Administration. Northwest Regional Office. Pollutional effects of pulp and paper mill wastes in Puget Sound. Portland, Oregon, March, 1967. 474 p.

16. Fenchel, T. The ecology of marine microbenthos. IV. Structure and function of the benthic ecosystem, its chemical and physical factors and the microfauna communities with special reference to the ciliated protozoa. Ophelia 6(1):1-182. 1969.

17. Hata, Y., et al. Microbial production of sulfides in polluted coastal and estuarine regions. In: Advances in Water Pollution Research, Second International Conference, Vol. 3, ed. by E. A. Pearson, Oxford, England, Pergamon, 1964. p. 287-302.

18. Haydu, E. P., H. R. Amberg, and R. E. Dimick. The effect of kraft mill waste components on certain salmonoid fishes of the Pacific Northwest. Tappi 35(12):545-549. 1952.

19. Ivanov, M. V. and L. S. Terebkova. Microbiological processes of hydrogen sulfide formation in Lake Solenoe II. Microbiology 28(3):387-391. 1959.

20. Orion Research Inc. Determination of total sulfide content in water. Cambridge, Mass. 1969. 2 p. (Applications Bulletin no. 12)

21. Orion Research Inc. Sulfide ion electrode, model 94-16. Cambridge, Mass. 1968. 29 p. (Instruction Manual)

22. Ostlund, H. G. and J. Alexander. Oxidation rate of sulfide in sea water, a preliminary study. Journal of Geophysical Research 68(13):3995-3997. 1963.

23. Servizi, J. A., R. W. Gordon, and D. W. Martens. Marine disposal of sediments from Bellingham harbor as related to sockeye and pink salmon fisheries. New Westminister, B. C., International Pacific Salmon Fisheries Commission. Progress report no. 23. 1969. 38 p.

24. Skopinstev, B. A., A. V. Karpov, and O. A. Vershinina. Study of the dynamics of some sulfur compounds in the Black Sea under experimental conditions. In: Soviet Oceanography, ser. 1964, issue no. 4, p. 55-72. (Translated from Transactions of the Marine Hydrophysical Institute of Sciences of the USSR)

25. Smith, Jr., L. L. and D. M. Oseid. Toxic effects of hydrogen sulfide to juvenile fish and fish eggs. Presented at 25th Purdue Industrial Waste Conference, Purdue University, Lafayette, Indiana, May 6, 1970. (In press)

26. Society of American Bacteriologists. Committee on Bacteriological Technic. Manual of microbiological methods. New York, McGraw-Hill, 1957. 315 p.

27. Sokolova, G. A. and Y. I. Sorokin. Bacterial reduction of sulfates in muds of Rybinsk reservoir. Microbiology 26(2):204-211. 1957.

28. Theede, H., et al. Studies on the resistance of marine bottom invertebrates to oxygen deficiency and hydrogen sulfide. Marine Biology 2(4):325-337. 1969.

29. Vamos, R. The release of hydrogen sulfide from mud. Journal of Soil Science 15(1):103-109. 1964.

30. Van Horn, W., J. B. Anderson, and M. Katz. The effect of kraft pulp mill wastes on fish life. Tappi 33(5):209-212. 1950.

31. Van Horn, W., J. B. Anderson, and M. Katz. The effect of kraft pulp mill wastes on some aquatic organisms. Transactions. American Fisheries Society 79:55-63. 1949.

32. Wells, R. A. Graduate student, Oregon State University, Dept. of Civil Engineering. Personal communication. Corvallis, Oregon. June 1972.

33. Wheatland, A. B. Some factors affecting the presence of sulphide in a polluted estuary. Journal of Hygiene 52(2):194-210. 1954.

34. Zobell, C. E. Organic geochemistry of sulfur. In: Organic geochemistry, ed. by E. A. Berger, Oxford, England, Pergamon, 1963. p. 543-578.

APPENDIX

APPENDIX: METHOD FOR SULFIDE DETERMINATIONS

Free sulfide concentrations were determined using an Orion Model 94-16 silver sulfide probe along with an Orion Model 90-02 double junction reference electrode. An Orion Model 407 specific ion meter was used in conjunction with the specific ion probe. The known subtraction method for sulfide determinations was used as outlined by Orion (21). Lead perchlorate was used as a sulfide complexing agent.

Since sulfides are very unstable in the presence of oxygen, a Standard Anti-Oxidant Buffer (SAOB) as developed by Orion was utilized (20). This SAOB fixes all of the free sulfides present in solution as the S^{2-} species and prevents further oxidation of this species. Exactly 10.0 ml. of sample were withdrawn from the reaction bottles directly into 10.0 ml. of the SAOB using a syringe.

The exact procedure for sulfide determinations used during experimentation was found to give the best results in previous investigations at Oregon State University (32). The 10.0 ml. of sample plus 10.0 ml. of SAOB were transferred to a 50 ml. beaker which contained a magnetic stirring bar. The specific ion probe assembly was then immersed in the solution. Also hooked to the probe assembly was a piece of surgical tubing with a piece of glass tubing inserted in one end. The other end of the surgical tubing was connected to a tank of purified nitrogen gas. The glass tubing was aligned flush with the

end of the sulfide probe, and nitrogen gas was slowly bubbled through the solution during the determinations. The beaker was also covered with a flexible rubber sheet. Nitrogen was bubbled through the solution in order to inhibit oxygen transfer during mixing.

After immersing the probe assembly in the solution, the mixture was stirred for several seconds and the initial millivolt potential was recorded. The mixer was then shut off, and the meter set to center scale. The mixer was started again, and the lead solution was carefully pipetted, dropwise, into the solution. When a desired reading on the known increment scale of the meter was obtained the mixer was turned off. The exact amount of lead solution added was recorded along with the meter reading after the needle had stabilized. With this information the concentration of free sulfides in solution could be determined mathematically.