

COMPLETION REPORT (A-011-ORE)

"Benthal Sulfide Release in
Aquatic Systems"

by

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INTRODUCTION

The purpose of this study was to better understand benthic systems with emphasis given to the sulfur cycle. The primary focus was directed toward the release of free sulfide from benthic systems.

High concentrations of free sulfides within the deposits and the release of free sulfides to the overlying water and atmosphere can be environmentally significant for a number of reasons; among these are the following:

1. Free sulfides, particularly hydrogen sulfide, are toxic at low concentrations to fish, crustaceans, polychetes and a variety of benthic microinvertebrates (10,11 12, 13, 16, 23). In tests which maintained nearly constant conditions, hydrogen sulfide concentrations below 0.075 mg/l (pH 7.6-8.0) were found to be significantly harmful to rainbow trout, sucker, and walleye, particularly to the eggs and fry of these fish (10).

2. The release of free sulfides can increase the benthic oxygen demand rate and thus lead to a decline in the aerobic zone of the deposit and a lowering of the DO concentrations within the overlying waters, particularly with the interfacial regions. Though these interfacial regions constitute a very small fraction of the estuarine water mass, they are of high ecological importance. In addition, if bottom deposits are physically disrupted, a reduction of dissolved oxygen within the water column due to the chemical oxidation of the total sulfides may occur.

3. The release of hydrogen sulfide to the atmosphere can cause an air pollution problem. Not only does hydrogen sulfide have an undesirable odor but it is also toxic. Moreover, the release of hydrogen sulfide from tidal flat areas may be a significant input of atmospheric sulfur (14)(15)(17).

SCOPE OF PROJECT

Initially, studies were attempted within both fresh water and estuarine systems. However, because of the limited size of this project, studies had to be confined to a smaller scale. It was decided not to pursue the fresh water studies to any extent. This decision was influenced by the following considerations:

1. Initial studies indicated that, for a number of fresh water systems the sulfate concentrations were approximately one hundred times lower than sulfate concentrations in marine waters. Thus, sulfate reduction can be expected to be substantially greater in marine systems. In addition, experiments indicated the oxidation of free sulfides were only slightly greater for estuarine waters compared to river waters (18). Thus, free sulfide release can be expected to be greatest in marine systems, particularly estuaries.
2. A number of sampling stations had been previously studied and procedures had been developed for analysis of these systems. The available data, however, was extremely limited.

The majority of funds from this project were employed to obtain additional meaningful data and to examine this data. Of the sixteen sets of data shown in Figures 1-5, twelve were collected and assembled under this study. Evaluation of all sixteen sets was conducted under this study.

The major contributions of this study have been (A) the collection of meaningful data of benthic systems and (B) an improved understanding of these systems with emphasis on the sulfur cycle.

DATA COLLECTED

The sample sites and analytical procedures have been previously described (2)(3)(4). The results of this field study are shown in Figures 1-5. Under this study, the evaluation of this data has been qualitative only. These qualitative results are discussed in the following section. Currently, a more quantitative evaluation of this data is being initiated under a separate study. A mathematical model is being developed to describe the chloride and sulfate profiles. It is anticipated that this study will lead to an improved understanding of the scour and mixing patterns which are important to this system.

DISCUSSION OF SYSTEM AND DATA

Inorganics and organics are deposited to estuarine benthic systems. Inorganics, including sands, silts and clays, are introduced into estuaries from the ocean, upstream rivers and localized runoff. Organics originate from sources outside the estuary and from primary production within the estuary. The system which results from such deposition is illustrated in Figure 6 (4).

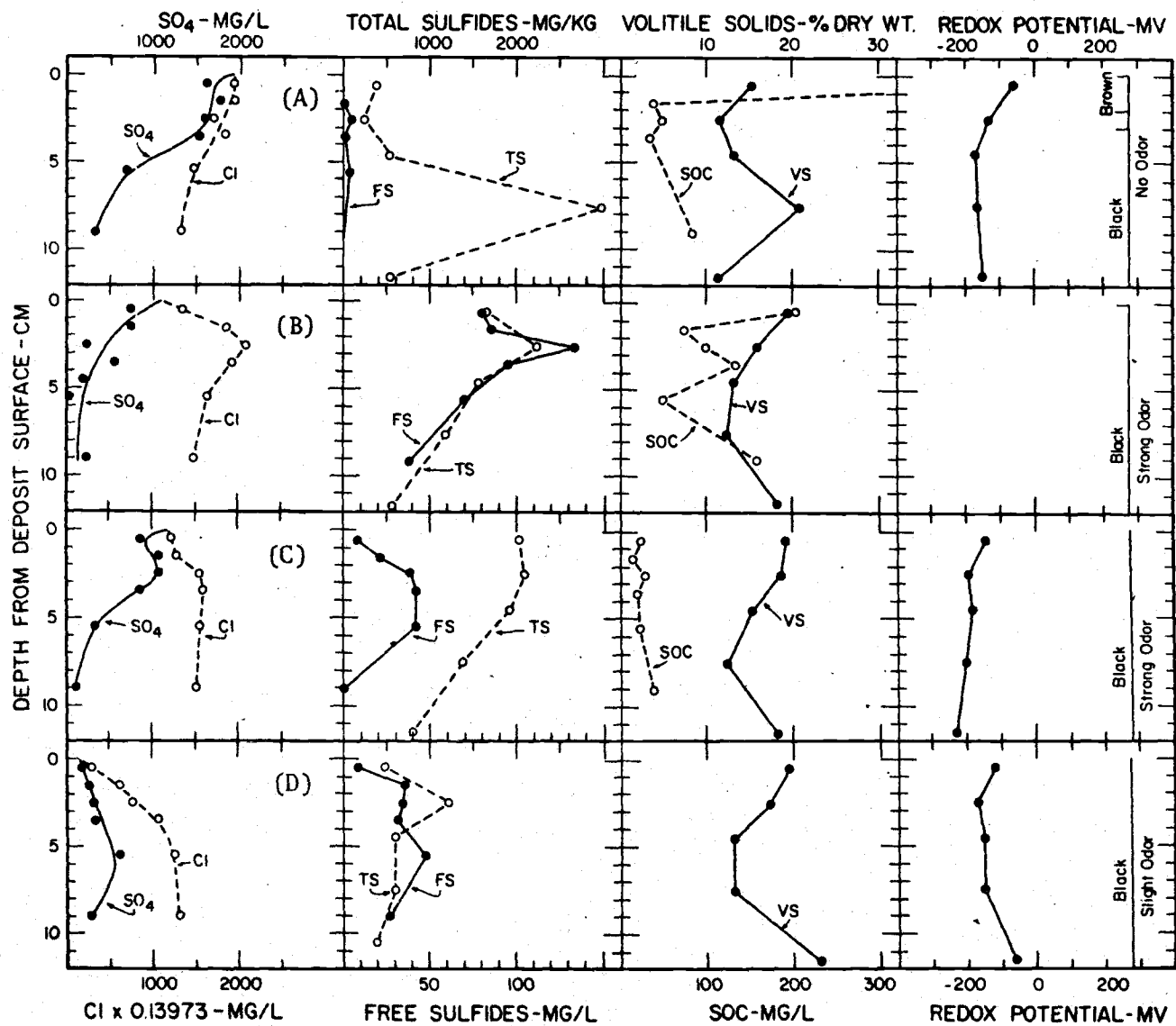


Figure 1. Benthic System, Isthmus Slough Tidal Flat Area; (A) 8/12/71, (B) 8/31/71, (C) 10/28/71, (D) 12/10/71.

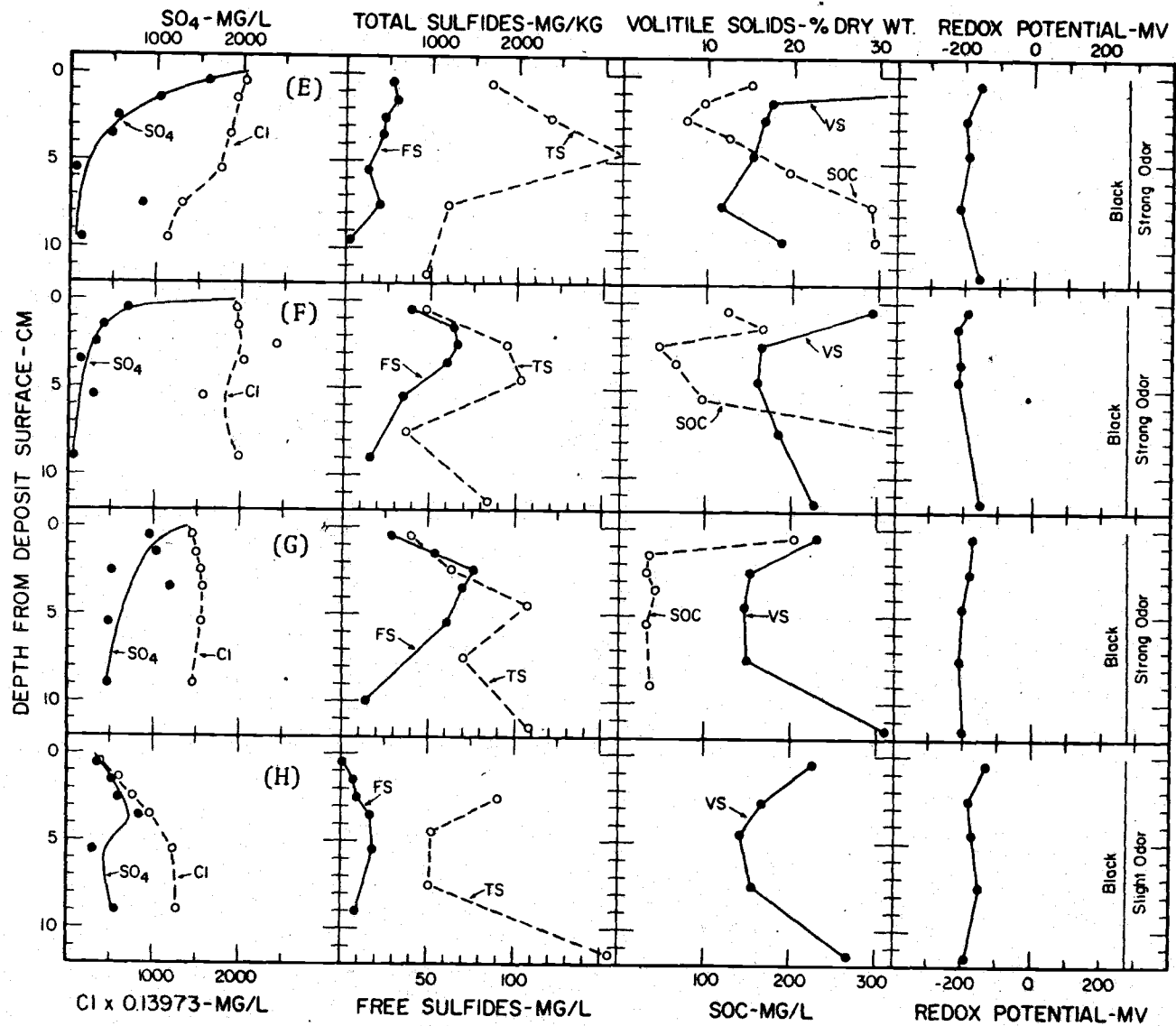


Figure 2. Benthic System, Isthmus Slough Tidal Flat Area; Near Shore;
 (E) 8/9/71, (F) 8/12/71, (G) 10/7/71, (H) 12/10/71.

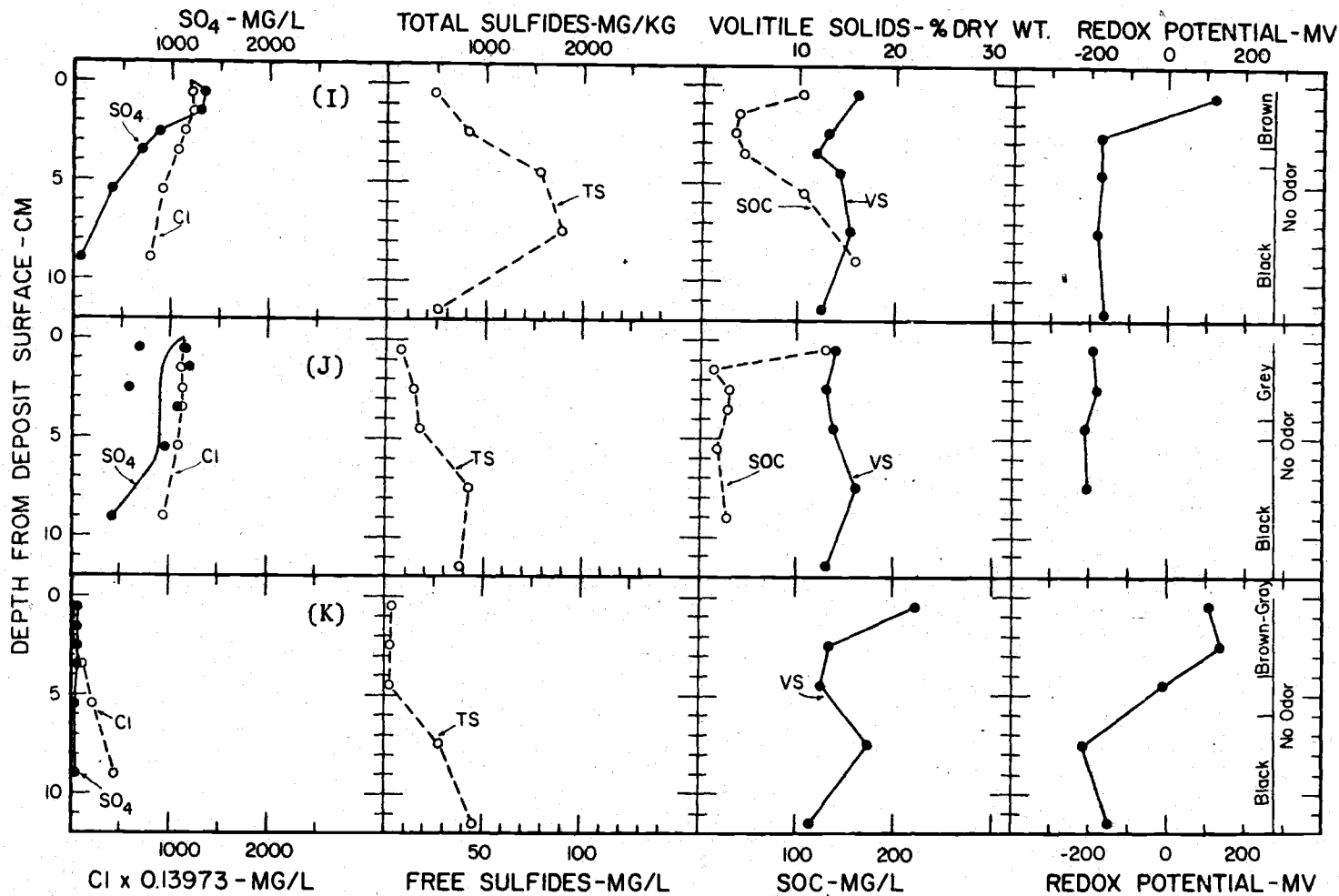


Figure 3. Benthic System Toledo Tidal Flat, Yaquina River; (I) 8/19/71, (J) 9/1/71, (K) 11/29/71.

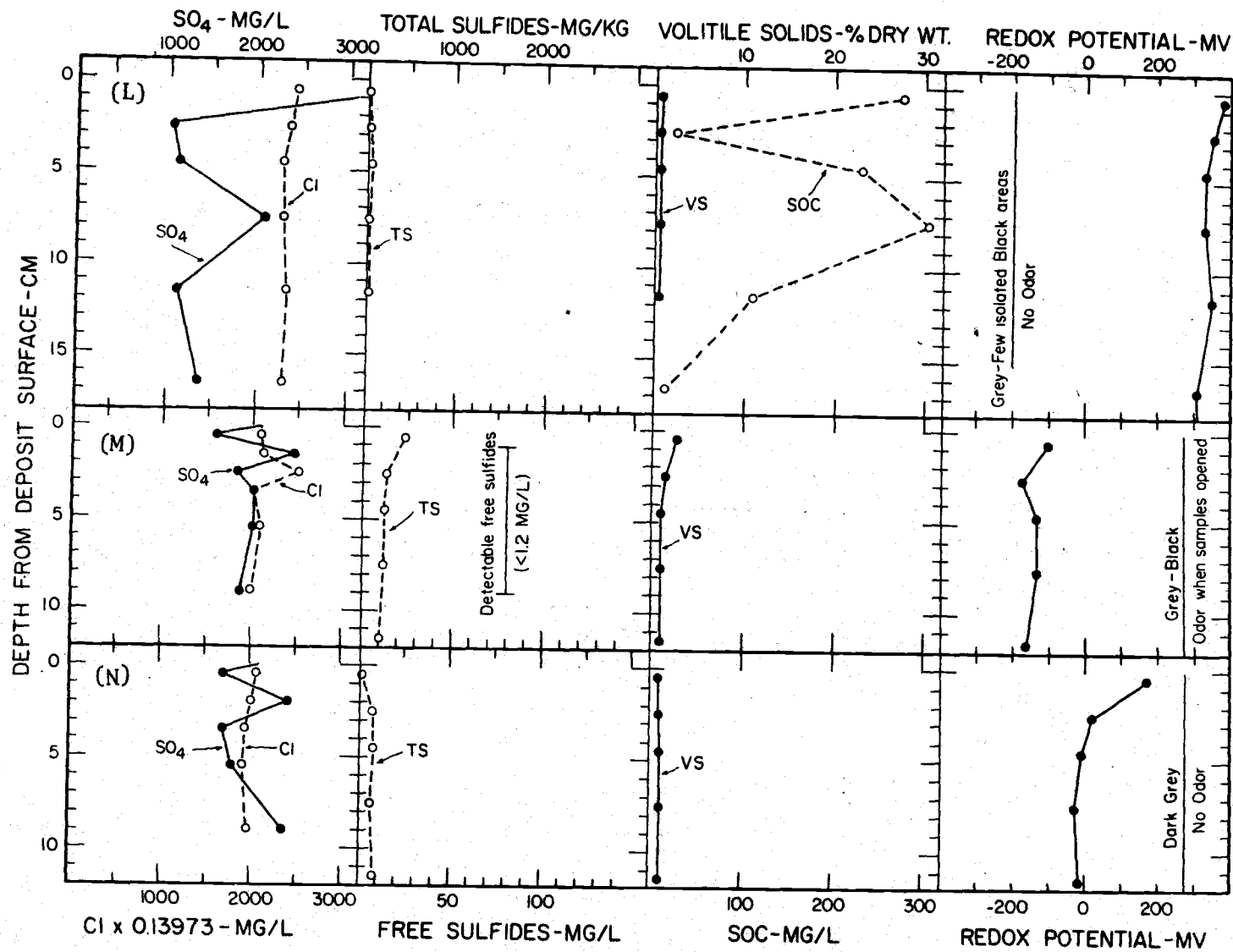


Figure 4. Marine Science Center, Tidal Flat Area, Yaquina Bay; (L) 9/30/71, (M) 12/2/71, (N) 12/3/71.

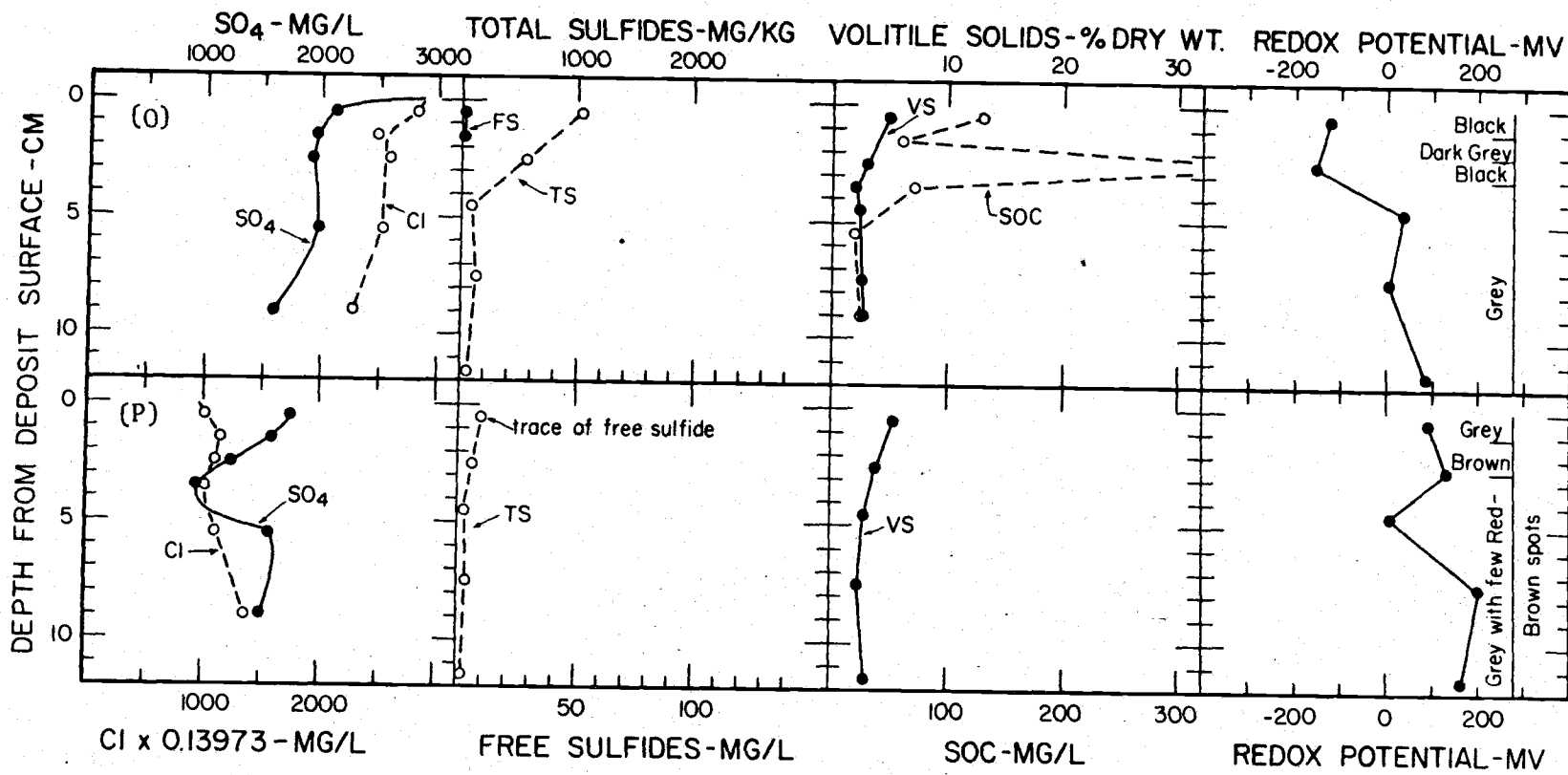
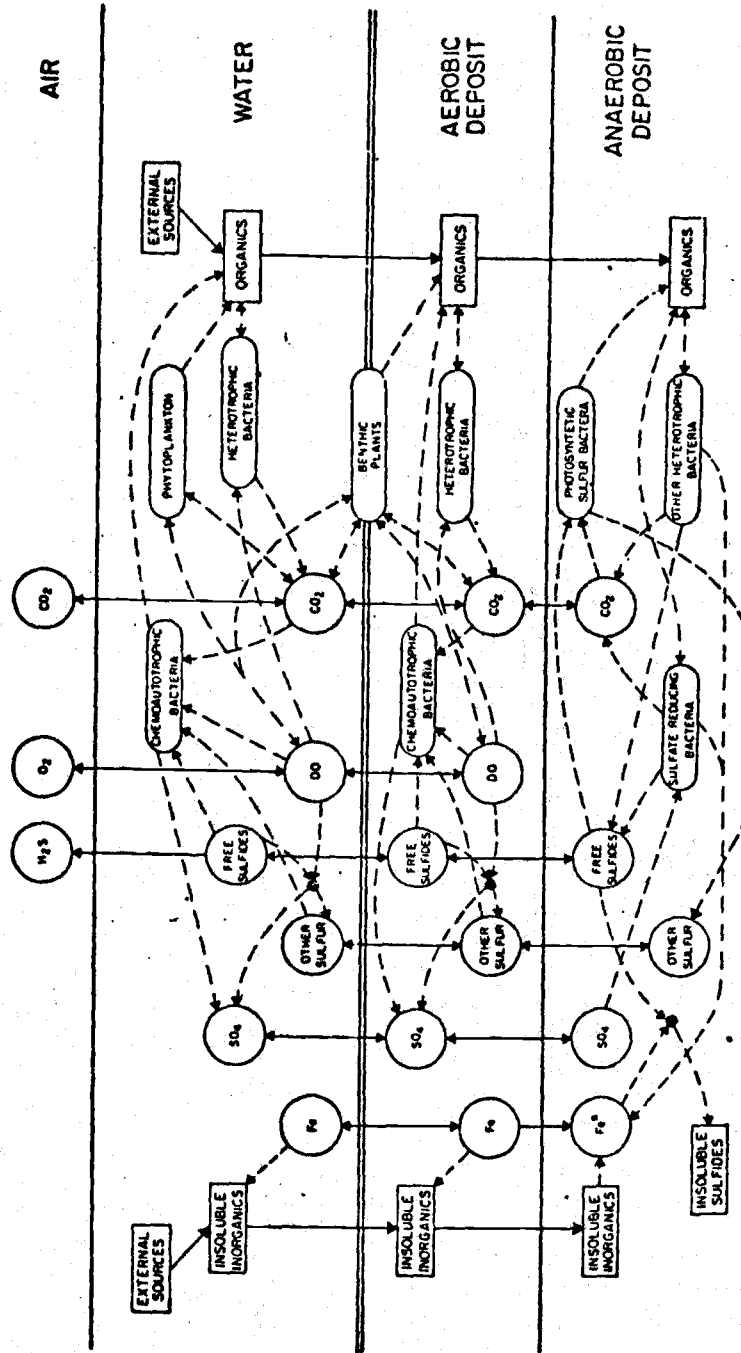


Figure 5. Sally's Bend Tidal Flat Area, Yaquina Bay; (O) 8/25/71, (P) 12/3/71.



SOLID LINES REPRESENT PHYSICAL TRANSFER PROCESS
 DASHED LINES REPRESENT CHEMICAL REACTION NOTED BY ●
 ● REACTIONS AVAILABLE FOR Fe, Zn, Sn, Cd, Hg and Cu

Figure 6. Estuarine Benthic System

The significant chemical transformations with the carbon, sulfur and nitrogen cycles are primarily mediated by bacterial metabolism with carbon from the deposited organics acting as the primary hydrogen donor. However, the type of bacterial decomposition occurring at any location is determined principally by the availability of hydrogen acceptors. When available, dissolved oxygen DO, is used as the hydrogen acceptor. In its absence and with the corresponding low Eh, conditions, sulfate becomes the principal hydrogen acceptor. Redox potentials are provided in column 4 in Figures 1-5. Sulfate reduction normally occurs when the redox potential is approximately -200 MV. Oxidizing conditions are indicated by a positive redox.

Because nitrate concentrations are nearly always far less than sulfate concentrations within estuarine systems, nitrate reduction, which will occur before sulfate reduction, is not usually significant. Nitrate profiles were not measured in this study. In most cases, however, nitrate would likely become depleted within a very short distance from the sediment surface. The absence of suitable concentrations of both oxygen and oxidized sulfur necessitates the use of endogenous hydrogen acceptors. (For a discussion of endogenous and exogenous hydrogen acceptors see reference (21)).

The availability of exogenous hydrogen acceptors (DO and sulfates) depends upon the mixing and advection within the deposits. Vertical mixing and thus the transport of exogenous hydrogen acceptors results from physical turnover of the deposits, and molecular diffusion. Sample set F (Figure 2) is the best example of a system predominantly controlled by molecular diffusion. The sulfate profile is quite sharp and sulfate likely

becomes limiting at approximately 5 cm from the sediment surface. Sample set A (Figure 1) and sample set I (Figure 3) provide examples of physical turnover to a depth of approximately 3 cm from the surface. Note the brown sediment color in turned over region and the higher redox in this region. Also, sulfates are relatively evenly mixed in this region and total sulfides are less here than at greater depths.

Advection through the deposits depends on the permeability of the deposits and the direction and magnitude of the hydraulic gradient. The greatest advection occurred through the sandy sediments of Figure 4 (19). As a result of this advection, sulfates were not depleted with depth, the sediments were not black, total sulfides were low and the redox was high except for sample set M. Advection through burrow holes occurred for the site shown in Figure 4. A tight algal mat covered the sediments of sample set O.

The reduction of sulfates by heterotrophic sulfate-reducing bacteria which utilize the sulfate ion as a terminal hydrogen acceptor (1) results in the release of hydrogen sulfide which is found in solution as part of the pH dependent system



In the present discussion, all components of the above relationship will be defined as "free sulfide". At a pH of 6.5-7.0, the free sulfide is approximately evenly divided between H_2S and HS^- with $\text{S}^{=}$ being negligible. Free sulfides are also produced during anaerobic putrefaction of sulfur containing amino acids, but this process is of negligible importance in the marine environment (9)(12).

Substantial free sulfides were only measured in the Isthmus Slough area (Figures 1 and 2). A distinctive odor (rotten eggs) was noted when free sulfides were measured (see Figures 1-5).

Free sulfides form insoluble compounds with heavy metals, particularly iron. Free sulfide quickly reacts with available iron within the deposits to form ferrous sulfide, FeS, which gives benthic deposits their characteristic black color (6). The results clearly show the relationship of the black sediment color (column 4) to the presence of combined sulfides listed as total sulfides (acid soluble) in column 3.

The input of iron into the deposits results primarily from the deposition of insoluble inorganics which contain ferric oxides and other insoluble forms of iron (7). Not all of this iron, however, is available to react with the sulfides.

Free sulfide concentrations within benthic deposits will remain at low levels (generally below 1 mg/l) when available iron is present. If available iron is sufficiently depleted, free sulfides within the anaerobic regions of deposits will increase. Free sulfide may diffuse to the aerobic regions of the deposits and into the overlying waters. Free sulfides have been measured in the waters above the Isthmus Slough deposits (3). Physical disruption of the deposits may also lead to the release of free sulfides.

Free sulfides are oxidized within the aerobic regions of the deposits and within aerobic waters. This reaction is extremely complex and appears to be catalyzed by the presence of metallic ions (8). Within oxygenated seawater, the half life of sulfide has been reported to vary

from ten minutes to several hours (9)(20). Studies indicate that estuarine waters stored for a period of time after collection will display slower oxidation rates of free sulfides than freshly collected waters (18). Since HS^- predominates at the pH of seawater, it has been proposed that the oxidation proceeds by the following reaction



Following the above chemical oxidation, the thiosulfate ion is more slowly oxidized to sulfate, probably with the intermediate production of other oxidized forms. Sulfur oxidizing bacteria of the genus Thiobacillus appear to be important in this final oxidation step (16)(22).

If the deposits are physically overturned or flushed with oxygenated water, ferrous sulfide will be oxidized. The oxygenated overturned sediments will normally return rapidly to anaerobic conditions. A portion of the oxidized ferrous sulfide iron will be returned to the sediment as available iron which can further react with free sulfide to form more ferrous sulfide. Thus, overturning or flushing of sediments leads to a recycling of available iron. The organic content of the sediments in Figure 3 (Toledo area) was nearly equal to that of the Isthmus Slough area (Figures 1 and 2) as indicated by the volatile solids (column 3). Free sulfides, however, were not measured at the Toledo site. This is likely due, in part, to the greater physical turnover of the sediments in the Toledo area (note the light color in the surface regions of sample sets I, J, and K). The Toledo site was open to currents and wave action while the Isthmus Slough area was protected by a dike.

The oxidation of ferrous sulfide (FeS) may result in the formation of elemental sulfur which, under anaerobic conditions, will react with ferrous sulfide to form pyrite (5). This reaction proceeds very slowly (on a time scale of months to years). The formation of pyrite, however, does mean that available iron can be relatively low. Thus, the amount of ferrous sulfide may serve only as a rough indicator of the amount of available iron that has been used within a sediment and the limitations of such an indicator must be recognized. It is planned that future studies will measure both pyrite and the chemical sulfide demand.

FUTURE WORK

Currently, a more quantitative evaluation of the data presented here is being conducted under separate funding.^(a) Particular emphasis will be given to the physical turnover of sediments which, as described, can be a controlling factor in the release of free sulfides.

It appears now that a meaningful rapid set of measurements can be developed for benthic systems and such an effort is now being pursued.

Detailed sampling, as shown in this report, will be expanded to include pyrite, chemical sulfide demand and ammonia. A replacement for the volatile solids measurement is being considered. Free sulfide measurement may be eliminated for efficiency and replaced by a lead acetate paper indicator test.

^(a) It was not possible to complete the mathematical model evaluation of the data shown in Fig. 1-5 under this limited study. It is anticipated that a professional paper with this data and a model will be completed within several months from the date of this report. Acknowledgement will be given to this study.

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