Oxygen Demand of US Waterway Sediments[1]

G. Fred Lee and R. Anne Jones
G. Fred Lee & Associates
El Macero, CA
ph 530 753-9630, fx 530 753-9956, em gfredlee@aol.com
www.gfredlee.com

Abstract

During the mid-1970*s, the federal Congress provided $30 million to the US Army Corps of Engineers to conduct a 5-yr research program to investigate the environmental impacts of dredged sediment disposal. As part of this program, the authors investigated the release of 30 contaminants from, and the oxygen demand of, a variety of US waterway sediments. A sediment oxygen demand test was developed by placing a few ml of sediment and aerated site water in a BOD bottle. Monitoring of the 0_2 concentrations during the one hour under completely mixed conditions was conducted. This test assessed the worst case oxygen demand by the suspension of dredged sediments in the water column. First-hour oxygen demands ranged from 42 to 930 g 0_2 m^3 wet sediment with typical values on the order of 500 g 0_2 m^3. The plots of oxygen concentration versus time during the first hour could generally be divided into an initial, rapid consumption followed by a slower rate of consumption. The initial, first order rates ranged from 0.005 to 0.064 mg/l 0_2 /min. The ratio of initial rate to final rate typically ranged from 2 to 10.

Field studies of the oxygen demand that occurred at open water dredged sediment disposal sites showed that there was no relationship between the oxygen demand of the sediment measured by the lab test and the oxygen depletion that occurred in the water column at the dredged sediment disposal site. This was due to the fact that unlike the test conditions, only a small part of the dumped sediment was mixed into the water column. The results of the field studies also showed that while open water dumping of dredged sediment would rarely cause water quality problems due to oxygen demand, the discharge of hydraulically dredged sediment by pipeline operations could be adverse to water quality-aquatic life-related beneficial uses of the water in the region of the disposal. The dredged sediment discharge from such operations forms a density current that moves along the bottom from the point of disposal.

The results of this study also provide information that is pertinent to assessing the oxygen demand of river and bay sediments upon suspension in the watercolumn that occurs with increased velocities of the overlying waters. For some aquatic systems, this is a critical period of sediment-related DO depletion. In order to properly predict the oxygen demand associated with sediment scour, it will be necessary to develop a much better understanding of the scour of cohesive sediments.

Key words: sediment oxygen demand, dredged sediment, water quality

---

[1] Report G. Fred Lee & Associates El Macero, CA (1999)

Introduction

The US Army Corps of Engineers (COE) has the responsibility for maintaining the navigation depth of many US waterways and annually dredges approximately 400 x 10^6 m^3 of sediments from US rivers, lakes, harbors, and coastal waterways. During the mid-l970*s, the COE undertook a $30 million, 5-yr Dredged Material Research Program devoted primarily to evaluating the environmental impacts of dredging and dredged sediment disposal. As part of this effort, the authors and their associates conducted a series of studies designed to evaluate the release of 30 contaminants from dredged sediment upon their suspension in the watercolumn.[1, 2] These studies included an evaluation of the oxygen demand of dredged sediment associated with open water disposal of hydraulically dredged sediment as assessed by laboratory tests and by field monitoring of the oxygen concentration during dredged sediment disposal operations. This report summarizes the results of these studies of the oxygen demand of dredged sediments, and the applicability of the findings to assessing the significance of the oxygen demand of sediments when suspended in the watercolumn.

Experimental Procedures

Approach

The overall approach was to collect sediment and water on which laboratory oxygen demand and other analyses would be conducted from an area cheduled to be dredged the following day. The disposal site was then intensely monitored during the time that sediments dredged from the area sampled the previous day, were being disposed at that location. Sampling boats were positioned in the disposal area to collect water samples and make ship-board measurements of dissolved oxygen (DO), temperature, etc. before, during, and after disposal such that changes in chemical characteristics of the watercolumn in the vicinity of the discharge (both upcurrent and downcurrent) would be detected. Water samples were collected immediately prior to and for an hour or so following disposal. Subsequent sections of thisreport provide additional description of specific monitoring procedures used for the disposal operations highlighted in this report. A detailed discussion of the approach used to monitoring each disposal operation is provided elsewhere.[1, 2]

Sample Collection

Samples of waterway sediments were collected from various sites at locations shown in Figure 1. Sediment grab samplers or corers were used to collect sediment generally from the upper 10 to 20 cm of the sediment in the particular navigation channel scheduled for dredging, near mid-channel. Samples were air freighted in 4-1, air-tight containers to the University of Texas-Dallas laboratories in Richardson, TX for processing and analysis. When it was not possible to analyze samples upon receipt, they were stored in the dark, at just above freezing for generally less than one week but not more than two weeks. Subsamples used for testing and analysis were taken from the interior of the sediment sample which had not previously been exposed to air.

Oxygen Demand Test

A sample of sediment for oxygen demand evaluation was transferred to a glove bag containing

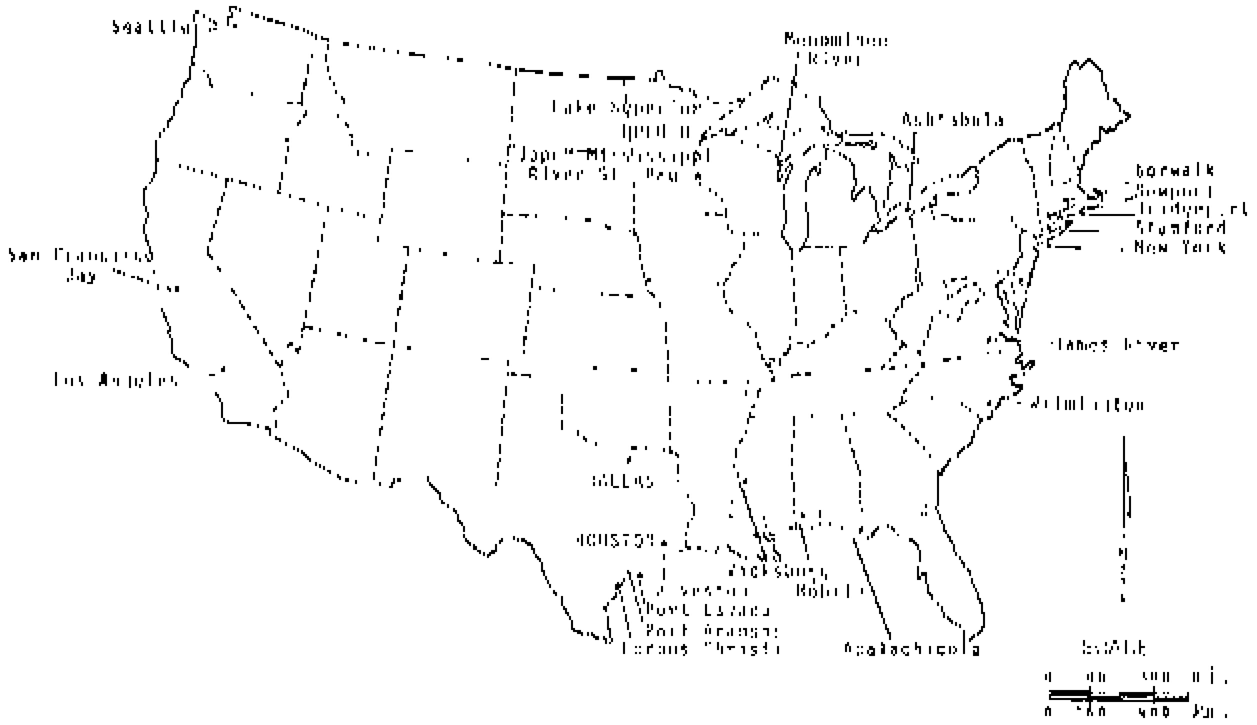


Figure 1. Dredged Sediment Sampling Locations (After Lee et al.^{2})

nitrogen gas, with care taken to avoid including any of the oxidized microzone (indicated by a reddish-brown color on the surface of the sediment). Under the N_2 atmosphere, the sediment was mixed with a glass stirring rod; approximately 20 ml were drawn into a plastic syringe that had the end removed to allow free flow of sediment into the barrel upon withdrawal of the plunger. The end of the syringe was capped with Saran Wrap; this prepared sample was stored in the dark at just above freezing until oxygen demand was determined. To conduct the oxygen demand test, the prepared syringe was uncapped and the first few ml of sample discarded to ensure minimal introduction of oxidized sediment. A measured volume between 2 and 10 ml of sediment was introduced into an approximately 300-ml BOD bottle containing a magnetic stirring bar. Water collected near the sediment sampling site was aerated and then added to fill the BOD bottle containing the sediment. A YSI membrane electrode BOD probe was inserted into the bottle and the magnetic stirrer started. DO readings were made on a YSI Model 54 dissolved oxygen meter at one-minute intervals during the first 10 minutes and then at five minute intervals for the next 50 minutes.

Sulfide Determination

A modification of the Iodometric Titration procedure described in Standard Methods[3] was used for the determination of total sulfides. Following Gardner[4], steam was used for H_2S stripping instead of the APHA *et al*[3]. -recommended inert gas. Also, following Bortleson,[5] potassium biniodate was substituted for the iodine solution.

Oxidation-Reduction Potential

Oxidation-reduction (redox) potential (Eh) was determined by placing a bright platinum electrode in the sediment. The probe was allowed to come to equilibrium before a reading was made on an Orion Model 8O1A Digital Ionanalyzer against a calomel reference electrode. The reading was corrected against an H_2 cell. Values were reported at ambient pH.

Other Measurements

Other measurements were conducted in accord with procedures specified in or equivalent to US EPA[6] or APHA *et al.*[3] Further information on experimental procedures, analytical methods, etc. has been presented by Lee, *et al.*[2]

Oxygen Demand Test Results

Results typical of the oxygen demand tests on dredged sediment are presented in Figure 2. In most cases, the oxygen decrease could be described as two consecutive first order reactions. The initial "first-stage" reaction exhibited a faster rate and usually had a duration of 5 to 10 minutes. The rate of the second-stage reaction was approximately five to ten times slower than the initial rate. Table 1 presents the overall first-hour oxygen demand data collected during this study. Also presented are values for selected bulk chemical parameters which could have an effect on the sediment oxygen demand. The highest demand per gram dry weight after one hour, 1.95 mg 02, was found in the sample from Apalachicola, FL Site No. 4. That sediment also had one of the higher first-hour oxygen demands calculated on a sediment volume basis, although the sample from Perth Amboy Channel exhibited the highest demand per cubic meter of

Table 1
Oxygen Demand and Bulk Characteristics of Sediments

Sample Site	Eh (mv)	Sulfide* (mg/kg)		Fe* (mg/kg)		Oxygen Demand First Hour		Percent Dry Wt.	Dry Wt. (g/cc)
		mean	SD	mean	SD	gO_2/m^3**	mgO_2/g*		
Mare Island	—	48		47,900	4,300	4.8x10^{2}	0.84	43.5	0.583
Rodeo Flats	—	258		42,800	20,000	5.7x10^{2}	0.96	43.8	0.589
Oakland	-198	1568	8	37,300	1,000	6.0x10^{2}	0.95	46.8	0.634
Los Angeles A-7	-234	2565	259	17,478	946	6.7xl0^{2}	1.15	43.6	0.583
Los Angeles C-2	-117	291	4	—	—	3.2x10^{2}	0.24	74.2	1.309
Newport A	+57	38	8	8,847	293	6.2xl0^{2}	0.55	67.4	1.127
Newport B	-92	93	12	—	—	2.2x10^{2}	0.22	64.0	0.979
Stamford	-173	2320	93	9,531	64	5.6x10^{2}	1.33	34.5	0.421
Norwalk 1	-151	2890	281	9,414	178	5.3x10^{2}	0.94	42.6	0.562
Norwalk 2	-160	2810	225	9,387	344	6.4x10^{2}	1.39	36.4	0.462
Apalachicola 2	-106	745	32	37,600	8,600	—	—	28.5	0.328
Apalachicola 3	-129	674	79	9,648	25	5.6x10^{2}	1.53	30.8	0.365
Apalachicola 4	-90	684	18	9,914	70	7.5x10^{2}	1.95	34.5	0.433
Apalachicola 5	-117	883	190	9,990	102	4.8x10^{2}	1.15	33.6	0.416
Duwamish 1	-64	13	8	15,581	44	42	0.03	79.6	1.401
Duwamish 2	-91	254	10	16,079	88	5.2x10^{2}	0.64	56.9	0.812
Duwamish 3	-111	247	13	15,892	220	5.6x10^{2}	0.64	59.7	0.891
Texas City Channel 1	-38	1205	108	23,200	300	5.0x10^{2}	0.66	52.6	0.761
Texas City Channel 2	-20	1251	95	17,400	4,700	4.8x10^{2}	0.64	51.4	0.745
Texas City Channel 3	—	—	—	33,300	2,300	—	—	—	—
Texas City Channel 4	-100	2519	10	26,260	238	6.0x10^{2}	1.21	38.5	0.495
Texas City Channel 5	-136	237	10	26,000	2,714	4.5x10^{2}	0.76	44.1	0.592
Texas City Channel 6	-124	1557	140	25,792	477	6.lxl0^{2}	1.17	40.0	0.520

Table 1 continues

Table 1 (continued)

Sample Site	Eh (mv)	Sulfide* (mg/kg)		Fe* (mg/kg)		Oxygen Demand First Hour		Percent Dry Wt.	Dry Wt. (g/cc)
		mean	SD	mean	SD	gO_2/m^3**	mgO_2/g*		
Galveston Bay Entrance Channel									
Buoy 1	+100	446	57	40,000	1,300	$3.6x10^2$	0.67	40.7	0.561
Buoy 9	—	—	—	13,300	2,100	$1.5x10^2$	0.16	41.2	0.552
Buoy 11	—	—	—	94,100	6,900	80	0.14	60.0	0.962
Galveston Channel	-87	1078	35	26,848	262	$5.9x10^2$	1.28	36.3	0.460
Port Lavaca	+40	166	7	21,000	1,100	$2.5x10^2$	0.42	44.6	0.603
Houston Ship Channel 1	-96	2962	78	20,055	0	$5.8x10^2$	1.42	34.3	0.416
Houston Ship Channel 2	-137	3483	291	19,778	161	$6.0x10^2$	1.80	28.2	0.333
Houston Ship Channel 3	-104	633	35	29,790	488	$5.2x10^2$	0.88	43.6	0.594
Vicksburg WES Lake	-75	278	17	—	—	$8.1x10^2$	1.01	54.8	0.802
Wilmington	-86	72	4	8,145	124	$1.5x10^2$	0.11	73.3	1.320
Mobile 1	-51	327	25	49,400	2,300	$5.1x10^2$	1.18	34.9	0.434
Mobile 2	-9	577	20	64,400	0	$6.3x10^2$	1.62	31.4	0.388
Upper Mississippi River 1	-172	5	4	11,820	700	$1.1x10^2$	0.07	83.4	1.488
Upper Mississippi River 2	-209	15	5	—	—	$1.7x10^2$	0.11	85.9	1.608
James River 1	-215	25	0	59,750	440	$6.2x10^2$	0.97	46.6	0.639
James River 2	-244	44	6	—	—	$7.3x10^2$	1.15	46.6	0.637
Bailey Creek	-2	166	5	37,100	4,500	$4.0x10^2$	0.27	80.0	1.493
Port of New York									
Bay Ridge Channel	-135	1190	27	15,900	10,300	$6.6x10^2$	0.90	47.6	0.735
Perth Amboy Channel	-109	1502	25	13,900	4,900	$9.3x10^2$	1.43	34.4	0.650
Perth Amboy Anchorage	-137	2373	121	14,800	7,300	$8.4x10^2$	1.29	39.7	0.652

Table 1 **(continued)**

Sample Site	Eh (mv)	Sulfide* (mg/kg)		Fe* (mg/kg)		Oxygen Demand First Hour		Percent Dry Wt.	Dry Wt. (g/cc)
		mean	SD	mean	SD	gO_2/m^3**	mgO_2/g*		
Menominee 1	-77	212	80	12,400	100	$5.0x10^2$	1.25	30.6	0.399
Menominee 2	-116	1133	26	9,600	100	$5.4x10^2$	1.14	38.8	0.476
Foundry Cove	-96	56	9	27,890	100	$5.2x10^2$	0.81	46.7	0.642
Ashtabula	—	—	—	30,540	1,840	$3.6x10^2$	0.4	55	—
Corpus Christi 1	—	—	—	8,300	10	$1.6x10^2$	0.2	70	0.80
Corpus Christi 2	—	—	—	27,400	8,780	$2.2xl0^2$	0.6	33	0.37
Corpus Christi 3	—	—	—	20,830	5,890	$2.5x10^2$	0.3	57	0.83
Corpus Christi 4	—	—	—	29,270	860	$2.1xl0^2$	0.6	30	0.35

Dash (—) indicates no data collected.

* Based on dry weight of sediment.

** Based on wet sediment.

A and B are replicate sediment samples collected at same location.

sediment for the first hour, 930 g 0_2. The lowest oxygen demand per gram dry weight for the first hour was 0.03 mg 0_2 in the Duwamish River Site 1 sediment sample. That sediment also exhibited the lowest demand per cubic meter for the first hour, 42 g 0_2. The majority of the samples had first-hour oxygen demands between about 500 and 650 g $0_2/m^3$; many were in the 200 to 400 g $02/m^3$ range.

The reproducibility of the oxygen demand test after the one-hour test period was good. The highest standard deviation between the dissolved oxygen readings of triplicate runs of the same sample was seen with the sediment from the James River Site No. 1, 0.6 mg /l. The lowest was found in the test of the Upper Mississippi River Site No. 2 sediment, 0.07 mg/l.

The reaction rates are presented in Table 2. Since various sediment to water ratios were used, the depletion rates were normalized based on volume. In normalizing, it was assumed that the relationship between reaction rates and sediment volume was linear, i.e., that a 2 ml volume of sediment in 300 ml would react at a rate two-thirds that of a 3 ml sediment sample in 300 ml. Several studies were conducted which verified that this approach was appropriate. The rates of oxygen depletion fit the following first order equation:

$$\log Ct = \log C_0 + kt$$

where Ct is the dissolved oxygen concentration at time t; C_0 is the initial oxygen concentration; k is the oxygen depletion rate constant; and t is time.

A wide range of first-stage rates was noted from a low of 0.005 mg/l 0_2 min^{-1} for the Wilmington, NC samples, to a high of 0.064 mg/l 0_2 min^{-1} in the Texas City Channel Site No. 6, and WES Lake (Vicksburg, MS) samples. The second-stage rates also had a large range of values from a low of 0•00l mg/l $0_2 min^{-1}$ for the Wilmington, NC and Corpus Christi Site No. 2 samples, to a high of 0.014 mg/l 0_2 min^{-1} in the sample from Los Angeles Harbor, Buoy A-7.

There were several samples where a single rate best described the data. As seen from Table 2, the rates were also varied, ranging from 0.001 mg 0_2 min^{-1} in one of the Upper Mississippi River sediments, to 0.02 mg/l 0_2 min^{-1} in a Texas City Channel sediment, about the same range as found for the second-stage rates for the other sediments. The ratios of the first to second-stage rates of oxygen depletion for the sediments investigated were compared and found to vary considerably among the sites (Table 2). They ranged from 1.8 for the sediment from Perth Amboy Channel to 21.3 for the WES Lake, Vicksburg, MS sample. These ratios have important implications for evaluating the potential impact of oxygen demand of sediments upon suspension in the watercolumn. The higher the ratio, the more likely that greater demand would be exerted near the point of sediment suspension (or dredged sediment disposal) in the watercolumn.

It is important, however, that the information developed from these ratios be closely tied with the actual rates of depletion, as part of assessing the degree of depletion at a site and implications for water quality there. Further, as discussed in a subsequent section, the actual amount of DO depletion that occurs at a site is controlled to a major extent by the hydrodynamics of the system rather than by the measured oxygen demand of the sediments. This is especially true for dredged sediment disposal or suspension of sediment, because the oxygen demand evaluation is made in completely mixed systems.

Because of the design of the evaluation system, the rates of reaction found in the laboratory portion of this study were controlled by chemical oxygen demand reactions rather than mixing. Each species exerted its own degree of influence in each sediment, creating a complex system in which the overall reaction took place. However, the two consecutive first order reactions may have been controlled by two different systems. The initial stage may be the result of the oxidation of reduced material, such as ferrous iron, sulfide, and polysulfide in the interstitial water. These constituents would be expected to be oxidized rapidly, as found in the faster initial rates. The slower, second-stage rates may be the result of the oxidation of reduced particulate material such as pyrite and FeS. These surface-controlled reactions take place at a slower rate. The single stage reactions may be controlled primarily by surface reactions, or by reduced constituents in the interstitial water, but both of these processes likely exert approximately equal influence. Gardner and Lee[7] studied the reactions between Lake Mendota, WI sediments and dissolved oxygen in similar, well-mixed laboratory systems. They found that these oxygen demand reactions proceeded for periods of months at a steady rate. The rates of oxidation they observed appeared to be controlled by the diffusion of dissolved oxygen through the hydrous oxide film on the surface of the particles.

Table 2 Reaction Rates for Oxygen Demand Test

Sample Site	Rate (mg O_2/L/min)			Initial:Final Ratio
	Initial	Single Rate	Final	
Oakland Harbor	—0.023		—0.011	2.09
Los Angeles A—7	—0.029		—0.014	2.07
Los Angeles C—2	—0.026		—0.003	8.67
Newport A*		—0.014		
Newport B	—0.006		—0.002	3.00
Stamford		—0.009		
Norwalk 1		—0.009		
Norwalk 2	—0.017		—0.009	1.89
Apalachicola 3	—0.026		—0.006	4.33
Apalachicola 4	—0.034		—0.009	3.78
Apalachicola 5	—0.016		—0.004	4.00
Duwamish 1		—0.001		
Duwamish 2	—0.030		—0.006	5.00
Duwamish 3	—0.033		—0.007	4.71
Texas City Channel 1		—0.020		
Texas City Channel 2		—0.018		
Texas City Channel 4	—0.023		—0.011	2.09
Texas City Channel 5	—0.024		—0.004	6.00
Texas City Channel 6	—0.064		—0.010	6.40
Galveston Bay Entrance Channel Buoy 1	—0.014		—0.004	3.50
Galveston Bay Channel	—0.025		—0.009	2.78
Port Lavaca	—0.016		—0.002	8.00

Houston Ship Channel 1	—0.018		—0.008	2.25

Table 2 (continued)

Sample Site	Rate (mg O_2/L/min)			Initial:Final Ratio
	Initial	Single Rate	Final	
Houston Ship Channel 2	—0.030		—0.008	3.75
Houston Ship Channel 3	—0.031		—0.007	4.43
Vicksburg, WES Lake	—0.064		—0.003	21.33
Wilmington	—0.005		—0.001	5.00
Mobile Bay 1	—0.031		—0.006	5.17
Mobile Bay 2	—0.031		—0.011	2 .82
Upper Mississippi River 1		—0.001		
Upper Mississippi River 2		—0.002		
James River 1	—0.036		—0.009	4.00
James River 2	—0.037		—0.010	3.70
Bailey Creek	—0.010		—0.004	2.50
Port of New York				
Bay Ridge Channel	—0.022		—0.009	2.44
Perth Amboy Channel	—0.024		—0.013	1.85
Perth Amboy Anchorage		—0.012		
Menominee 1	—0.025		—0.003	8.33
Menominee 2	—0.019		—0.005	3.80
Foundry Cove	—0.027		—0.003	9.00
Ashtabula Harbor	—0.012		—0.004	2.86
Corpus Christi 1	—0.006		—0.002	3.00
Corpus Christi 2	—0.012		—0.001	12.00

Corpus Christi 3	—0.006	—0.002	3.00
Corpus Christi 4	—0.006	—0.002	3.00

*A and B are replicate sediment samples collected at same location.
Dash (—) indicates not applicable.

Relationship Between Sediment Characteristics and Oxygen Demand Test Results

Bulk characteristics of the sediments examined, percent dry weight, oxidation-reduction potential, and total sulfide and total iron content, are presented in Table 1. The sediments percent dry weight values ranged from about 28 to 86% with a mean value of about 50%. In the authors[2] dredged sediment oxygen demand evaluations, correlations between first-hour oxygen demand and weight percent sediment have been a $r^2 = 0.37$.

Redox potential for the sediments studied ranged from +100 mv to -244 mv. Only three of the sediments were found to be in an oxidizing or positive Eh state: Newport, RI, GBEC Buoy 1 (the most seaward site), and Port Lavaca, TX. It can be concluded that most sediments are in a reduced oxidation-reduction state and, therefore, would likely contain significant concentrations of chemicals which would exert an oxygen demand. The reducing conditions of the sediments were also evidenced by the presence of sulfide. The range in the total sulfide concentrations was large, from 5 mg/kg to 3,483 mg/kg dry weight; these samples were from the Upper Mississippi River Site No. 1 and Houston Ship Channel Site No. 2, respectively. The mean sulfide concentration was 928 mg/kg dry weight. Even the samples having a positive redox potential contained sulfide. It has been reported[9] that the highest oxidation-reduction potential at which sulfide species will be formed is +110 mv and the lowest is -500 mv. The Eh values for all sediments investigated in this study were within this range, and sulfide was found in each sample analyzed. When compared statistically, there was not a significant relationship between Eh and total sulfide concentration in the sediments with a $r^2 = 0.08$. This would be expected, however, because the Eh provides an indication of whether or not sulfide can form, not of the extent of formation. The formation of sulfide is more related to the suitability of the particular environment for sulfate reduction by microorganisms.

The other major reduced species in the sediment which would have a major impact on the immediate oxygen demand is iron in the form of Fe II. The iron form reported in Table 1 was total iron in the dry sediments; no attempt was made to differentiate between Fe II and Fe III although it is likely that most of the iron present in the samples was in the Fe II form. Total iron ranged from 8,145 mg/kg in sediment from Wilmington, NC to 94,100 mg/kg in the sediment sample from GBEC Buoy 11. The mean was found to be about 25,000 mg/kg for all sediments tested

Calculations were made to determine the theoretical oxygen demand of each sediment based on the sulfide and iron content. It was assumed that all of the iron in the sediment was in a reduced state and that the oxidation of the two reduced species followed these reactions:

$$HS^- + 2\ 0_2 = SO_4^{=} + H^+$$

$Fe^{2+} + 1/4\ 02 + H = Fe^{3\sim} + 1/2H_2O$

Presented in Table 3 are the theoretical oxygen demands based on the above equations, the demand realized after one hour, and the percentage of the theoretical demand realized in that time. The percentage of the demand realized ranged from a low of 1.3 in the Duwamish River Site No. 1 sediment to about 70 in the Apalachicola Site No. 4 sediment. The mean percent of the theoretical demand (based on the iron and sulfide present) that was exerted by the sediments tested during the one-hour period, was 20 %. From these data it can concluded that the oxygen demand of a sediment cannot be predicted based on the total iron and total sulfide content alone.

The data were examined to determine if a relationship between the bulk concentrations of total sulfide or total iron and oxygen uptake could be described. The r^2 values for these two relationships were 0.32 and 0.01, respectively, indicating the lack of strong regressions for these data. Thus, as expected, neither total sulfide nor iron alone can be used for estimating the first hour oxygen demand of a sediment. From these findings it can concluded that bulk characteristics such as total sulfide, total iron, oxidation-reduction potential, and dry weight cannot be used individually or in combination to estimate the one-hour oxygen demand of a sediment. One of the primary reasons is the complexity of the reactions of iron sulfide and other surface reactions. Another is the importance of hydrodynamics in controlling oxygen demand exertion. Therefore, at this time and for the foreseeable future, oxygen demand can only be determined by empirical methods.

It is important not to confuse the results of these abiotic oxygen demand results with biochemical oxygen demand (BOD) processes that can take place in ambient waters and sediments. Biotic oxygen demand at the BOD concentrations typically found in natural water systems is a much slower process with first order rate constants of about 0.1 $day^{-1.}$

Relationship Between Oxygen Demand Test Results and Oxygen Depletion Observed During Open Water Dredged Sediment Disposal

Dumping Operations

There were basically two types of dredged sediment disposal operations monitored. One was the dumping of sediments at a location far removed from the dredging site via hopper dredge or barge. Sediments mechanically dredged were placed on a barge and were towed to the dump site. A hopper dredge vessel contains large bins into which the hydraulically dredged sediment slurry is pumped; much of the excess water is allowed to overflow. The dredge proceeds to a disposal area and dumps the sediment into the watercolumn by opening doors on the bottom of the bins. Normally, each dump from a hopper dredge will involve a few thousand cubic meters of sediment. Most of the sediment falls directly to the bottom as a mass, reaching the bottom a few seconds after release. A turbid cloud is formed from the suspension of sediment from the edges of the mass of dumped sediment as it proceeds downward through the watercolumn. The turbid cloud moves downcurrent and is dispersed within an hour or so of the dump.[1, 10] It was the concentration of contaminants and DO in this turbid cloud that was of primary interest in this investigation.

Table 3
Sediment Oxygen Demand

Sample Site	Oxygen Demand (mg O_2/g dry wt)		
	Theoretical	Realized	Percent
Mare Island	6.96	0.84	12.07
Rodeo Flats	6.65	0.96	14.44
Oakland	8.48	0.95	11.20
Los Angeles A—7	7.63	1.15	15.06
Newport A*	1.34	0.55	40.95
Newport B	1.45	0.22	15.14
Stamford	6.01	1.33	22.15
Norwalk 1	7.13	0.94	13.19
Norwalk 2	6.96	1.39	19.96
Apalachicola 3	2.73	1.53	56.04
Apalachicola 4	2.79	1.95	69.94
Apalachicola 5	3.20	1.15	35.97
Duwamish 1	2.26	0.03	1.33
Duwamish 2	2.81	0.64	22.77
Duwamish 3	2.77	0.64	23.10
Texas City Channel 1	5.73	0.66	11.51
Texas City Channel 2	4.99	0.614	12.82
Texas City Channel 4	8.80	1.21	13.75
Texas City Channel 5	4.20	0.76	18.10
Texas City Channel 6	6.81	1.17	17.18
G B E Channel Buoy 1	6.62	0.67	10.12
Galveston Channel	6.00	1.28	21.33

Port Lavaca	3.34	0.42	12.57

Table 3 (continued)

Sample Site	Oxygen Demand (mg O_2/g dry wt)		
	Theoretical	Realized	Percent
Houston Ship Channel 1	8.80	1.42	16.14
Houston Ship Channel 2	9.80	1.80	18.37
Houston Ship Channel 3	5.53	0.88	15.90
Wilmington	1.31	0.11	8.39
Mobile Bay 1	7.73	1.18	15.26
Mobile Bay 2	10.37	1.62	15.62
Upper Mississippi River 1	1.70	0.07	14.11
Upper Mississippi River 2	1.72	0.11	6.34
James River 1	8.61	0.97	11.27
James River 2	8.65	1.15	13.30
Bailey Creek	5.65	0.27	4.78
Port of New York			
Bay Ridge Channel	4.66	0.99	21.25
Perth Amboy Channel	4.99	1.43	28.63
Perth Amboy Anchorage	6.87	1.29	18.79
Menominee 1	2.20	1.25	56.84
Menominee 2	3.64	1.14	31.22
Foundry Cove	4.11	0.81	19.72

*A and B are replicate sediment samples collected at same location.

The monitoring procedure for this type of disposal operation involved positioning a sampling boat 100 m or so downcurrent of the dump site. Measurements of light transmission were made to determine when the turbid cloud had reached and had passed the sampling vessel at various depths within the watercolumn. An example of the type of turbidity patterns found during dredged sediment disposal is shown in Figure 3. In this hopper dredge disposal of sediments from the Galveston Bay Entrance Channel (Buoys 1-3), the turbid cloud reached the sampling vessel about 30 m downcurrent, 2 to 3 minutes after the dump began, and concentration which returned to pre-dump levels within about 2 minutes of the arrival of the turbid cloud (Figure 4).

Figure 5 shows a different pattern of DO concentration during the barge disposal of mechanically dredged New York harbor (Perth Amboy Anchorage) sediments, at the Mud Dump Site in the New York Bight. During this dump, which was monitored from about 100 m down bottom current, there was an increase in the near-bottom water*s dissolved oxygen concentration during the passage of the turbidity cloud. Such an increase was noted during all three New York dumps and occurred despite the fact that the oxygen demand of these sediments had been among the highest found for the sediments evaluated. The reason for the increase in bottom water DO with the passage of the turbid cloud relates to the fact that the disposal site waters were density stratified and the ambient DO concentration of the bottom waters was lower than that of the surface waters. The dump of sediments caused an entrainment of surface waters into the bottom waters, thereby increasing their dissolved oxygen concentration.

It has been concluded that the open water dumping of dredged sediments derived from either hopper or mechanical dredging operations would not be expected to cause a significant dissolved oxygen depletion in the watercolumn at or near the dredged material disposal site. Because of the entrainment phenomenon, a dumping operation may actually increase the short term DO concentration in the hypolimnetic waters. Further, it is evident that because of entrainment and other hydrodynamic factors, no simple relationship can be developed between the results of the oxygen demand test developed by Lee et al[2]. and the oxygen depletion that will occur in the watercolumn at or near an open water dredged material dump site.

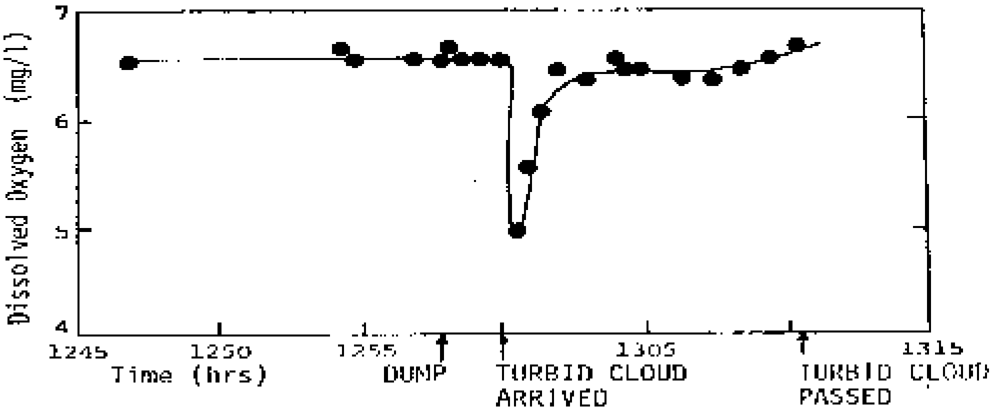


Figure 4. Dissolved Oxygen Concentrations in Near-Bottom Water during Disposal of Galveston Bay Entrance Channel Buoy 1-8 Sediments (After Lee *et al.*[2])

0

Pipeline Discharge Operations

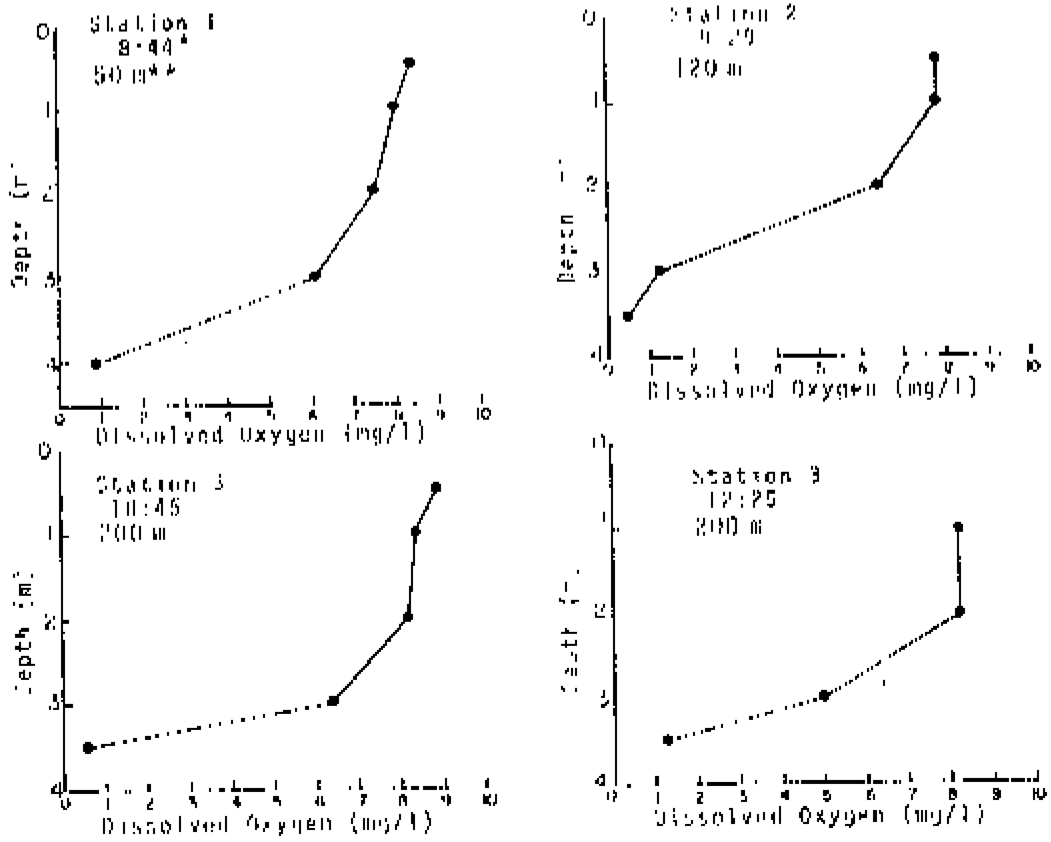
The other general type of dredged sediment disposal operation investigated was the pipeline disposal of hydraulically dredged sediments. This commonly used method involves the slurrying of the sediment and the transport of the sediment via pipeline to an off-channel location. The discharge point for this type of operation generally receives a more or less continuous flow of dredged sediment slurry for a few hours to a day or more. The sediment slurry discharge, which is typically on the order of 10 to 30% sediment, sinks to the bottom and moves with the bottom current, forming a turbid plume about 0.5 to 1 m thick. Four pipeline disposal operations were monitored. At three of the four locations (James River, Apalachicola Bay, and Mobile Bay) the discharges were anoxic and similar patterns of DO behavior in the receiving waters were found. There was generally an inverse relationship between the turbidity and DO concentrations. Figure 6 shows representative DO concentration profiles at various locations directly downcurrent from the Mobile Bay discharge. In this case, measurements were made in the watercolumn from about 0.5 m beneath the water surface to a few cm above the sediment water interface. It is evident from the examination of Figure 6 that even as far as 200 m from the Mobile Bay, AL discharge, there was appreciable oxygen depletion near the sediment water interface. At the fourth pipeline disposal operation monitored (Upper Mississippi River), the discharge from the pipeline was oxic, containing several mg/l DO. While the DO was depressed near the point of discharge, within a few tens of meters, DO concentrations within the turbid plume were at ambient levels.

Discussion

It has become clear from these studies that in order to predict dissolved oxygen depletion associated with open water dredged sediment disposal operations, a much better understanding of the hydrodynamics of the density current and the disposal area must be available. It is also evident that while it would likely be rare that significant oxygen depletion problems would occur in association with open water dumping of dredged sediment, water quality problems related to DO depletion could develop near the point of discharge for a pipeline disposal operation. Of particular concern would be the effects of the dissolved oxygen depletion in the turbid plume on benthic and epibenthic organisms.

Suspended sediment-related oxygen depletion is not restricted to dredged sediment disposal; it can also occur in shallow bays or rivers when increased flows or wind-induced turbulence suspends bottom sediments into the watercolumn. It is well-known that in certain rivers which accumulate significant amounts of sludge, the most crucial period for aquatic life in terms of the adequacy of dissolved oxygen occurs with the first major rising of the hydrograph that causes sediment scour after an extended low-flow. Rivers such as the Little Miami River near Cincinnati, OH and the Trinity River near Dallas, TX have shown significant DO depletion with increasing hydrographs.

The typical oxygen demand studies involving laboratory cores or in situ "bell jar-chambers" measurements do not properly account for the high oxygen demands associated with the accumulated ferrous iron and sulfide species that are present in sediments which would exert a rapid oxygen demand upon suspension of the sediments in the watercolumn. In order to properly monitor this type of oxygen demand, which for some systems may be the most important, it will be necessary to obtain a much better understanding of the influence of the velocity of the overlying waters on the suspension of cohesive sediments.



* Time of measurement

** Distance between discharge and sampling site

Figure 6. Dissolved Oxygen Profiles during Pipeline Disposal of Mobile Bay Sediments (After May et al.[2])

Summary and Conclusions

With few exceptions, the sediments in US waterways near urban centers are anoxic. Upon suspension of these sediments in the watercolum, the reduced iron and sulfur species exerted an inorganic chemical oxygen demand which had a first order rate constant on the order of 0.02 mg O_2 mg/l min^{-1} when a few ml of the sediment were mixed into several hundred ml of water. This oxygen demand can typically be described as having two components: a higher rate exerted over the first 5 to 10 minutes of exposure of the sediments to oxygen-containing waters, followed by a lower rate which may extend over a period of days, weeks, or months, apparently controlled by the diffusion of oxygen through a hydrous oxide film formed on the surface of iron sulfide and polysulfide particles. This abiotic oxygen demand may result in sufficient depletion of oxygen to impair water quality when increased water velocity suspends river or bay sediments. The suspension of such sediments may, in some aquatic systems, represent one of the most important sources of oxygen depletion.

It is apparent that oxygen demand modeling efforts which do not include the short-term, high intensity demand associated with sediment suspension may have limited applicability to describing the true impact of sediment suspension on water quality-impairment of beneficial uses of a water. In order to properly describe the abiotic, short-term, high intensity oxygen demand of sediments, it will be necessary to better describe the relationships between water velocity and cohesive sediment suspension in rivers and the shallow waters of lakes and bays.

Acknowledgments

The US Army Corps of Engineers Dredged Material Research Program contracts DACW 39-75-C-0l02 and DACW 39-76 C-01l7 administered through the Environmental Laboratory, US Army Engineer Waterways Experiment Station, Vicksburg, MS provided support for the laboratory and field studies for this investigation. The authors acknowledge the assistance provided by D. Homer, then a graduate student at the University of Texas at Dallas in sample collection, analysis and in drafting sections of the report[2] from which sections of this paper were drawn.

References

1. Jones, R. A., and Lee, G. F., "Evaluation of the Elutriate Test as a Method of Predicting Contaminant Release during Open Water Disposal of Dredged Sediment and Environmental Impact of Open Water Dredged Material Disposal, Vol I: Discussion," Technical Report D-78-45,US Army Engineer Waterways Experiment Station, Vicksburg, MS (1978).

2. Lee, G. F., et al., "Evaluation of the Elutriate Test as a Method of Predicting Contaminant Release during Open Water Disposal of Dredged Sediment and Environmental Impact of Open Water Dredged Material Disposal, Vol II: Data Report," Technical Report D-78-45, US Army Engineer Waterways Experiment Station, Vicksburg, MS (1978).

3. American Public Health Association (APHA), et al., Standard Methods for the Examination of Water and Wastewater, 13th ed., APHA, New York (1971).

4. Gardner, W. S., Oxygenation of Lake Sediments, M.S. Thesis, University of Wisconsin, Madison, WI (1964).

5. Bortleson, G. C., The Chemical Investigation of Recent Lake Sediments, M.S. Thesis, University of Wisconsin, Madison, WI (1970).

6. US EPA, Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, US EPA Cincinnati, OH (1974).

7. Gardner, W. S., and Lee, G. F., “Oxygenation of Lake Sediments,” Air Water Poll. 9, 553 (1965).

8. Lee, G. F., *et al.*, “Research Study for the Development of Dredged Material Disposal Criteria,” Technical Report D-75-4, US Army Engineer Waterways Experiment Station, Vicksburg, MS (1975).

9. Baas-Becking, L.G.M., *et al.*, “Limits of the Natural Environment in Terms of pH and Oxidation Reduction Potentials,” J. Geol. 68, 243 (1960).

10. Lee, G.F. and Jones, R.A., "Water Quality Aspects of Dredging and Dredged Sediment Disposal," In: Handbook of Dredging Engineering, McGraw Hill pp. 9-23 to 9-59, (1992). An updated version of this chapter which will appear in the second edition of this handbook is available from http://www.gfredlee.com (1999).