Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand
Part I – Origin of Rapid Sediment Oxygen Demand [1]

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May 2007

Some urban streams experience rapid depletion of dissolved oxygen (DO) associated with major stormwater runoff events. In some situations, the DO depletion can be sufficient to rapidly cause low DO that can lead to fish kills. This report is Part I of a three-part discussion that examines the role of aquatic sediments in causing the rapid depletion of DO in some urban and rural streams associated with stormwater runoff events that suspend sediments into the watercolumn where they exert oxygen demand.

Also, focus is given to the potential for similar, rapid DO depletion in US navigable waterways (river and harbor systems) associated with the exertion of sediment oxygen demand when sediments become suspended into the watercolumn during storms and open water disposal of dredged sediments. While sediment oxygen demand is typically said to be associated with relatively slow biotic reactions (decomposition of organics), there are situations in which abiotic (inorganic) reactions play a major role in DO depletion in a waterbody watercolumn. Examples of these situations are discussed herein.

Part II expands on the discussion of sediment oxygen demand and includes examination of the role of planktonic (suspended) algal death/decomposition in causing oxygen demand in the watercolumn of lakes and channels.

Part III discusses the role of aquatic plant nutrients in causing low DO in waterbodies that leads to sediment toxicity.

Impact of Low DO on Fish.
Lee and Jones-Lee (2003) summarized the effects of decreased DO on fish and other aquatic life based on the information in the US EPA guidance document for the DO water quality criteria (US EPA, 1986). According to C. Delos (Health and Ecological Criteria Division, Office of Science and Technology, Office of Water, US EPA, Washington DC) (Personal communication, 2003) the US EPA believes that this information is still current. DO concentrations between the water quality criterion and several mg/L below the criterion would be expected to slow fish growth rate; the amount of impact is proportional to the amount of depletion below the criterion. There is, however, a critical

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[1] Reference as Lee, G. F., and Jones-Lee, A., "Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand Part I – Origin of Rapid Sediment Oxygen Demand," Report of G. Fred Lee & Associates, El Macero, CA, May (2007).

DO level of about 2 to 3 mg/L; if the DO remains at or below that level for a period of time, significant mortality will occur in most fish populations.

Oxygen Demand Reactions.
The oxygen concentration in a waterbody is the result of oxygen demand associated with oxygen demanding substances in the watercolumn and sediments. Both biotic (biochemical oxygen demand—BOD) and abiotic (non-biological—inorganic)-based reactions consume DO in waterbodies. Aquatic plant (algae and macrophytes-floating and attached water weeds) photosynthesis can add significant DO during the daylight hours. Bacterial and aquatic plant respiration consumes oxygen. Diurnal (night/day) DO changes in urban streams and other waterbodies with substantial aquatic plant populations can be several mg/L. Low nighttime DO can result in violations of DO water quality standards unless the averaging of diurnal DO is allowed. US EPA and some states allow this averaging; California does not.

Typically biochemical oxygen demand reactions are relatively slow compared to some inorganic abiotic reactions with DO that occur in aquatic sediments. The typical domestic wastewater and dead algal BOD reactions are about 70% completed in five days. Baird and Smith (2002) and Bowie et al. (1985) have provided detailed discussion of the typical BOD reactions. As discussed below, inorganic reactions, which are the primary cause of the rapid DO depletion that occurs in urban streams during stormwater runoff events, take place in a few minutes to a few hours.

Gas Exchange Reactions with the Atmosphere. The DO concentration in a waterbody depends on the DO saturation value (i. e., the amount of DO that a water will hold in equilibrium with the atmosphere). The saturation concentration depends on the temperature and salinity of the water, and barometric pressure. Atmospheric aeration will add DO to the waterbody when the DO is below saturation, and remove DO to the atmosphere when the water is supersaturated with DO. As discussed by Chapra (1997) and Bowie et al. (1985), the rate of gas exchange reactions with the atmosphere is governed by the water turbulence at the surface/water interface. While the turbulence of urban streams increases during runoff events, gas exchange reactions rarely are a major factor in preventing the rapid DO depletion that occurs associated with stormwater runoff events.

Nomenclature
The chemical symbols used in this Newsletter with Roman numerals, such as Fe(III), S(-II) designate the element and its oxidation state; the Roman numeral indicates the number of electrons gained or lost from the elemental state. This approach does not indicate the chemical species present in a water or sediment.

Inorganic DO Demand Reactions.
The inorganic chemicals primarily responsible for DO depletion during runoff events are precipitates with iron (in the form of ferrous iron (Fe^{2+})) and with sulfur (in the form of sulfide and polysulfides (referred to herein as "sulfides")). Stumm and Lee (1960) presented a comprehensive review of the aqueous environmental chemistry of iron in,

"Chemistry of Aqueous Iron." This review is updated in Stumm and Morgan (1996). Iron exists in aquatic systems (water and sediments) in the form of ferrous iron (Fe II) and ferric iron (Fe III). (The II and III designations refer to the oxidation states of the iron.) Ferrous iron is somewhat soluble in anoxic (oxygen-free) waters; it has limited solubility in the presence of sulfides, such as in contact with sediments. Ferric iron is highly insoluble in oxic waters where it precipitates as ferric hydroxide (hydrous oxide). Ferric iron is not stable under anoxic (oxygen-free) waters; there it is reduced to ferrous iron. In the neutral to slightly alkaline pH range typical of surface waters, the reactions between ferrous iron and "sulfides" and DO are extremely rapid. Stumm and Lee (1961) reported that the reaction between ferrous iron and DO followed the rate expression,

$$\underline{d(FeII)/dt} = -k(Fe\ II)\ (O_2)\ (OH^-)^2$$

The rate of this reaction is first order with respect to ferrous iron and DO (i.e., directly proportional to ferrous iron and DO concentrations); it is second-order with respect to the pH ($(OH)^2$). This means that for a one-unit change in pH (a 10-fold hydrogen ion concentration change) the rate of reaction is changed 100-fold. At near-neutral pH and at typical iron and oxygen concentrations in aquatic systems, the reaction between ferrous iron and dissolved oxygen is essentially completed in a few minutes. The rate of reaction decreases fairly rapidly under somewhat acidic conditions. Stumm and Lee (1961) found that many other chemicals, such as traces of copper, catalyze this reaction, causing the rate to greatly increase.

Sulfur exists in aquatic systems as sulfate ($SO_4^=$), elemental sulfur, various sulfur oxide species (sulfite, thiosulfate, and others) and as sulfides (S -II species, and sulfide/polysulfides (S^{-II}/S^{-I}, H_2S, and HS^-). Sulfides are oxidized by dissolved oxygen to form oxidized forms, and eventually sulfate. Chen and Morris (1972) found that the reactions of sulfide species and DO are fairly rapid. If the water has a pH of less than about 7, the oxidation of the sulfides stops at elemental sulfur. This reaction accounts for the finding of elemental sulfur in the sediments of many waterbodies.

DO Depletion Problems in Urban Streams
The Lee (2004) and Lee and Jones-Lee (2004a, 2005) reviews of urban stream and lake water quality issues were discussed in Newsletter 7-6/7,
(http://www.members.aol.com/apple27298/swnews767.pdf). As discussed therein, DO depletion in urban streams associated is commonly associated with stormwater runoff events and can be significantly adverse to water quality in the streams.

City of Stockton, CA DO Depletion Situation. An example of severe DO depletion in urban waterways associated with stormwater runoff is the situation that was found by the DeltaKeeper (2000) (W. Jennings and his associates) in the early 2000s and described by Lee and Jones-Lee (2003, 2004c) and Lee (2003). The city of Stockton has several freshwater tidal sloughs (waterways) that are connected to the San Joaquin River and the Sacramento/San Joaquin Delta. The DeltaKeeper found that there were fish kills in several of these sloughs associated with the first major stormwater runoff event of the fall. It was found that the DO in the sloughs dropped to zero or near-zero just after the

runoff event began. As discussed by Lee and Jones-Lee (2003, 2004b,c) and Lee (2003) the rapid depletion of DO just after the runoff event began was likely caused by the exertion of the oxygen demand of ferrous sulfide precipitates that had accumulated in the city's storm sewers.

Other DO Depletion Situations. Lee et al. (2001) studied the stormwater runoff-related water quality issues of the Upper Newport Bay (Orange County, California) watershed. They reported that according to findings of the Orange County Public Facilities and Resources Department (stormwater management agency), there were DO depletion problems in San Diego Creek, a tributary of Upper Newport Bay. They also reported that the Trinity River, just downstream from the city of Dallas, TX, also experiences DO depletion problems associated with stormwater runoff events.

Graczyk and Sonzogni (1991) investigated the impact of stormwater runoff on DO in several Wisconsin streams using continuous recording of DO during the stormwater runoff event. One of the streams was Black Earth Creek, a rural, high-value trout stream located west of Madison, WI. The author (G. F. Lee) is familiar with the characteristics of Black Earth Creek through studies conducted on it by the University of Wisconsin Madison Water Chemistry Program graduate students while he was on the faculty there. Graczyk and Sonzogni (1991) found that a stormwater runoff event in the summer of 1985 led to low DO in the stream which led to a fish kill. They discussed potential causes of the low DO in that creek and indicated that additional study would be needed to evaluate this situation, and stated,

"It is commonly believed that runoff from heavy rainfall is not detrimental to the oxygen content of rural streams free from industrial and municipal discharges. However, evidence is presented of low dissolved oxygen concentrations during high flows (caused by agricultural runoff during summer rainstorms) in southern Wisconsin streams. Continuous monitoring of streams with in situ oxygen meters indicated a rapid decrease in dissolved oxygen with a rise in the hydrograph." "Loss of DO is important because it appears to be associated with fish kills and declining sport fish populations in streams in the region."

Based on the characteristics of the creek, it is likely that that stormwater runoff event led to the suspension of Black Earth Creek sediments which had accumulated ferrous iron and sulfides, which in turn, consumed DO when suspended in the watercolumn associated with the runoff event. While regulatory agencies and others sometimes attribute fish kills associated with runoff, to pesticides carried to the stream by the runoff from the watershed, low DO associated with stormwater runoff events can be a cause of fish kills. Conventional stormwater runoff monitoring is not adequate to evaluate this type of situation; continuous recording of DO is necessary.

Overall it can be concluded that stormwater runoff in urban streams and in some other waterbodies can lead to significant DO depletion that, in some situations, can be of sufficient magnitude to violate water quality standards and adversely affect aquatic life. The rapid depletion of dissolved oxygen associated with stormwater runoff events is due

to reactions between DO and ferrous iron and sulfides. In order to examine the occurrence and significance of DO depletion associated with stormwater runoff, the typical stormwater runoff monitoring would need to be expanded to include repetitive monitoring of the receiving waters over the day or so following the start of the runoff event.

US Waterway Sediment Oxygen Demand
During the 1970s, G. Fred Lee and his graduate students at the University of Texas at Dallas conducted about $1 million of studies on the potential water quality impacts of sediments dredged from US waterway navigation channels and disposed of in open/deeper waters (Lee et al., 1978 and Jones and Lee, 1978). Those studies were conducted as part of the US Army Corps of Engineers Waterways Experiment Station's Dredged Material Research Program (DMRP), a $30 million, 5-year program whose overall primary objective was the evaluation of the potential environmental impacts of open water disposal of contaminated dredged sediments. The Lee et al. studies focused on developing criteria for the open water disposal of contaminated dredged sediment. They included taking sediments from about 100 locations typically near urban/industrial areas throughout the US, and measuring and evaluating the release of about 30 potential pollutants (heavy metals, nutrients, pesticides, and PCBs) from those sediments using the elutriate test and toxicity tests. The elutriate test simulates the suspension of dredged sediments associated with open water disposal of hydraulically dredged sediments. The results of those studies were summarized in Lee and Jones-Lee (2000) and Jones-Lee and Lee (2005).

As part of their DMRP studies Lee et al. addressed the concern that open water disposal of dredged sediments could lead to significant DO depletion at the disposal site. D. Homer (1980) conducted studies designed to assess the oxygen demand in US waterway sediments by suspending a few mL of the subject sediment in continuously stirred water in a BOD bottle and measuring the depletion of DO over time using a membrane electrode. Those studies provided insight into the magnitude of the rapid exertion of the inorganic oxygen demand from US waterways sediments. They also provided information on the factors that influence the rate of exertion that could lead to low-DO problems in waterbodies. As summarized by Jones and Lee (1978) and Lee and Jones (1999), those studies showed that the oxygen demand of the sediments studied followed the same pattern that was found by Gardner and Lee (1965) (discussed in Newsletter 10-5), that there was an initial, rapid rate of oxygen demand lasting about 5 to 10 minutes followed by a slower rate of DO consumption that took place over a considerable period of time. The rate of the second reaction was approximately five to ten times slower than the initial rate.

The highest demand *per gram dry weight* after one hour, 1.95 mg O_2, was found in the sample from Apalachicola, FL Site No. 4, while the sample from Perth Amboy Channel, New Jersey, exhibited the highest demand *per cubic meter* of sediment for the first hour, 930 g O_2. The lowest oxygen demand per gram dry weight for the first hour was 0.03 mg O_2 in the Duwamish River (near Seattle, WA) Site 1 sediment sample. The lowest demand per cubic meter for the first hour was observed in the Duwamish River Site No. 1

sediment, 42 g O_2. Many of the sediments evaluated had oxygen demand values on the order of 500 g O_2/m^3 sediment.

Overall it can be concluded that US waterway sediments have a substantial reservoir of inorganic oxygen demand that has the potential to cause significant water quality problems when the sediment is suspended in the watercolumn.

Oxygen Demand at Dredged Sediment Disposal

Dredging of US waterway sediments takes place by either hydraulic dredging (in which the sediments are sucked into a pipeline by a pump located on the dredge) or by mechanical lifting of the sediment. During hydraulic dredging, the sediments are slurried in the approximate ratio of one volume of sediment in four volumes of water. These slurried sediments are either place in hoppers (bins) on the hopper dredge or pumped via pipeline to an open water disposal site or to a "confined" on-land disposal area. Mechanical dredging is accomplished using a clamshell grab; the sediments are removed into a closable bucket and then dumped onto a scow (flat-bottom boat). The scow transports the dredged sediment to a disposal area in open waters, or to an on-land disposal site.

Hydraulic Dredging. Hydraulic dredging is illustrated in Figure 1. The slurrying results in the mixing of the sediments with water, which tends to promote the release of constituents associated with the sediment and interstitial water into the slurry water. In hopper dredging, excess water is typically allowed to drain off from the hopper bins at the dredging site or during transport to the disposal site, to optimize efficiency of sediment removal.

Figure 1. Diagrammatic Representation of Hydraulic Dredging
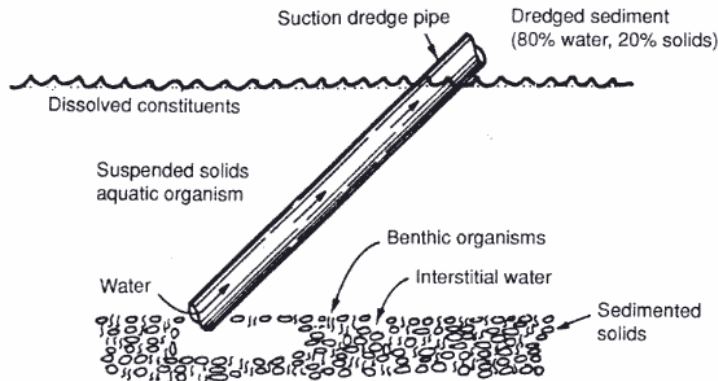
Hopper Dredged Sediment Disposal. Figure 2 illustrates the watercolumn during disposal of dredged sediment from a hopper dredge. When the hopper-dredge is at the designated disposal location, the hopper doors (located at the bottom of the hopper bins) are opened and the sediments are released. Most of sediment rapidly descends as a fairly

cohesive mass. As indicated in Figure 2, the descent of the dredged sediments from the hopper to the bottom of the watercolumn forms a turbid cloud in the waters of the region.
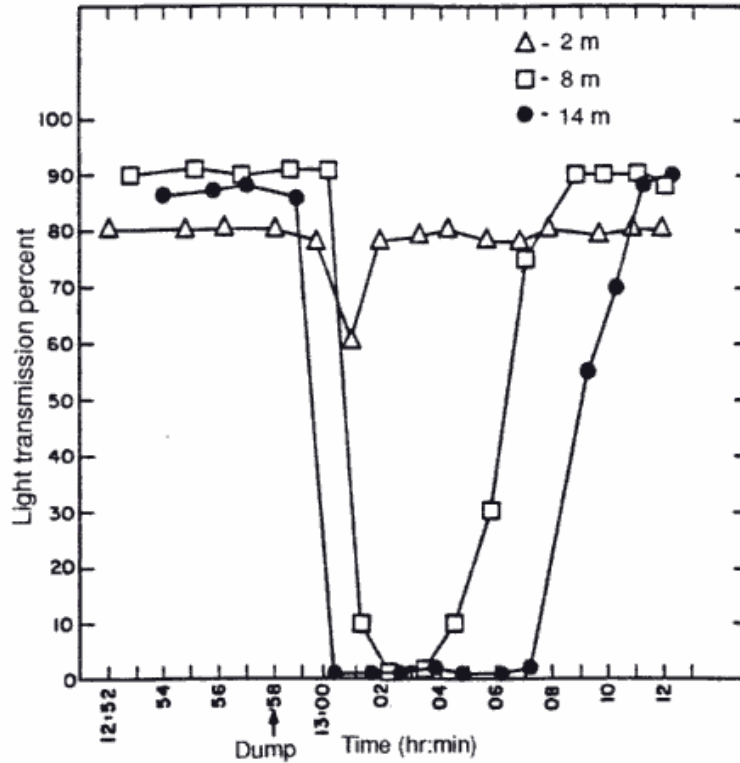
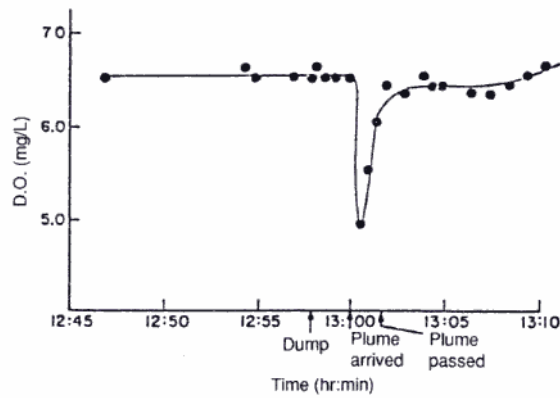**Figure 2 Hopper Dredge Disposal of Dredged Sediment**
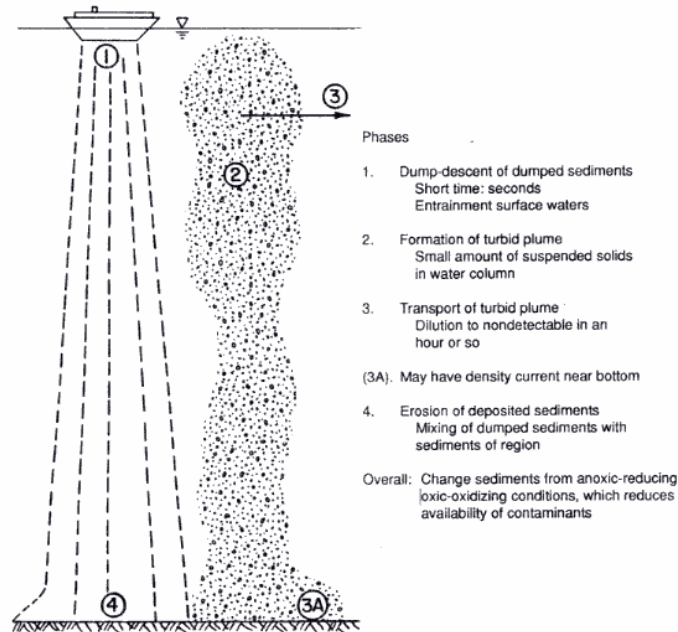
In their evaluation of the nature and water quality impacts of dredging and dredged sediment disposal, Lee et al. (1978) monitored the watercolumn during more than 10 open-water disposal operations by measuring more than 30 physical and chemical parameters at various depths in the watercolumn before, during and after the passage of the turbid plume for each. Figure 3 shows the characteristic pattern of turbidity marking the passage of the turbid plume during open-water disposal of dredged sediment (based on a monitored dredged sediment disposal operation at the New York Bight Mud Dump Site off the New Jersey coast, with the Corps of Engineers dredge, the *Essayons*, the hoppers of which hold 8,000 cu. yds. of sediment.) As indicated in this figure, near the surface (2-meter depth) the turbidity persisted at a location a few tens of meters down current from the dump for about 2 minutes. Near the bottom at 14 meters, it took the turbid plume turbidity about 7 minutes to pass the monitoring site down bottom-current from the disposal site. The plume typically dispersed to indistinguishable from ambient turbidity of the disposal area in about one hour.

Figure 4 shows the DO depletion in the surface water turbid plume as it passed the monitoring site down surface-current. As shown, even though very large amounts of sediment containing large amounts of oxygen-demanding materials were dumped, only a small depression of DO concentration occurred at the monitoring site.

Figure 3 Passage of the Turbid Plume

Figure 4. Dissolved Oxygen Concentration in Near-Surface Waters during Passage of Turbid Plume from Hopper-Dredge Disposal of Dredged Sediment

Figures 3 and 4 both demonstrate that the turbid plume of sediment characteristic of hopper-dredged sediment disposal in open water was a very short-term, transitory phenomenon. Associated with the turbid plume, Lee et al. (1978) found that there was, in some instances, some increase in concentration of some chemical constituents in this turbid cloud as well as some decrease in the dissolved oxygen concentration as is shown in Figure 4. The possible duration of exposure of aquatic organisms to elevated concentrations of constituents within that plume would be expected to be on the order of minutes to a few hours, too short to cause adverse impacts in an open-water disposal site

8

environment. Furthermore, most released contaminants would be scavenged by ferric hydroxide in an oxic disposal site watercolumn.

In the studies conducted by Lee et al. (1978), the only constituent of potential concern released was ammonia. The potential impact of ammonia on aquatic organisms at an open-water disposal site would have to be reviewed on a site-by-site basis since it would be controlled largely by the sensitivity of the organisms there and the rate of dilution.

The turbid plume associated with open water dumping of mechanically dredged sediment is even less pronounced than with hopper-dredge disposal because the mechanically dredged sediment is a more cohesive mass. It was concluded by Lee et al. (1978) that open-water disposal of even contaminated sediments would not be expected to cause water quality problems in the disposal site watercolumn because of the short exposures that aquatic organisms could experience from such releases.

Figure 5 shows the typical disposal situation for hydraulic dredging and pipeline disposal.

Figure 5 Hydraulic Dredging with Open-Water Pipeline Disposal
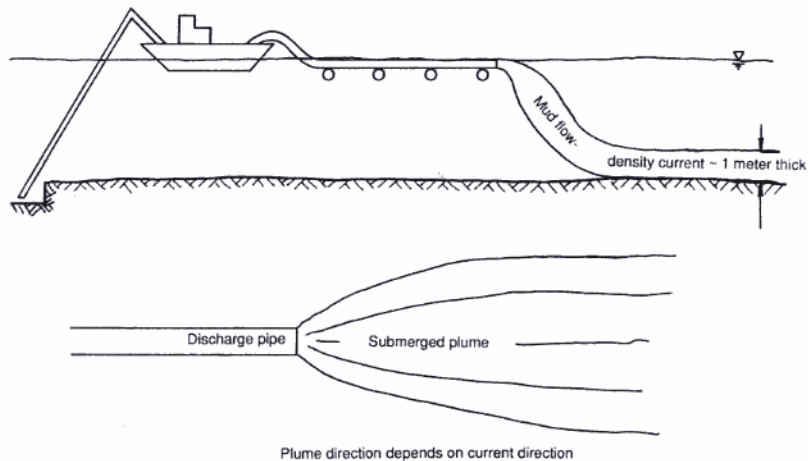
The pipeline disposal situation is significantly different from that of dumping of mechanically or hopper-dredged sediments in open waters. In that process, the dredged sediment slurry is transported via pipeline to the disposal location where it is discharged. The slurry sinks to the bottom and moves down current as an approximately one-meter-thick density current along the bottom. This density current has been found to persist for thousands of meters from the point of discharge during disposal operations. Because this dredged sediment density current is typically characterized by low DO and/or the release of constituents such as ammonia, its presence at a location for extended periods of time (many hours to a day or so) could represent a significant adverse impact on aquatic organisms residing on the bottom in the path of the current. Ordinarily, however, such density currents do not persist in one location for extended periods because of the intermittent nature of pipeline disposal operations owing to frequent mechanical adjustments and the movement of the dredge. Further, the point of discharge is frequently moved because of the accumulation of sediments near the point of discharge.

The high rapid oxygen demand of US waterway sediments is only a source of oxygen demand that causes DO depletion of significance to water quality when the sediments are mixed into the watercolumn such as pipeline disposal of dredged sediments. Also of potential concern would be during storms when the bedded sediments are suspended into the watercolumn.

Overall
The inorganic oxygen demand of aquatic sediments has the potential to cause significant DO depletion in streams and rivers when suspended into the watercolumn. The key to whether or not a significant DO depletion occurs is the degree to which the sediments are suspended in the watercolumn, such as during storms.

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