AN ABSTRACT OF THE THESIS OF

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Title: BIODEGRADABILITY AND OXYGEN UPTAKE STUDIES ON RESUSPENDED ESTUARINE BOTTOM SEDIMENTS

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A study was conducted to determine the oxygen uptake rate of resuspended estuarine bottom sediments and the biodegradability of the organic matter released during resuspension.

Oxygen uptake was measured on a Gilson Differential Respirometer and the percent biodegradability was calculated by determining the soluble organic carbon on a Beckman Carbonaceous Analyzer.

A preliminary study was conducted to determine if estuarine sediments contained sufficient bacteria to exert a measurable oxygen uptake or if additional bacterial seed was required. The oxygen uptake rates of unseeded and seeded sediments were compared and the results indicated that additional seeding was not necessary.

Another preliminary study was conducted to evaluate the effect of storage time at 4° C on the oxygen uptake rate of resuspended estuarine bottom sediments. The oxygen uptake rate of an

homogenized sample was measured up to eight days after collection. Results indicated that the oxygen uptake rate was not seriously effected by storage at 4°C within the time interval tested.

Oxygen uptake rates and percent biodegradability of four estuarine sediment samples were measured. The oxygen uptake rates varied from 2 to 360 μl O_2/gram/hr. Percent biodegradability was calculated from soluble organic carbon measurements and varied from 10.4% to 81.0%. The volatile solids content of the sediment and the soluble ferrous iron, free sulfide and sulfate concentrations in the interstitial water were also measured. The data were statistically analyzed for correlation between these parameters and the oxygen uptake rate and percent biodegradability.

Experimental results indicated that the oxygen uptake rate was directly related to both the volatile solids content of the sediment and the soluble organic carbon released during resuspension. The percent biodegradability of the carbonaceous material released during resuspension of the sediments was found to be related to the soluble organic carbon and the free sulfide concentration in the interstitial water.

Biodegradability and Oxygen Uptake Studies on Resuspended Estuarine Bottom Sediments

by

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BIODEGRADABILITY AND OXYGEN UPTAKE STUDIES ON RESUSPENDED ESTUARINE BOTTOM SEDIMENTS

I. INTRODUCTION

General

Dredging in and around estuaries has become an accepted practice throughout the country, however concern has recently arisen over the possible detrimental effects of dredging to the delicate balance of life in these estuaries. Even though dredging operations are considered to be a major cause for concern, very little research has been done to evaluate its effects on the environment.

The role that bottom deposits play in the oxygen balance of streams, lakes and estuaries has been evaluated and mathematical models have been developed to describe these effects. Oxygen depletions have been observed in the area of dredging operations but the causes of these depletions have not been determined. Therefore, not only must quantitative evaluations be made of the oxygen depletions that occur but the causes should also be studied.

When sediments are disturbed and suspended most of the particles will settle rapidly but a significant portion of small particles will remain in suspension and possibly cause environmental damage by increasing turbidity. Also as the sediments are suspended, dissolved organic matter may also be released into the water and be made readily available for biodegradation.

The Solid Waste Management Office of the United States Environmental Protection Agency reported that in 1970 over 52 million tons of dredge spoil from the coastal areas of the United States were disposed of by ocean dumping (20) compared to 39 million tons in 1968 (6). This comparison emphasizes the increase in dredging activity over the past few years, but it may not be entirely valid since some states such as California had instituted the practice of disposing of dredge spoil on land by 1970. The advent of the supertanker and other deep-draft vessels will increase the amount of dredging required in the future for maintenance of deeper channels.

Purpose

This study was undertaken to determine the oxygen uptake rates of resuspended estuarine bottom sediments and the biodegradability of the organic matter released during resuspension, and to correlate the data to some chemical properties of the sediment. Another objective was to develop the required methodology for handling and studying estuarine sediments since previous research to develop these methods has been scarce.

II. LITERATURE REVIEW

The oxidation of bottom sediments has been studied by a number of investigators and a number of methods for study have been used. In 1938, Waksman and Hotchkiss (22) studied the oxygen consumption of sediments by placing the sediment in sealed bottles and measuring the oxygen depletion with time by the Winkler technique. They concluded that sediments consisting of sandy mud created a greater oxygen demand than sandy sediments. Anderson (2) studied the distribution of organic matter with depth and its availability for decomposition by the oxygen consumed per gram of organic carbon. The distribution of carbon in the mud varied considerably with depth as well as the availability for decomposition. He also used the bottle technique and determined the dissolved oxygen by the Winkler method. Edwards and Rolley (9) and Rolley and Owens (18) observed the oxygen consumption of sediments of undisturbed cores using the polarographic method for oxygen determination proposed by Knowles, Edwards and Briggs (13). In both of the above papers the authors tried to establish some correlation between the rate of oxygen consumption and chemical parameters of the sediment. Some of the chemical parameters measured were the organic carbon content, dehydrogenase activity, humic acid content and Kjeldahl nitrogen. In both studies no correlation could be found between these parameters and the rate of oxygen consumption. More recently, Hanes and Irvine (12) and Davison and Hanes (7) studied the oxygen uptake rates of benthal systems by placing a layer of sediment in a large plexiglas reactor sealed to the atmosphere and measuring the oxygen consumption continuously with a dissolved oxygen meter and probe. They found that once consolidation of the bottom deposits was complete the oxygen uptake was independent of the depth of the deposit. Berg (4) in 1970, used a respirometer to study the oxygen uptake of bottom sediments with very good results. He concluded that the sediments did not require external seeding to initiate the biochemical reactions. Martin (14) studied the activity of sediments in core sampling tubes and measured the dissolved oxygen by the Winkler method. He also tried to determine the oxygen demand of dissolved gases in the sediment to distinguish between biological and chemical oxygen demand. He concluded that the chemical demand was minimal.

With the exception of Berg (4), all of the above investigators have studied the oxygen consumption of bottom sediments in a quiescent condition with gentle agitation of the overlying water. However, some general conclusions have been stated in common by these workers despite differences in the methods used. First, the rate of oxygen consumption could not be correlated with the amount of organic matter present (2, 9, 17, 22). Second, although quiescent conditions had been maintained, some of the investigators have noted that any disturbance that results in scouring and resuspension of the sediment, however slight it may be, would increase the rate and amount of oxygen consumption (4, 7, 9, 14, 22).

The actual effects of dredging have been studied to a much lesser extent. While sampling in the general area of dredging activity, before and during the actual operations, Brown and Clark (5) noted that the dissolved oxygen was much lower while dredging was in progress. They theorized that the resuspension of the bottom sediments was the primary cause of this depletion. Gannon and Beeton (11) studied the effects of dredged sediments from the Great Lakes on the amphipod Pontoporeia and found high mortality rates in cases where the sediment originated in harbors as opposed to open lake sediments. Servizi, Gordon and Martens (19) evaluated oxygen depletion, hydrogen sulfide production and turbidity from sediments at a proposed dredging site in Bellingham Harbor, Washington. The site consisted of two areas, one that received the effluent from a wood pulping mill and the other in the open harbor. The sediments were placed in large tanks and bioassays on juvenile salmon were performed after disturbing the sediments. The authors concluded that when the sediments containing putrefied wood fibers were disturbed they were harmful to salmon as a result of turbidity and hydrogen sulfide toxicity.

III. EXPERIMENTAL STUDIES

Materials and Methods

Sampling

Core samples were taken from various locations on the Umpqua and Coos Estuaries on the Southern Oregon coast. Samples were taken by pushing either six foot by two inch diameter aluminum tubes into the bottom by hand from a boat, or where areas were accessible on foot, 18 inch by two inch diameter plexiglas tubes were used. After samples were collected, the tubes were sealed with rubber stoppers and transported to the laboratory and placed in storage at 4° C. In some cases duplicate cores were taken to extract the interstitial water from the sediment to measure some chemical parameters. The water was obtained by using an interstitial water sampler like the one developed by Reesburg (16) as shown in Figure 1. The water samples were prepared in the field and returned to the laboratory for analysis.

The approximate sites for the sampling at the Umpqua and Coos Estuaries are shown in Figures 2 and 3, respectively. The sampling sites were chosen from areas of future dredging operations or past industrial use. These sites also enabled collection of sediments with different physical and chemical characteristics. Water

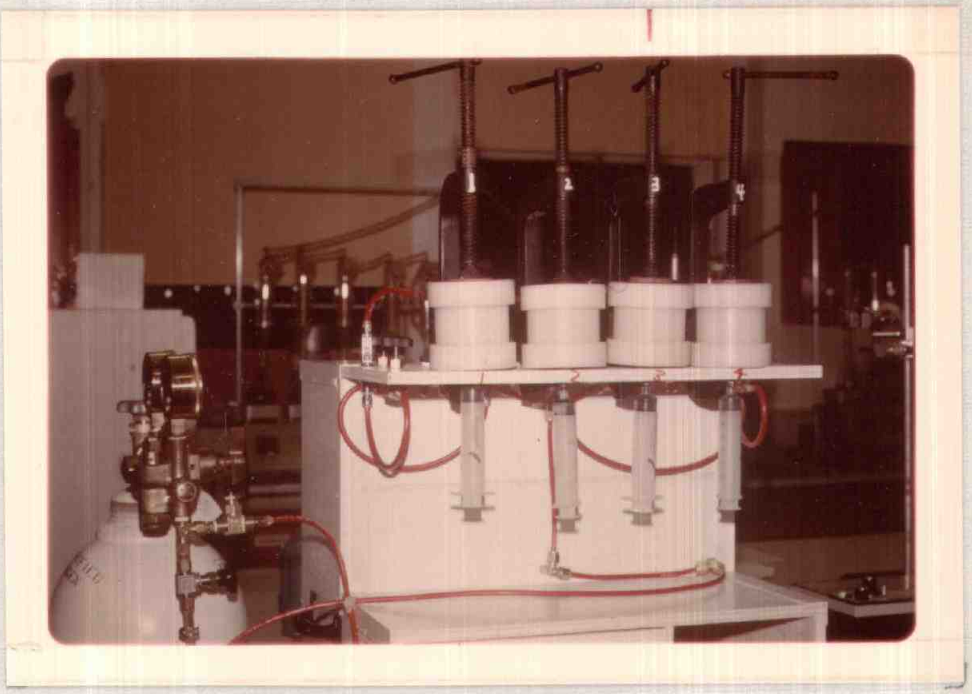

Figure 1. Interstitial water sampler.

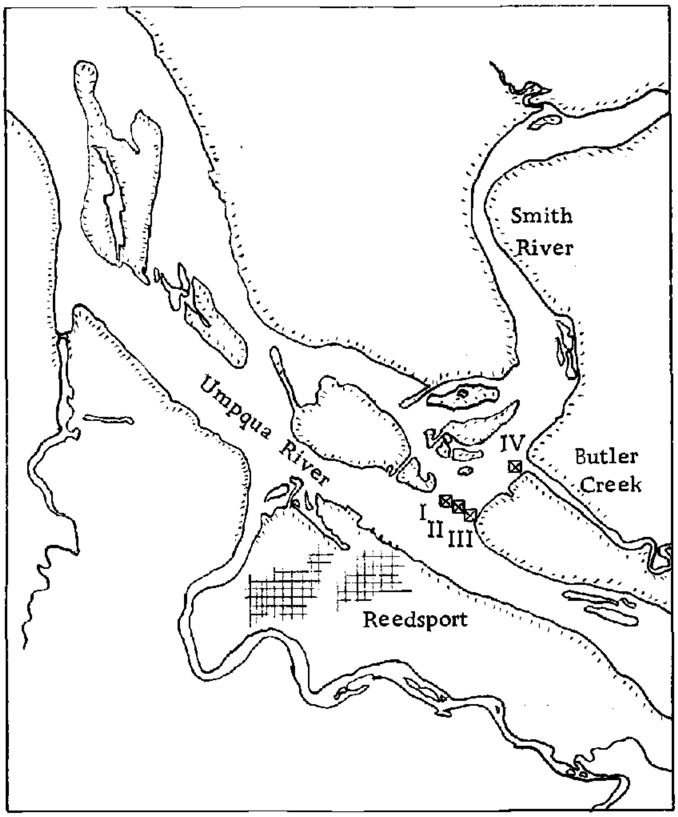

Figure 2. Smith River on the Upper Umpqua Estuary at Reedsport, Oregon. (Estuarine bottom sediment samples I, II, III and IV.)

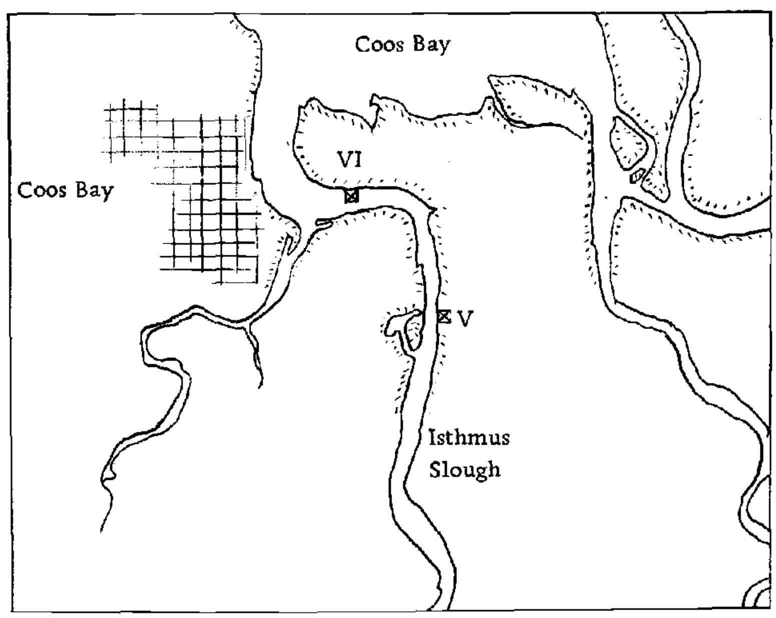

Figure 3. Isthmus slough on the Coos Estuary at Coos Bay, Oregon. (Estuarine bottom sediment samples V and VI.)

samples were collected and stored in 20 liter carboys at 4° C.

Laboratory Apparatus

The following equipment was used in this investigation:

1 - Beckman Carbonaceous Analyzer Model #137879

1 - Beckman Spectrophotometer Model DB

1 - Gilson Differential Respirometer

2 - "Magnestir" Magnetic Stirrers

1 - Orion Specific Ion Meter Model 407

1 - Orion Silver/Sulfide Probe Model 94-16A

Laboratory Analyses

Oxygen Uptake. Oxygen uptake rates and ultimate oxygen demand were determined on a Gilson Differential Respirometer as shown in Figure 4 using 125 ml Gilson flasks. Forty ml samples of suspended sediment were used. Oxygen uptake was read directly on a micrometer calibrated in microliters and corrected to standard temperature and pressure. All oxygen uptake studies were carried out with the water bath set at 20° C. All procedures were performed as recommended in the manufacturer's instruction manual (8) and in Manometric Techniques (21). Oxygen uptake rates were expressed in microliters O_2/gram suspended solids (dry weight)/hour.

Soluble Organic Carbon. Soluble organic carbon (SOC) analysis

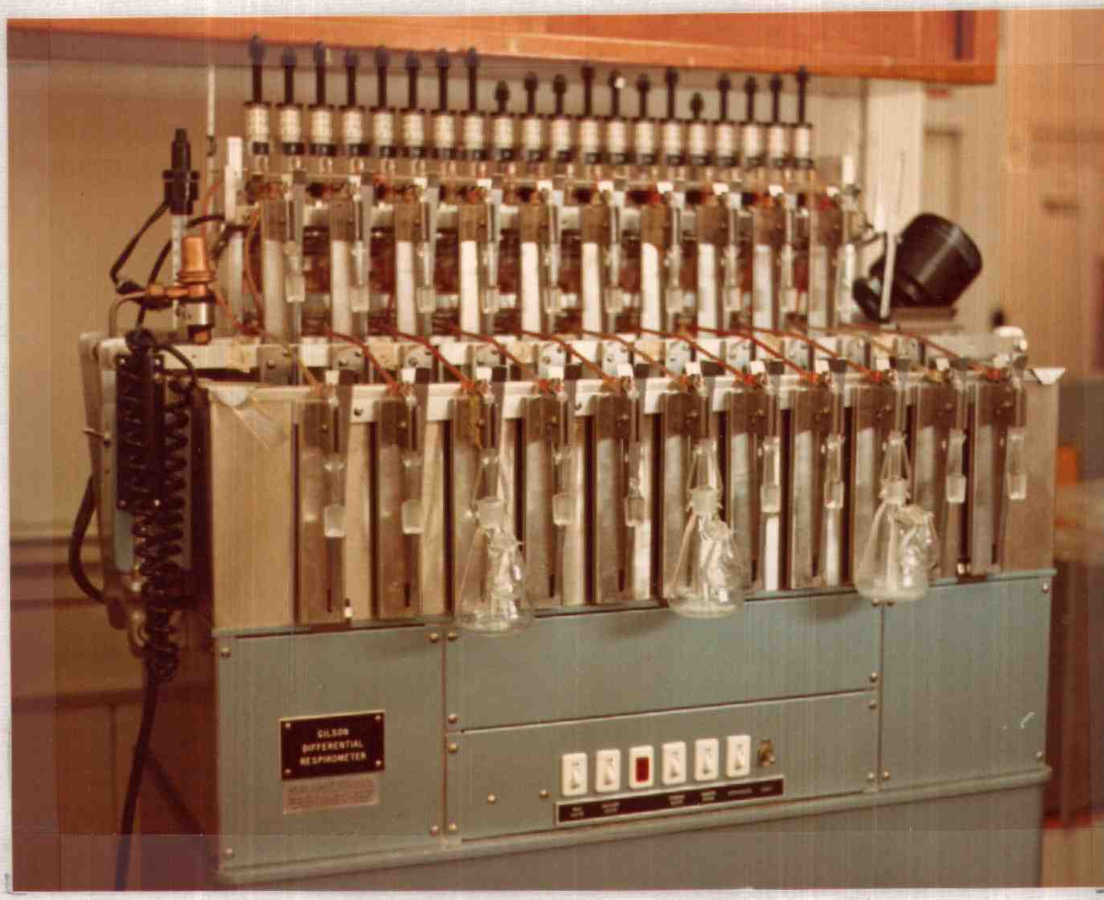

Figure 4. Gilson Differential Respirometer.

was performed using a Beckman Carbonaceous Analyzer equipped with an infrared analyzer. All procedures recommended in the manufacturer's instruction manual (3) were followed. Potassium acid phthalate was used to prepare standards for calibration of the analyzer.

Total and Volatile Suspended Solids. All analyses of total and volatile suspended solids were performed according to the procedures outlined in Standard Methods for the Examination of Water and Wastewater (1).

Soluble Ferrous Iron. Soluble ferrous iron in the interstitial water of the sediments was analyzed colorimetrically by the Phenanthroline method as outlined in Standard Methods (1) with the following modifications. Fifty ml sample volumes are recommended when Nessler tubes are used for the analysis, however samples of only two to three mls were obtained from the interstitial water sampler. Therefore, five ml sample cells were used for this determination and all reagent volumes were correspondingly reduced by a factor of ten.

Free Sulfide Concentration. Free sulfides ($S^{=}$, HS^{-} and H_2S) in the interstitial water of the sediments were analyzed by the Known Subtraction method using an Orion Specific Ion Meter and an Orion Silver/Sulfide probe. All procedures recommended in the manufacturer's instruction manual (15) were followed.

Sulfate Concentration. Sulfate concentrations in the interstitial water of the sediments were analyzed by the Automated Chloranilate method. The procedures outlined in the FWPCA Methods for Chemical Analysis of Water and Wastes (10) were followed.

Preliminary Studies

Effects of Seeding Sediment Samples

Introduction. Bacterial numbers will increase the rate of organic decomposition as measured by oxygen uptake rate but the effect may be limited by the amount of organic matter present. This limiting condition should therefore be exhibited by reaching a maximum oxygen uptake rate that will be maintained regardless of the number of bacteria present.

In this phase of the investigation, identical portions of sediment were seeded with different amounts of bacteria and compared with an unseeded sample. The purpose of this was twofold; first, to determine the maximum oxygen uptake rate of the resuspended sediment and second, to determine if there are sufficient bacteria in the sediment and water to achieve a measurable oxygen uptake rate. The results were used to determine if sediments can be studied in the "natural" condition or if additional seeding will be necessary.

Technique. A core sample (Core II) of sediment was taken from the Umpqua estuary at the mouth of the Smith River at Reedsport, Oregon (Figure 2). The sample was returned to the laboratory and placed in storage at 4° C.

The following procedure was used for preparation of the samples and measurement of oxygen uptake. The sample was first allowed to come to room temperature. The sediment was then placed in a one-liter beaker and water from the sampling area was added. The beaker was placed on a magnetic stirrer and mixed to keep the sediment in suspension. Forty ml samples were withdrawn while stirring continued and placed in 125 ml Gilson flasks. One set of flasks was not seeded while the other sets of flasks were inoculated with 1.0, 2.0, 4.0 and 8.0 mls of bacterial seed. The seed was obtained by aerating 250 mls of water, collected at the sampling area, that had been enriched with nutrient broth for 24 hours. Before the bacterial seed was introduced into the flasks, it was centrifuged, washed and resuspended in estuarine water three times. Another set of flasks, each containing 40 mls of estuarine water without sediment were also prepared for measurement of baseline oxygen uptake. The flasks were mounted on the respirometer and permitted to reach thermal equilibrium in the water bath set at 20° C. Measurement of oxygen uptake began with gentle agitation of the flasks at 106 oscillations per minute throughout the measurement period.

Duplicate 10 ml samples were withdrawn from the sample beaker for total and volatile suspended solids analysis.

Results. The cumulative oxygen uptake data are plotted in Figure 5. As expected the oxygen uptake rate increased with increasing amounts of seed until a maximum rate was achieved. The curves for the unseeded flasks and the flasks inoculated with 1.0 ml of seed could not be distinguished so only the data for the unseeded flasks were plotted in Figure 5. The oxygen uptake rate for the unseeded resuspended sediment was 44.6 µl O_2/gram/hr. The maximum oxygen uptake rate of 54.5 µl O_2/gram/hr was reached with 4.0 mls of bacterial seed and since the rate did not change for 8.0 mls only the data for the flasks containing 4.0 mls were plotted.

The data from this sample and from additional samples analyzed by the same technique (not shown) suggest that estuarine bottom sediments contain extensive bacterial populations. Therefore, the oxygen uptake of resuspended estuarine bottom sediments can be studied without adding external bacterial seed.

Evaluation of Sample Storage Techniques

Introduction. Samples containing organic matter are subject to biological decomposition during storage even at low temperatures. This decomposition may seriously effect the results of analyses designed to measure concentrations of organic matter or biological activity of the samples. Berg (4), while studying the oxygen uptake

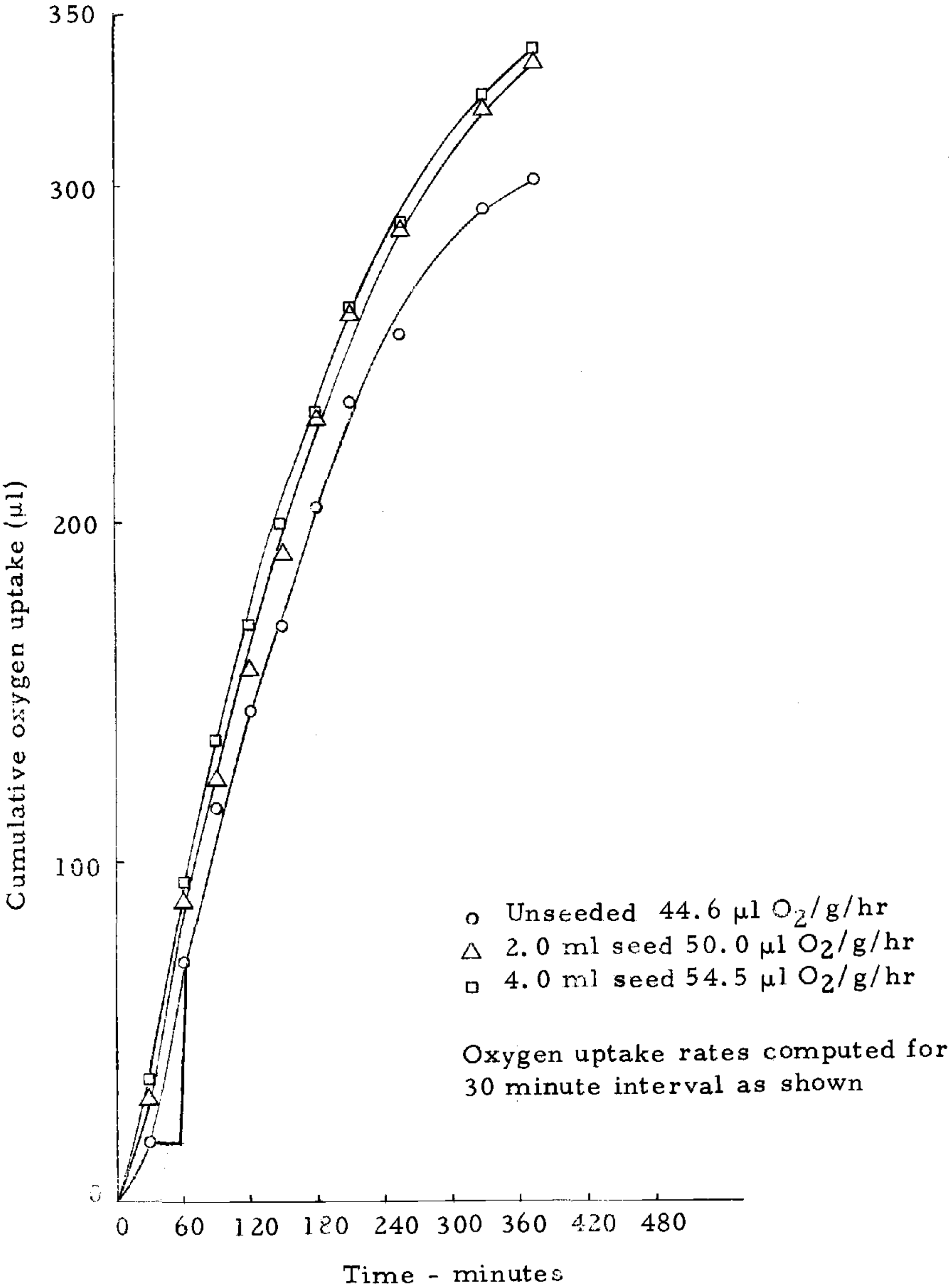

Figure 5. Cumulative oxygen uptake vs. time for unseeded and bacterially seeded estuarine bottom sediments. (Core II, from Smith River at the Umpqua Estuary on the southern Oregon Coast.

of bottom sediments at Seattle University found that . . . "The magnitude of the maximum oxygen uptake rate is sensitive to the elapsed storage time of the samples. Storage at 4° C does not eliminate this problem."

The purpose of this phase of the investigation was to determine the effect of storage time at 4° C on the biological activity of samples of bottom sediment as measured by the rate of oxygen uptake. The results will be used to determine a maximum storage time for other samples to be collected for this study.

Technique. A core sample (Core I) was taken from the Umpqua Estuary at the mouth of the Smith River at Reedsport, Oregon (Figure 2). The sample was returned to the laboratory and homogenized in a Waring blender. The oxygen uptake was measured on a portion of the sample within 24 hours of collection. The remaining portion was stored at 4° C for subsequent oxygen uptake measurements at 2, 4 and 8 days after collection.

The procedure for preparation of the samples and measurement of oxygen uptake outlined in the previous section on the effects of seeding sediment samples was followed except in this case the samples were not seeded.

Results. The cumulative oxygen uptake data are plotted in Figures 6, 7, 8 and 9. The data was corrected for the baseline oxygen uptake so the curves reflect uptake due to the sediment only.

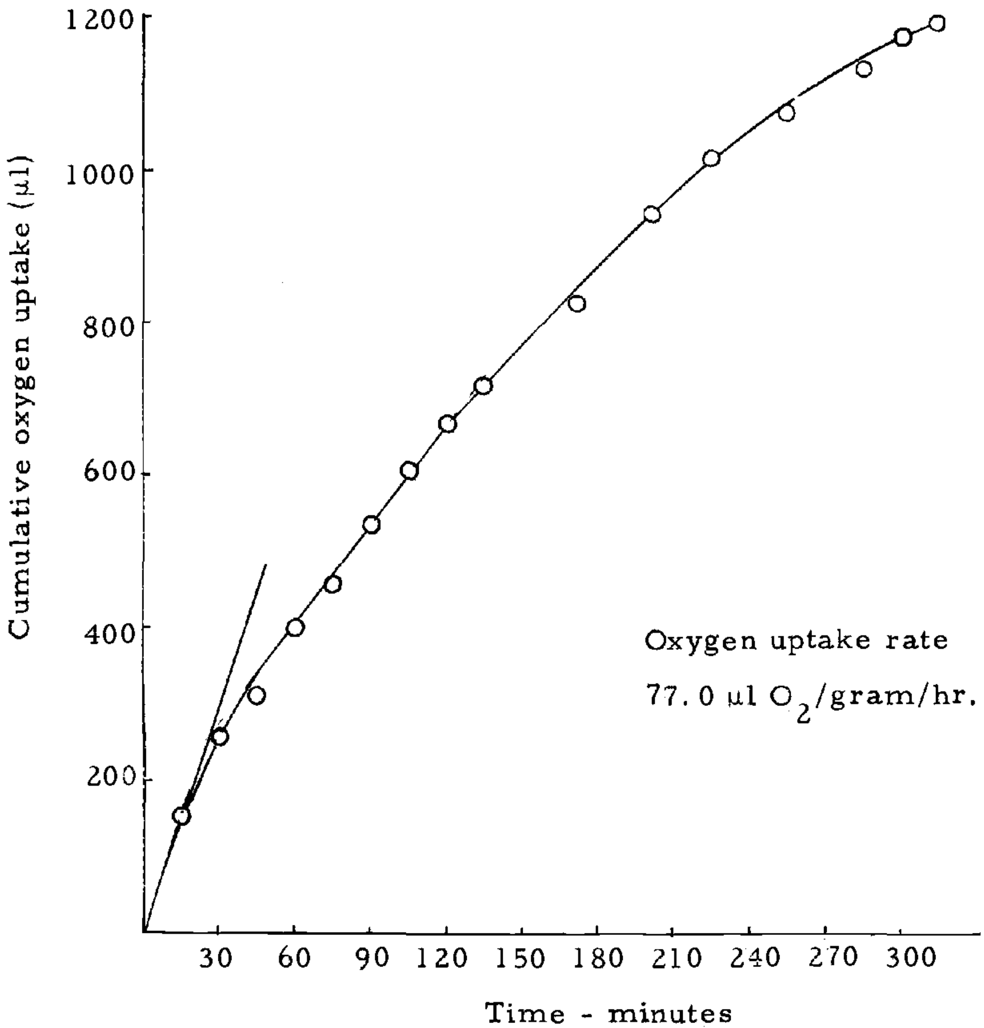

Figure 6. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment after storage at 4° C for 1 day. (Core I from the Smith River at the Umpqua Estuary on the southern Oregon Coast.)

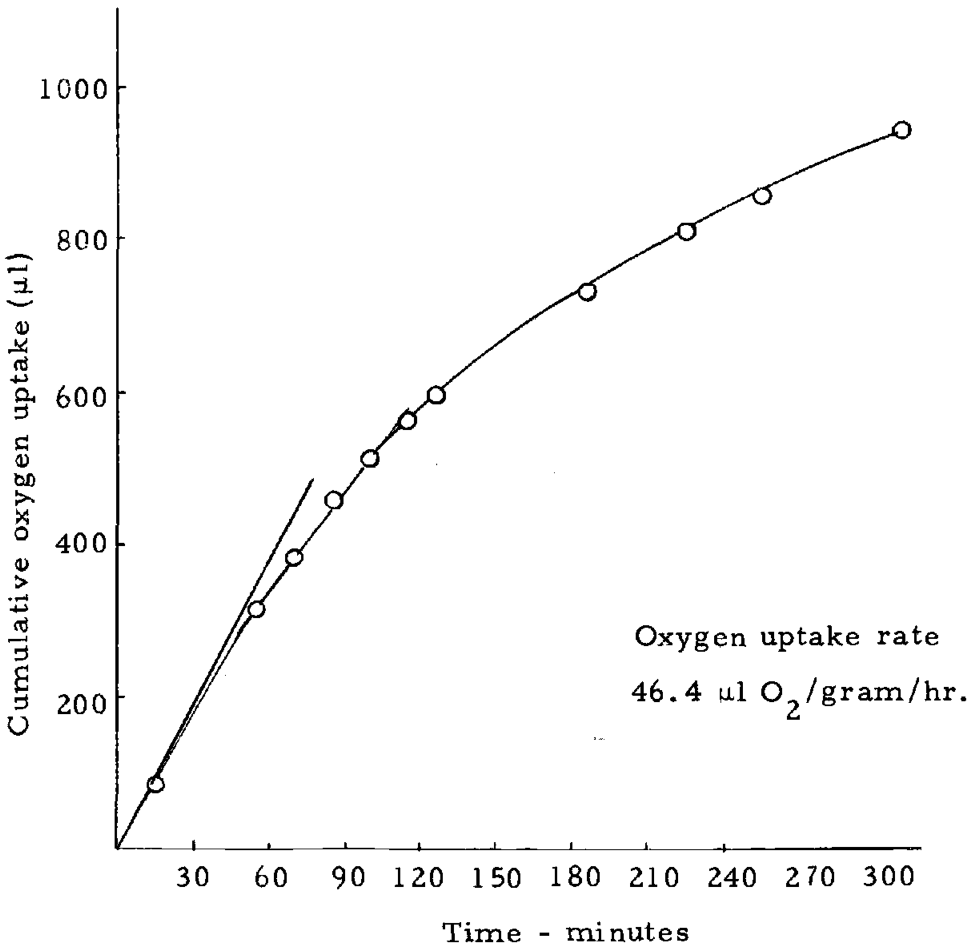

Figure 7. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment after storage at 4° C for 2 days. (Core I from the Smith River at the Umpqua Estuary on the southern Oregon Coast.)

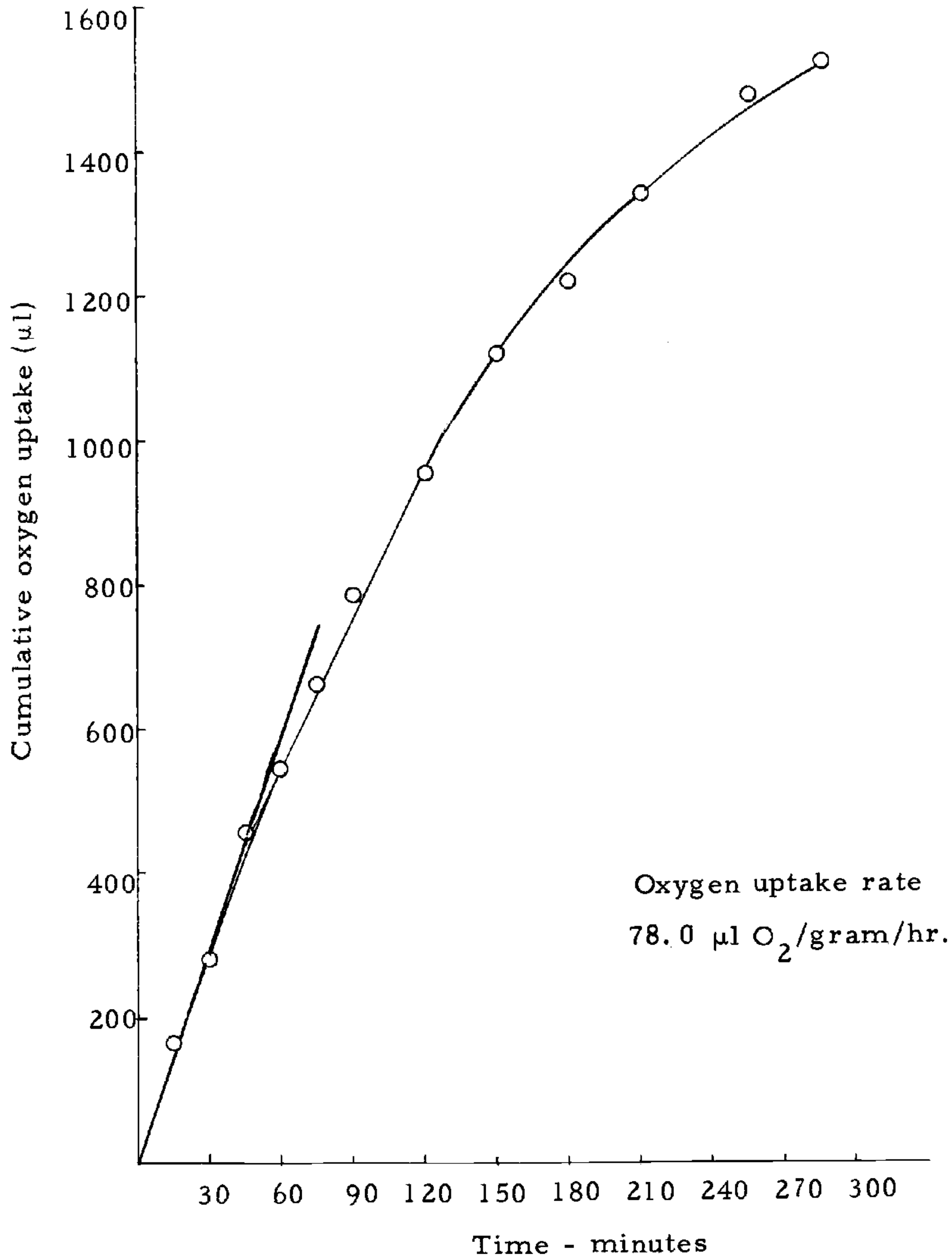

Figure 8. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment after storage at 4° C for 4 days.
(Core I from the Smith River at the Umpqua Estuary on the southern Oregon Coast.

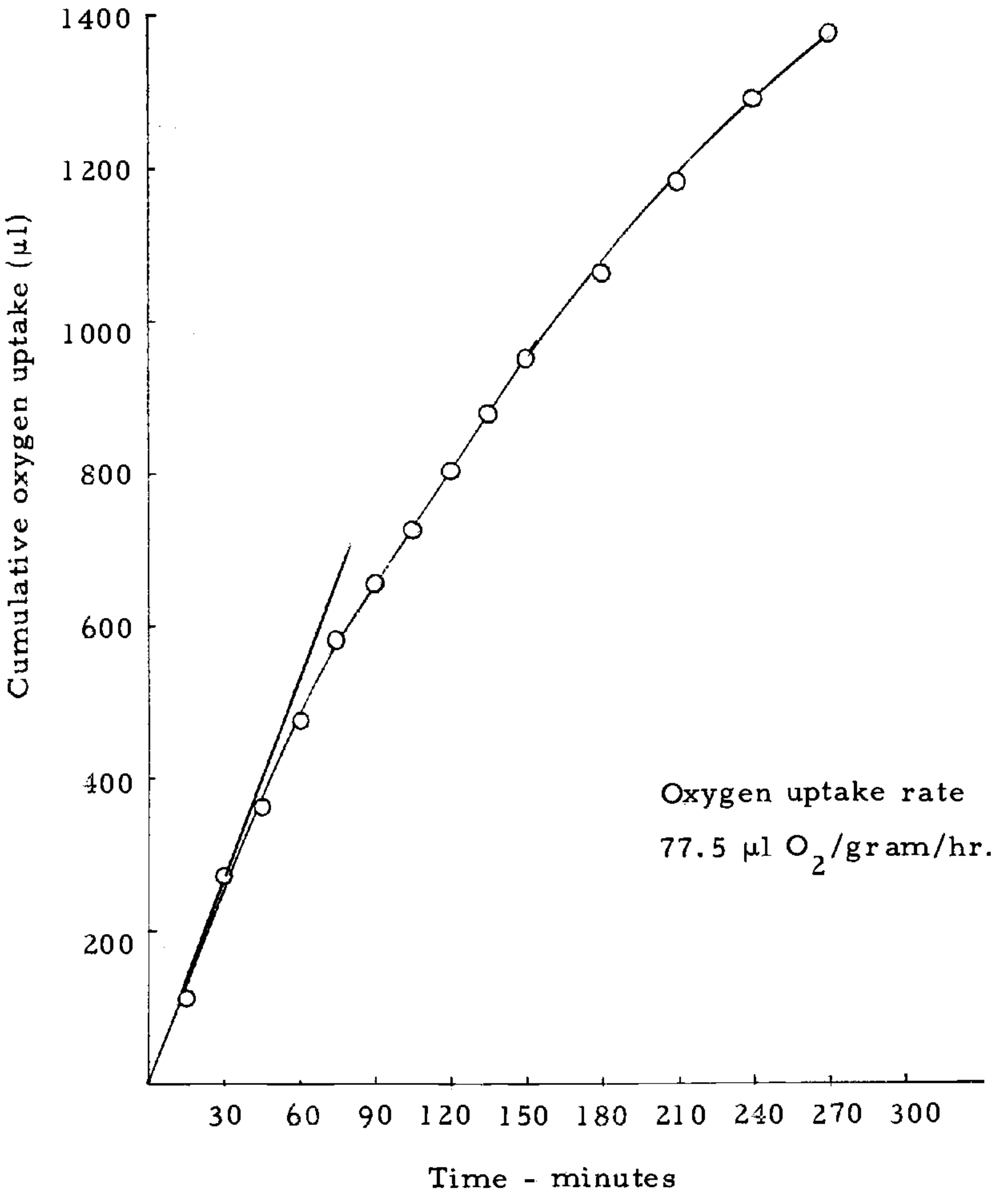

Figure 9. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediments after storage at 4° C for 8 days.
(Core I from the Smith River at the Umpqua Estuary on the southern Oregon Coast.)

The oxygen uptake rates are expressed in microliters (μl) O_2/gram/hr. The curves represent average data from triplicate samples analyzed concurrently. The oxygen uptake rates were computed from the initial 15 minutes of uptake to provide a common interval for comparison. The rates were then plotted versus storage time in Figure 10. The range of the oxygen uptake rate for the triplicate samples analyzed each day is also plotted to illustrate the limits of experimental error.

The data for days one, four and eight indicate no change in oxygen uptake rate. While there is fluctuation in the rate on day two, based on the consistency of the data for the other three days, it appears that this fluctuation may be attributed to other sources of error. Storage time at 4°C within the time interval studied has not seriously effected the oxygen uptake rate.

Oxygen Uptake and Biodegradability of Sediments

Introduction

The total oxygen demand due to combined biological and chemical oxidation in resuspended sediments can be determined by respirometry (4). Furthermore, the biological oxygen demand may be estimated by calculating the oxygen equivalent to the soluble carbonaceous material metabolized.

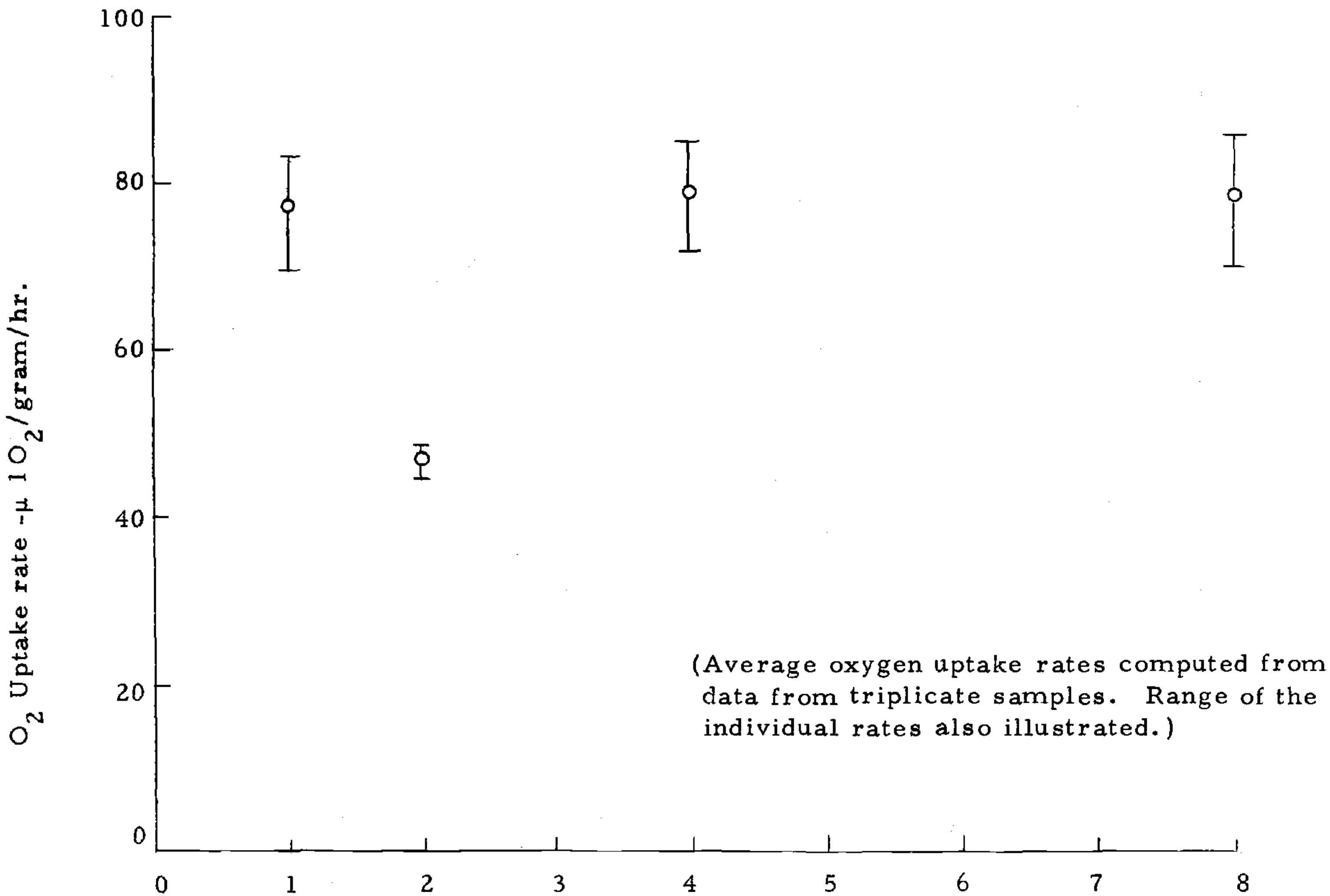

Figure 10. Oxygen uptake rate vs. storage time at 4°C. (Core I, estuarine bottom sediment from Smith River at the Umpqua Estuary on the southern Oregon Coast.)

Soluble carbonaceous material is metabolized by both heterotrophic and chemotrophic bacteria; however, ZoBell (24) found negligible chemotrophic activity in oceans and estuaries. Therefore, the following expression may be used to represent the biological oxidation of organic matter in estuarine sediments,

$$\text{Organic Matter} + O_2 \xrightarrow{\text{Organisms}} CO_2 + H_2O + \text{Organisms} + \text{Energy}$$

However, specific knowledge of the various constituents of the organic matter is needed for precise calculation of the oxygen required in the above expression. Since the organic matter in sediments is heterogeneous, precise calculation of the oxygen demand is not possible. The utilization of the organic matter in sediments by bacteria can be measured by the change in soluble organic carbon. Therefore, the biological oxygen demand can be estimated with reasonable accuracy by calculating the oxygen equivalent to the carbon utilized as follows,

$$nC + nO_2 \longrightarrow nCO_2$$

The organic matter in estuarine sediments will not be degraded entirely since some of the material is refractory. The percent biodegradability can be determined by determining the amount of soluble organic carbon utilized and dividing by the amount present initially,

$$\% \text{ Biodegradability} = \frac{\text{Initial SOC (mg/l)} - \text{final SOC (mg/l)}}{\text{Initial SOC (mg/l)}} \times 100$$

The purpose of this phase of the investigation was to measure the oxygen uptake of resuspended estuarine bottom sediments and to determine the percent biodegradability of the organic matter released during resuspension. The volatile solids content of the sediment and the soluble ferrous iron, free sulfide and sulfate concentrations in the interstitial water were measured and these parameters were statistically analyzed for possible linear correlation with oxygen uptake rate and percent biodegradability.

Technique

The following procedure was followed for preparation of the samples and measurement of oxygen uptake and soluble organic carbon. After the samples were removed from storage and allowed to come to room temperature, they were placed in a one-liter beaker and water from the sampling area was added. The beaker was placed on a magnetic stirrer and mixed to keep the sediment in suspension. Forty ml samples were withdrawn and placed in three 125 ml Gilson flasks. Another set of three Gilson flasks, each containing 40 mls of estuarine water without sediment, were also prepared for measurement of baseline oxygen uptake. The flasks were mounted on the respirometer and permitted to reach thermal equilibrium in the water bath set at 20° C. Measurement of oxygen uptake began with agitation of the flasks at 106 oscillations per minute continued throughout the measurement period.

Duplicate 10 ml samples of the mixture were withdrawn from the sample beaker for determination of total and volatile suspended solids.

Additional samples were also withdrawn from the beaker and filtered through glass-fiber filters that had been fired at 400° C for four hours for measurement of initial soluble organic carbon (SOC). After completion of oxygen uptake measurements, samples were withdrawn directly from the Gilson flasks and filtered as before to measure the SOC remaining. The filtrate was poisoned with a one gram/liter mercuric chloride solution and stored at 4° C for subsequent analysis.

The data from this phase of the investigation was statistically analyzed for correlation between chemical parameters of the sediments and oxygen uptake rates and percent biodegradability.

Results

In order to further characterize each sediment a general description follows. Core III was a sample from the mouth of the Smith River on the Umpqua Estuary (Figure 2). It was a six inch core taken from a depth of 33 to 39 inches. The sediment was brownish-grey silty sand containing small pieces of bark.

Core IV was a six inch surface core from the Smith River below Butler Creek on the Umpqua Estuary (Figure 2). The sediment was light brown sand and small gravel. There was little organic matter apparent in the sediment. Both Core III and IV were taken from a boat in approximately six feet of water.

Core V was an eight inch surface core taken from a tidal mud flat at Isthmus Slough on the Coos Estuary (Figure 3). The sediment was taken from under a two inch mat of algal growth. Purple sulfur bacteria were evident on the surface of the mud flat. The sediment was black for about the first three inches and the remainder was dark grey. The smell of hydrogen sulfide was evident while sampling.

Core VI was a six inch surface core taken from the bank of the navigation channel at Isthmus Slough on the Coos Estuary (Figure 3). The sediment was light grey sand under a thin layer of brownish ooze. Small sections of blackened mud were scattered throughout the sand. The smell of hydrogen sulfide was again evident while sampling at this site.

The cumulative oxygen uptake data for the four sediment samples are plotted in Figures 11, 12, 13 and 14. The oxygen uptake rates, computed for the initial 30 minute interval, are also shown. Not only do the physical characteristics of the sediment differ, but the oxygen uptake rates varied from 2 to 360 μl O_2/gram/hr (Table 1).

Since the velocity of biological reactions is known to depend on the amount of substrate available, the oxygen uptake rates were

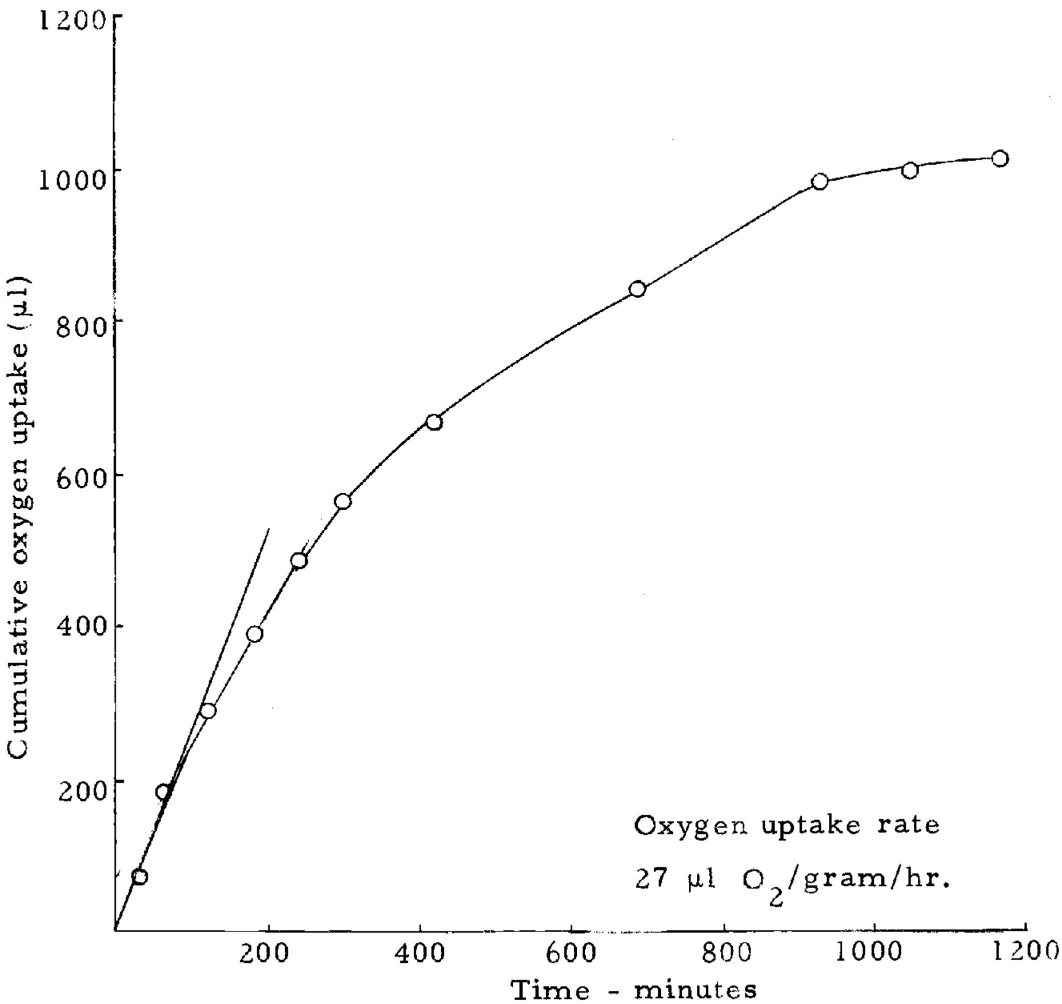

Figure 11. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment.
(Core III from the Smith River at the Umpqua Estuary on the southern Oregon Coast.)

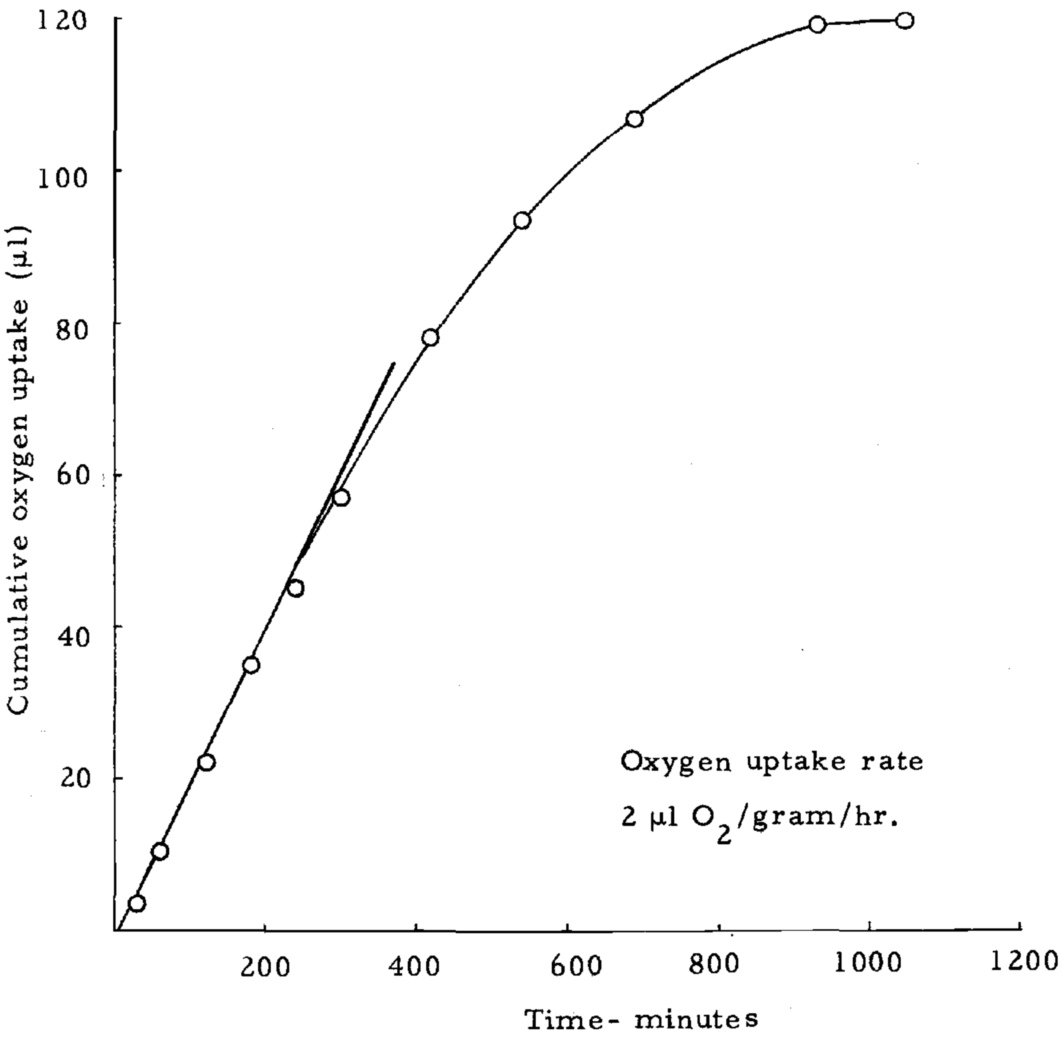

Figure 12. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment.
(Core IV from Smith River at the Umpqua Estuary on the southern Oregon Coast.)

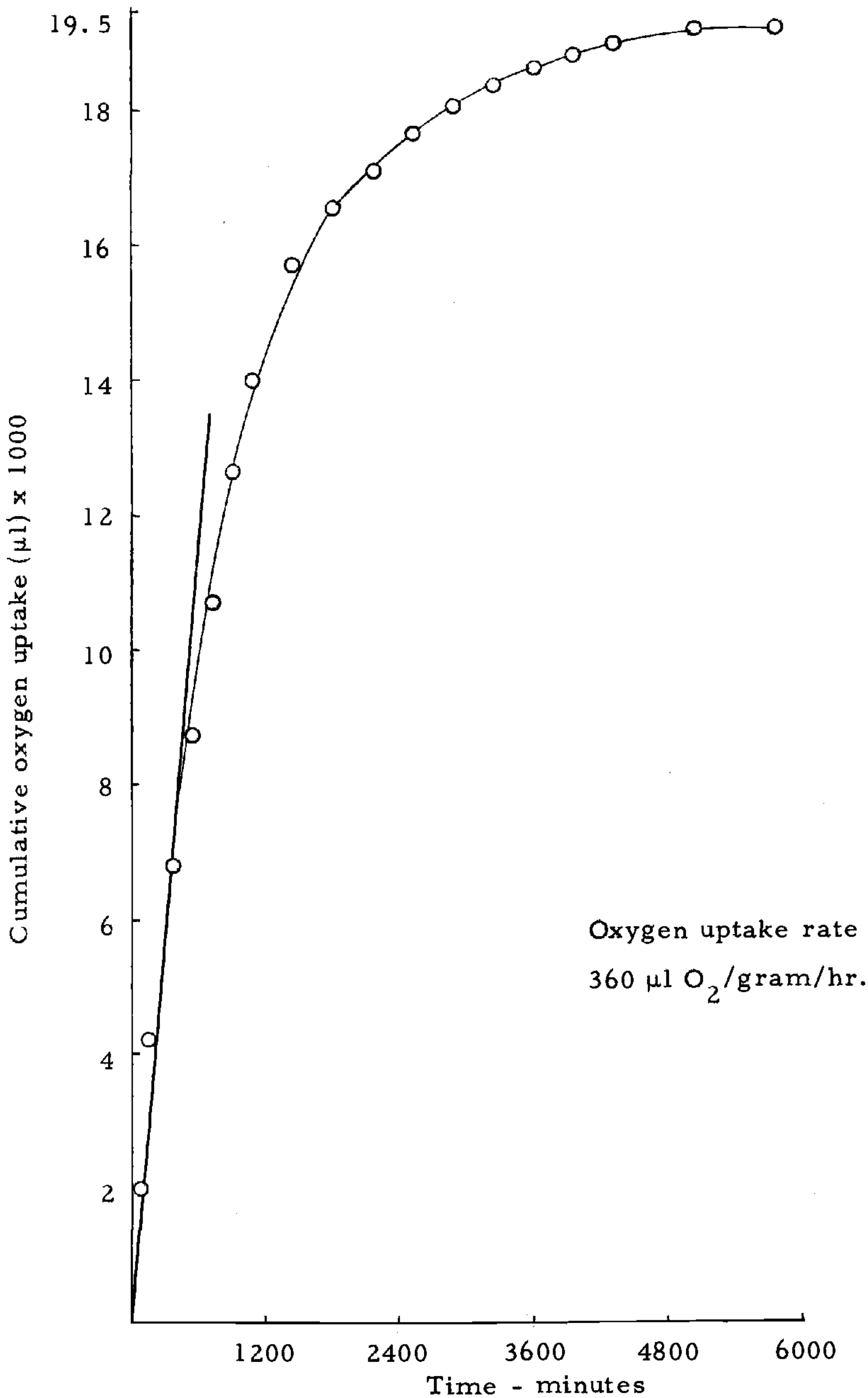

Figure 13. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment.
(Core V from Isthmus Slough at the Coos Estuary on the southern Oregon Coast.)

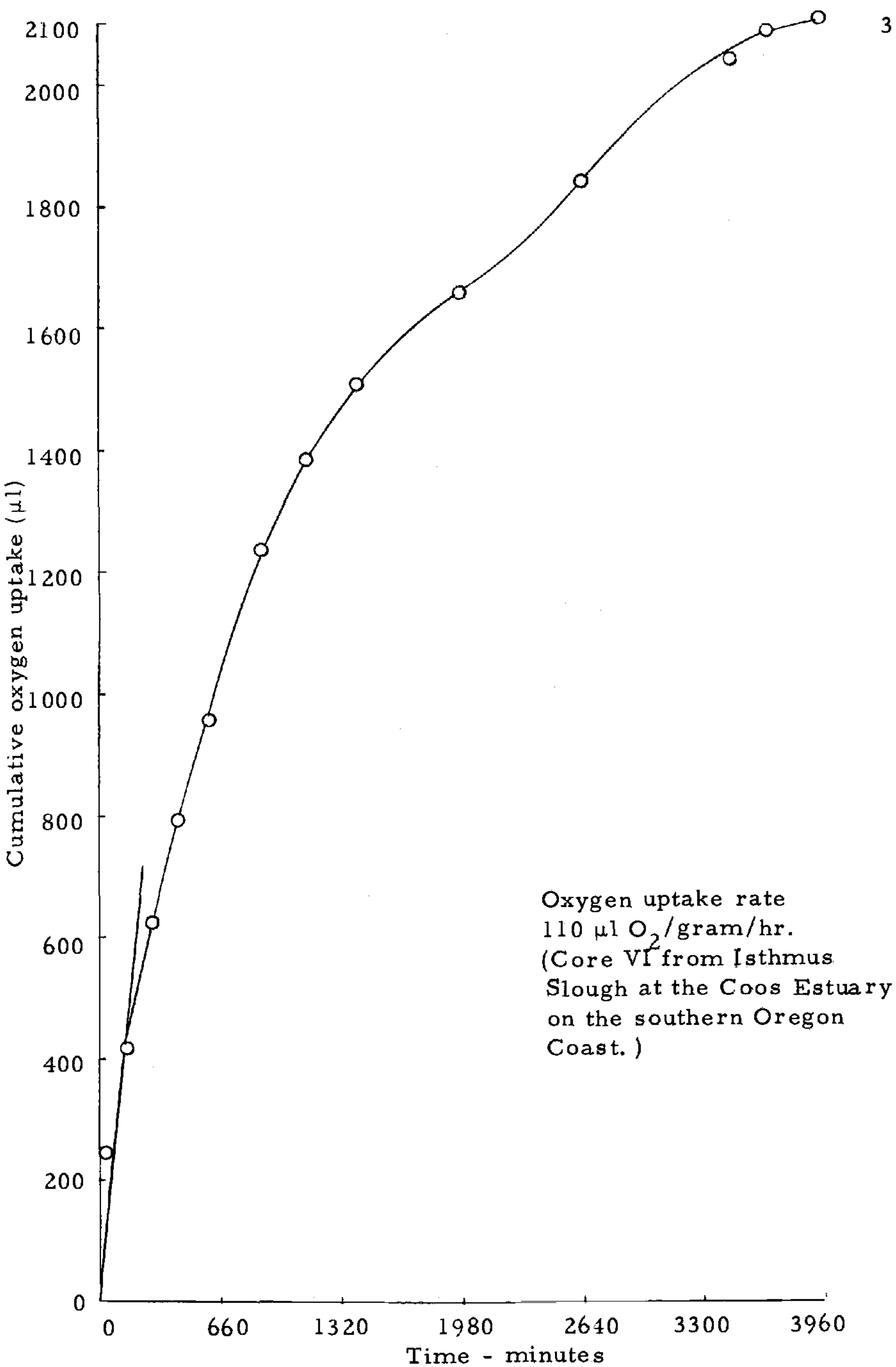

Figure 14. Cumulative oxygen uptake vs. time for resuspended estuarine bottom sediment.

Table 1. General description, chemical parameters and oxygen uptake rate of resuspended estuarine bottom sediments. (Cores III, IV, V and VI.)

	General Description	O_2 uptake rates ul O_2/gr./ hr.	Sulfate mg./l	Free Sulfides mg./l	Soluble Ferrous Iron mg./l	% Vol. S. S.	Initial SOC mg./l
Core III	brown-grey silty sand	27	126	0	>40	4.2	--
Core IV	light brown sand-gravel	2	---	0	>40	1.4	2.9
Core V	black to dark grey mud	360	160	12	22	14.7	72.0
Core VI	light grey sand - some black mud	110	672	19	32	8.9	37.1

plotted versus the volatile solids content of the sediments (see Figure 15) to determine if a relationship existed between these parameters. The degree of correlation between the oxygen uptake rate and the volatile solids content was determined by computing the correlation coefficient. The coefficient was 0.96 indicating that a linear relationship did exist between these parameters.

The soluble organic carbon (SOC) released during resuspension of sediments was measured to determine the amount of substrate available to organisms. In Figure 16, the initial SOC concentrations for Cores IV, V and VI were plotted versus the oxygen uptake rate. The correlation coefficient of 0.98 suggests that increasing amounts of carbonaceous material was an indication of incomplete degradation so that this material was available for further decomposition when the sediments were resuspended.

In order to determine if increasing amounts of SOC were an indication of incomplete degradation, the percent SOC degraded was calculated. The initial and final concentrations of SOC present during oxygen uptake were measured to determine the bacterially available SOC and to compute percent biodegradability (Table 2). Percent biodegradability was then plotted versus the initial SOC present in Figure 17 and the degree of correlation was computed. The correlation coefficient was 0.94 indicating the linear relationship existing between these parameters. The initial SOC

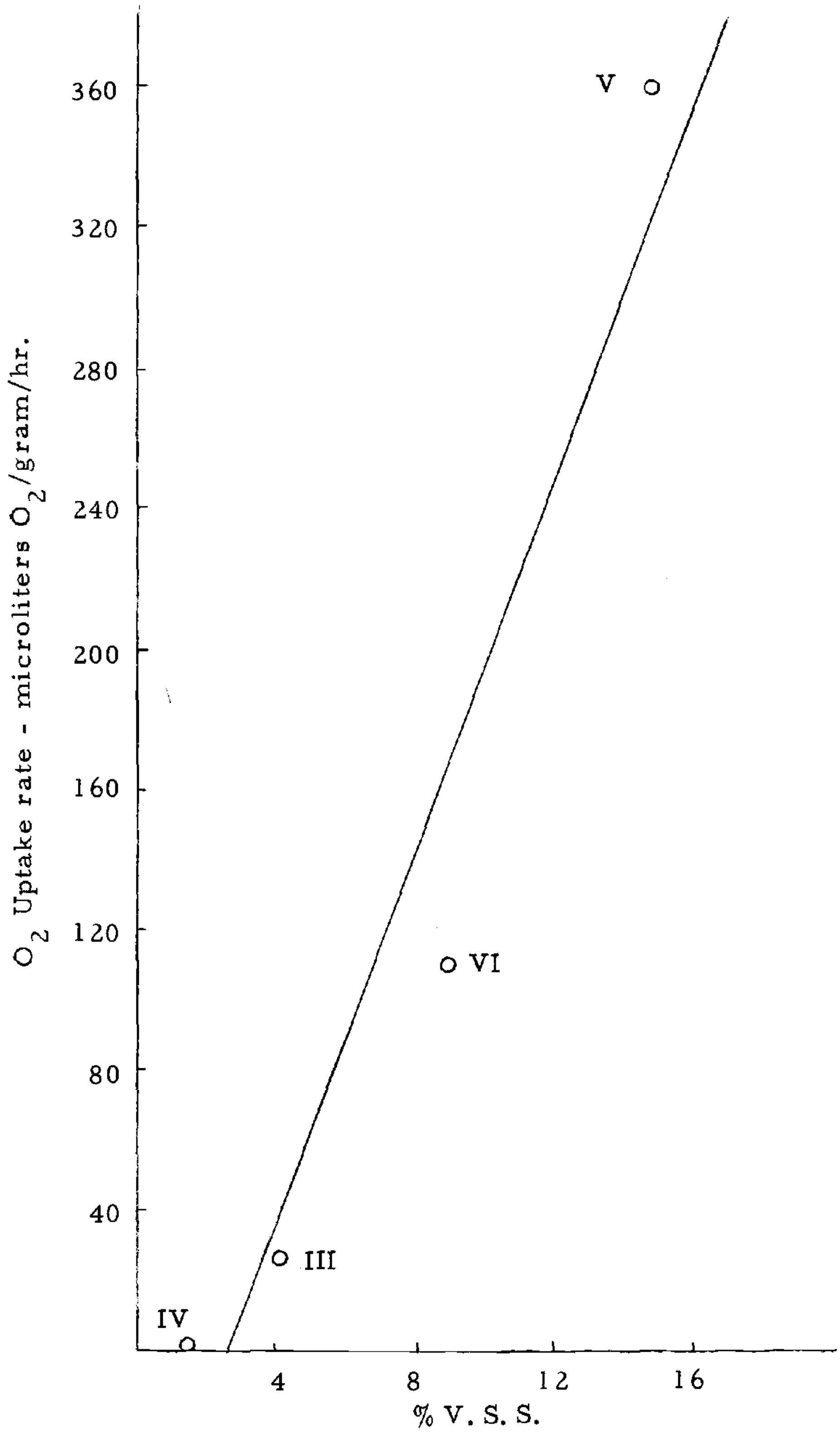

Figure 15. Oxygen uptake rate vs. % volatile suspended solids of resuspended estuarine bottom sediments. (Cores III, IV, V and VI.)

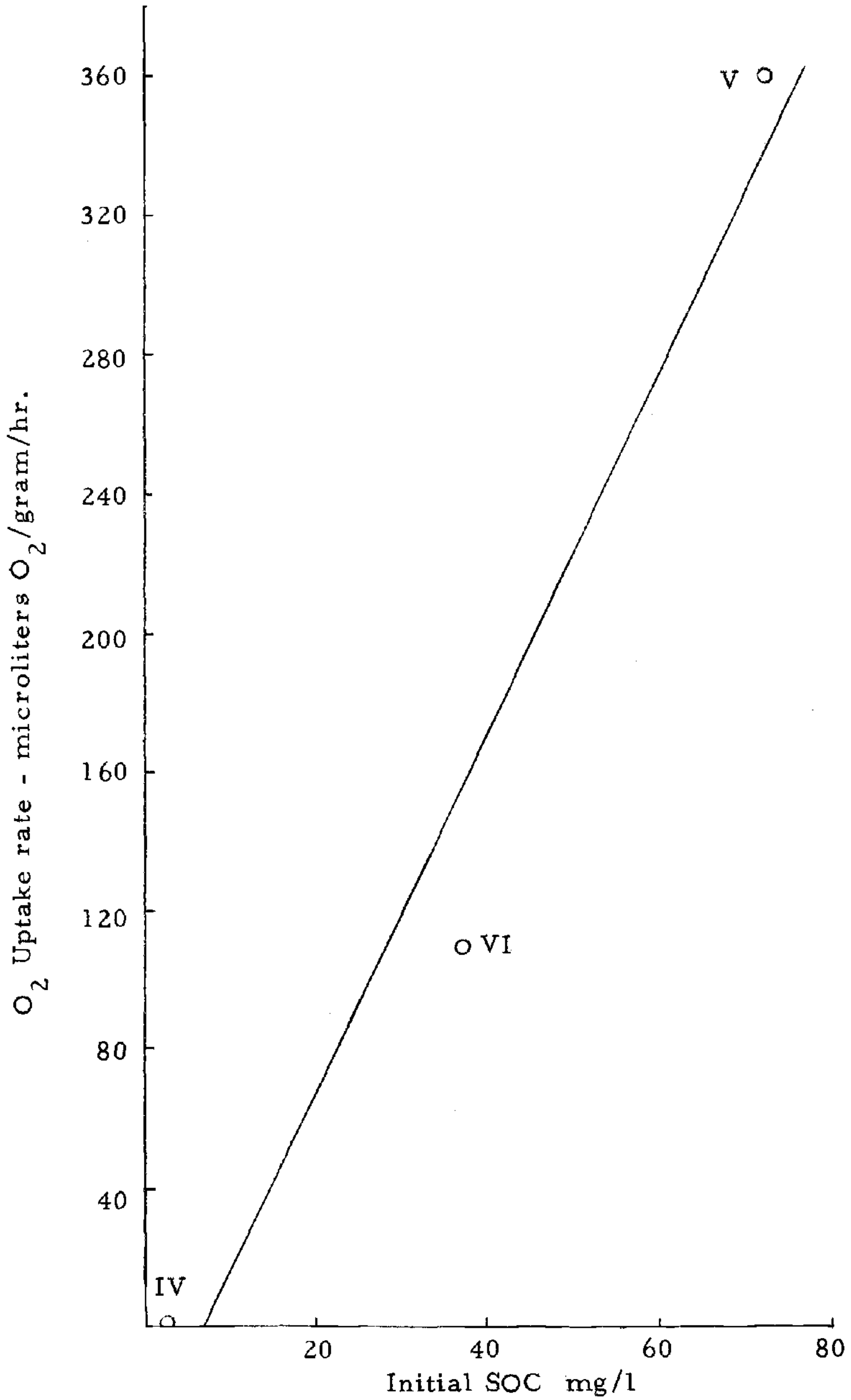

Figure 16. Oxygen uptake rate vs. initial soluble organic carbon concentration of resuspended estuarine bottom sediments. (Core IV, V and VI.)

Table 2. Experimental soluble organic carbon and total oxygen demand data for resuspended estuarine sediments. (Cores IV, V and VI.)

	Initial SOC mg./l (1)	Final SOC mg./l (2)	SOC utilized (3)	Biodegradability % $(3)/(1) \times 100$	Total Exp't O_2 Demand ul. (4)	Theoretical O_2 Demand Biol. ul (5)	% Biological O_2 Demand $(5)/(4) \times 100$
Core IV	2.9	2.6	0.3	10.4	119	22.4	18.8
Core V	72.0	13.6	58.4	81.0	19,240	4350	22.6
Core VI	37.1	11.8	25.3	68.2	2106	1866	88.5

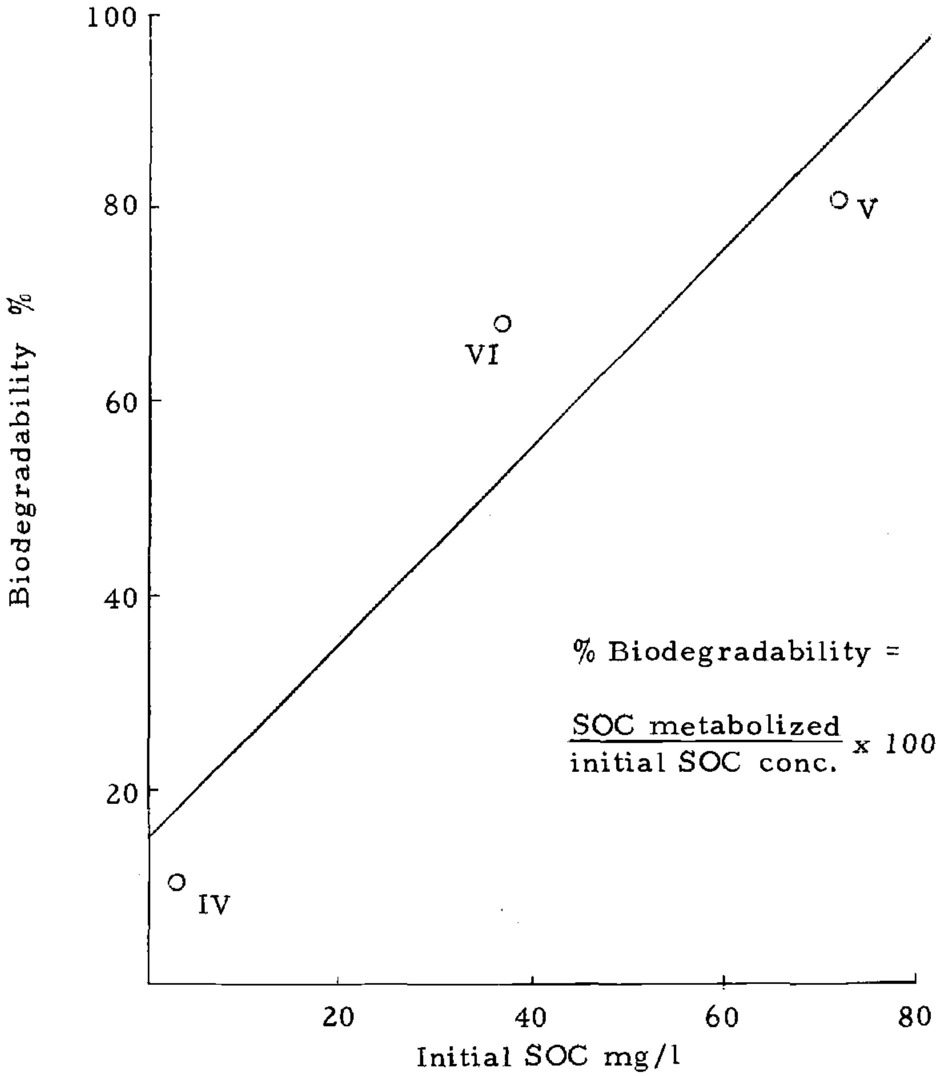

Figure 17. % Biodegradability vs. initial soluble organic carbon concentration of resuspended estuarine bottom sediments. (Cores IV, V and VI.)

released during resuspension appears to indicate an increasing amount of carbonaceous material available to the organisms for subsequent degradation.

Once the amount of carbonaceous material metabolized was determined by measuring the change in SOC, the equivalent oxygen was calculated. Results from this method of calculation will admittedly differ from the theoretical oxygen demand by either overestimating or underestimating the oxygen demand for individual organic compounds. However, since estuarine sediments contain a heterogeneous mixture of organic compounds, the difference from the theoretical demand will be minimal.

Therefore, the theoretical biological oxygen demand estimated by this method was used to calculate the biological fraction of the total oxygen demand of the sediments as follows,

$$\% \ O_2 \text{ utilized biologically} = \frac{\text{Theoretical biological } O_2 \text{ demand}}{\text{total } O_2 \text{ demand}} \times 100$$

The results are listed in Table 2.

Biological oxygen demand, as estimated by the above technique, accounted for a relatively small fraction of the total oxygen demand for Core IV (18.8%) and Core V (22.6%). However, the biological demand appeared to be predominant in Core IV (88.5%).

Finally, the free sulfide concentration in the interstitial water of the sediments were measured (Table 1). The presence of free sulfides is evidence of anaerobic conditions caused by the deposition of large amounts of organic matter. When these sediments are resuspended, the organic matter will be subject to aerobic degradation. Therefore, free sulfides in the interstitial water may indicate a source of highly degradable organic material. To determine if a relationship existed between the free sulfide concentration and the percent biodegradability, the data was plotted in Figure 18. The correlation coefficient for this relationship was 0.85 suggesting that free sulfides in the interstitial water indicated a large source of organic material that was subsequently degraded when the sediments were disturbed and molecular oxygen was introduced.

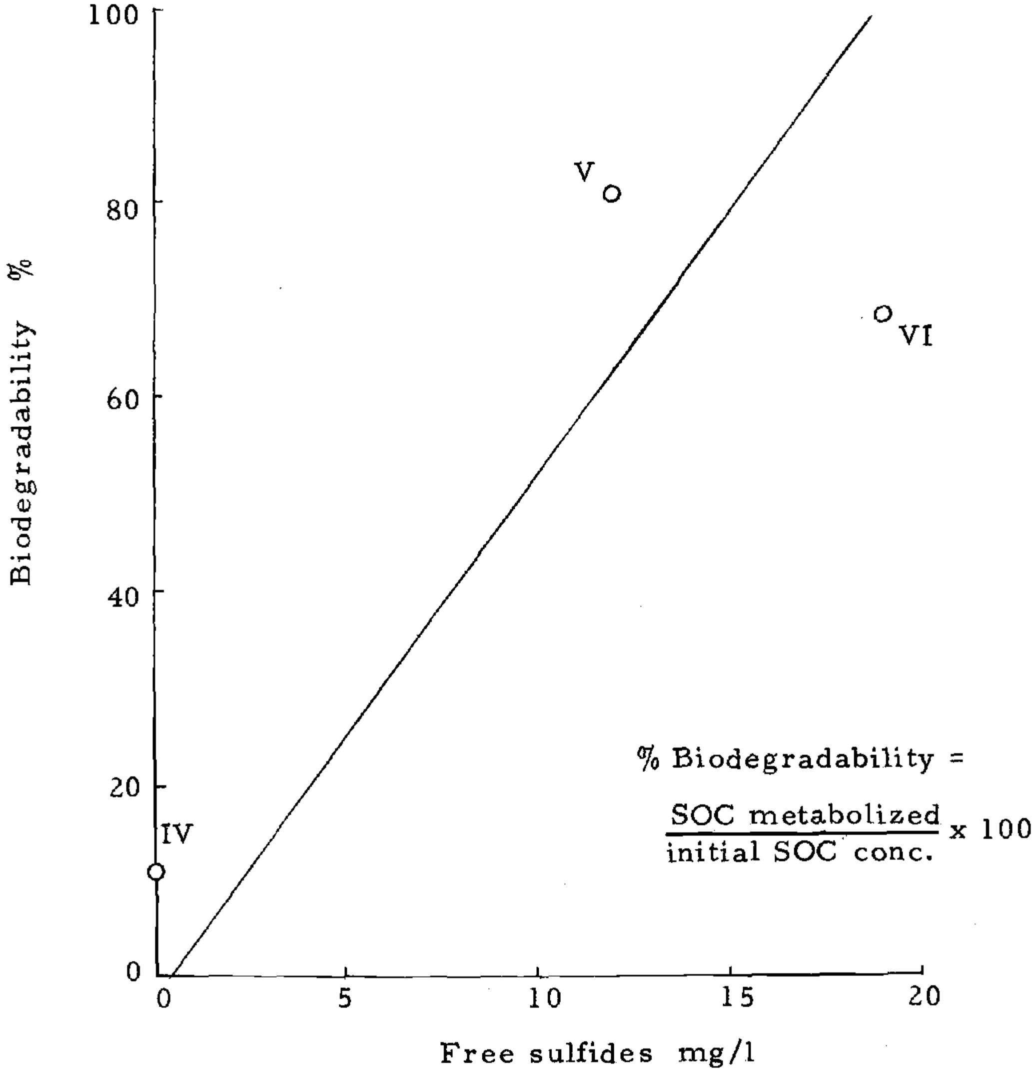

Figure 18. % Biodegradability vs. interstitial free sulfide concentration for resuspended estuarine bottom sediments.
(Cores IV, V and VI.)

IV. DISCUSSION

The purpose of this study was to determine the oxygen uptake rate of resuspended estuarine bottom sediments and the biodegradability of the organic matter released during resuspension. The technology for studying resuspended sediments in situ has not been well developed, therefore it was necessary to collect samples in the field and study them under controlled conditions in the laboratory.

A number of successful methods for approximating in situ conditions in the laboratory and measuring oxygen uptake have been reported, however respirometry was selected for this study for the following reasons. First, there are relatively no interferences in measuring oxygen uptake by respirometry compared to chemical or electrometric techniques. Second, respirometry provides direct, continuous measurement of oxygen uptake. Finally, respirometers provide the agitation necessary to keep sediments in suspension without additional equipment.

Preliminary studies were conducted because previous research defining the collection and handling of sediments has been scarce. The first consideration was to minimize disturbing the sediments during collection. The core tubes used for sampling enabled the investigator to collect samples and transport them to the laboratory and still maintain the consolidation of the sediment.

Since sediment samples had to be stored before analysis, the effect of storage time on the oxygen uptake was evaluated. As shown in Figure 10, the oxygen uptake rate seemed uneffected by storage time. ZoBell (23) found changes in the bacterial population in sediments and water samples collected off the California coast. However, the changes were only evident after the samples had been stored for periods of one to two months. He also reported that Butkevich found that most bottom dwelling organisms were active at temperatures of -3°C to -7°C (24), but the rate of activity was considerably reduced from the rates at higher temperatures. These observations support the notion that biological activity in samples stored at 4°C will be minimal.

Although minor changes in the activity of sediment samples may occur due to storage at 4°C, it is apparent from the data presented in this study that the changes are not significant after 8 days of storage of 4°C. However, the samples used in the other phase of this investigation were analyzed within 24 hours of collection.

In order to study the oxygen uptake rate and biodegradability of resuspended sediments in the laboratory, relatively small samples would be used. However, by using small sample sizes, the number of bacteria present may be a limiting factor. The magnitude of the oxygen uptake rate and the degree to which the organic matter is degraded will depend on the number of viable bacteria in the sediment and water. Therefore a preliminary investigation was conducted to compare the oxygen uptake rate of resuspended sediment samples containing only the natural flora with samples inoculated with additional bacterial seed.

To study this effect a sample of estuarine bottom sediment was resuspended in water from the sampling area. The oxygen uptake rate for an unseeded portion of the mixture was compared to the rates for equal portions inoculated with increasing amounts of bacterial seed. From the plot of the data in Figure 5, it is evident that there was little difference between the oxygen uptake rates for the unseeded and seeded samples. For example, the oxygen uptake rate for the unseeded sample was 87% of the maximum. The data suggests that the bacterial seed was readily acclimated to the carbonaceous material in the sediment since there were no significant lag periods in oxygen uptake. From a comparison of the data for the unseeded and seeded flasks, the sediment apparently contained an extensive bacterial population. This observation enabled the investigator to study oxygen uptake rates of resuspended sediments without additional seeding.

The cumulative oxygen uptake of resuspended estuarine bottom sediments is the result of both a chemical and a biological oxygen demand and each may affect the oxygen uptake rate. Therefore the cumulative oxygen uptake data for four sediment samples were plotted in Figures 6, 7, 8 and 9. The oxygen uptake rates were computed and they ranged from 2 to 360 μl O_2/gram/hr. The various chemical parameters for each sediment sample were analyzed and listed in Tables 1 and 2. In order to understand the nature of the oxygen consumption by the resuspended sediments, the data were statistically analyzed for linear correlation between oxygen uptake rates and the chemical parameters.

Since estuarine bottom sediments have previously been shown to contain extensive bacterial populations (Figure 5), oxygen uptake rate will depend on the amount of substrate available for heterotrophic degradation. In this study the volatile solids content and the initial soluble organic carbon (SOC) released during resuspension were measured to determine the amount of substrate available to the organisms.

In Figure 15 the volatile solids content was plotted versus oxygen uptake rate for each sediment. The initial SOC concentration was also plotted versus oxygen uptake rate in Figure 16. The correlation coefficients between volatile content and oxygen uptake rate, and between initial SOC and oxygen uptake rate were 0.96 and 0.98 respectively. A linear relationship has been established between the amount of substrate available to organisms and the oxygen uptake of resuspended sediments. From the linear relationships established between volatile solids content, SOC and oxygen uptake rate, it appears that increasing amounts of organic matter in estuarine sediments indicate incomplete in situ degradation, and therefore, result in higher oxygen uptake rates.

In order to determine if the initial amount of carbonaceous material is an indication of the amount of potentially degradable material, the percent biodegradability was calculated. The linear relationship between initial SOC and percent biodegradability is illustrated in Figure 17. The data confirm that high concentrations of soluble organic carbon in sediments are the result of incomplete degradation. Sediments containing high concentrations of organic matter are subject to further degradation upon resuspension and result in higher oxygen uptake rates.

Free sulfides in estuarine sediments indicate large amounts of organic matter putrefying under anaerobic conditions. Eventually decomposition in these sediments will decrease as the organic matter becomes stable to further anaerobic degradation. However, this organic matter can still be degraded if molecular oxygen is introduced since it has been estimated that up to 90% of the bacteria in bottom deposits are facultative aerobes (24). Figure 18 illustrates that a relationship did exist in this study between the free sulfide concentration in the interstitial and the percent biodegradability of the carbonaceous material. While free sulfides do not directly measure the amount of organic material in sediments, they do indicate its presence in large amounts and that it may be degraded further if the sediments are disturbed and oxygen is introduced.

An estimate of the biological fraction of the total oxygen demand was made by calculating the percent oxygen utilized by bacteria in metabolizing the soluble organic carbon of the sediments (Table 2). Based on this estimate, the biological oxygen demand accounted for 18.8% and 22.6% of the total demand for Cores IV and V, respectively. The data seemed to be consistent with the characteristics of these sediment samples. Core IV consisted of coarse sand and gravel and contained very little organic matter (2.9 mg SOC/l). The biological oxygen demand was not expected to be the predominant factor in this case. Core V contained a large amount of SOC (72 mg/l) but it also contained large quantities of soluble ferrous iron (22 mg/l) and free sulfides (12 mg/l). The oxygen demand from the oxidation of these reduced inorganic compounds predominated over the biological oxygen demand. However, the estimated biological oxygen demand for Core VI was inconsistent with the data. The free sulfide concentration (19 mg/l) and soluble ferrous iron (32 mg/l) would seem to again indicate a predominant chemical oxygen demand. But the estimated biological oxygen demand was 88.5%

Therefore, based on the data, the relative proportion between the biological and chemical oxygen demand cannot be correlated with the chemical parameters measured in this study.

To summarize, the magnitude of the oxygen uptake rate and the degree of degradation of the organic matter released during resuspension of estuarine bottom sediments can be predicted from other parameters. These parameters are the volatile solids content, the soluble organic carbon and free sulfide concentration in the interstitial water. This can be a valuable tool for rapid evaluation of the environmental impact of dredging operations.

V. CONCLUSIONS

I. Increasing volatile solids and soluble organic carbon concentrations indicate incomplete *in situ* degradation of organic matter in estuarine sediments. This organic matter is subject to further degradation when the sediments are resuspended.

II. Oxygen uptake rate of resuspended estuarine bottom sediments increases with increasing volatile solids and soluble organic carbon concentrations since larger quantities of degradable organic material are released during resuspension.

III. Total oxygen demand of resuspended estuarine bottom sediments is the result of chemical and biological oxidation. The data from this study indicate that chemical oxygen demand may be the predominant factor.

IV. Sample storage time at 4°C did not effect oxygen uptake studies of resuspended estuarine bottom sediments. The oxygen uptake rate did not change for a sediment sample stored up to eight days after collection.

V. Estuarine bottom sediments contain extensive bacterial populations that enable the study of oxygen uptake and biodegradability without additional bacterial seed.

VI. The environmental impact of dredging operations can be determined by measuring the volatile solids content and soluble organic carbon concentration of estuarine bottom sediments and the free sulfide concentration in the interstitial water.

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