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This issue of the Stormwater Runoff Water Quality Science/Engineering Newsletter is devoted to a review of the **role of aqueous chemistry of iron in controlling the release of potential pollutants upon resuspension of aquatic sediments**. There is a myriad chemical contaminants present in many aquatic sediments. It is often presumed that such contaminants are released to the watercolumn during sediment resuspension, and there, adversely impact aquatic life and other beneficial uses of the water. However, extensive laboratory and field studies of about 100 contaminated sediments from across the US that specifically addressed such release showed that of about 30 common heavy metals, organic compounds, and other potential pollutants, only manganese II and ammonia were released/remained in the water column after sediment resuspension. These results show that the chemistry of aqueous iron controls the availability of many contaminants in resuspended sediment. The formation of ferric hydroxide during sediment suspension into the watercolumn as the result of the reaction between ferrous iron in the sediments and dissolved oxygen in the watercolumn leads to rapid scavenging of many contaminants in the $Fe(OH)_3$ precipitate. The scavenged contaminates are redeposited in the sediments. This Newsletter presents a preprint of a paper that reviews the role of the aqueous chemistry of iron as it relates to controlling the release of potential pollutants from resuspended sediments.

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Role of Iron Chemistry in Controlling the Release of Pollutants from Resuspended Sediments[1]

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Introduction

There is justified concern about potential water quality impacts of sediment-associated chemical contaminants when the sediments are resuspended into the watercolumn. However, approaches being developed and implemented for the evaluation and management of sediment-associated contaminants do not, in general, reflect an understanding of the aqueous environmental chemistry of sediment-associated contaminants. One major deficiency is that they do not consider the role of iron in controlling the release and impact of many such contaminants. While it is commonly assumed that the suspension of bedded sediments leads to the release of sediment-

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associated chemicals to the watercolumn where they will be available to affect water quality, unless the aqueous chemistry of iron is considered, assessments made will not be reliable in directing control toward real problem areas.

G. F. Lee has been involved in the investigation and application of information on the chemistry of iron in aquatic systems for over 45 years. Stumm and Lee (1960) presented a comprehensive review of the aqueous environmental chemistry of iron in aquatic systems. The text, Aquatic Chemistry, (Stumm and Morgan 1996 and earlier editions dating to 1970) also provides detailed information on iron chemistry in aquatic systems. Although the role of iron chemistry in influencing the release of chemicals from sediments has been well-established in the literature for decades (see reviews by Lee, 1970, 1975 and Lee and Jones-Lee, 2000), it is poorly reflected in the evaluation of the water quality impacts of suspension of contaminated sediments. For example, during the past two years the US EPA Superfund, Corps of Engineers, S-SW HSRC, US Navy, NOAA and Sediment Management Work Group have held conferences devoted to management of contaminated sediments. The 2003 workshop was devoted to Environmental Stability of Chemicals in Sediments Workshop (http://www.sediments.org/sedstab03.html);
the October 2004 workshop was devoted to addressing Uncertainty and Managing Risk at Contaminated Sediment Sites (http://www.smwg.org/initialframe.htm). In neither of those workshops was the role of iron chemistry mentioned as a key issue controlling the release of pollutants from suspended sediments, yet in both, participants noted the importance of incorporating iron chemistry into evaluating the release of potential pollutants from contaminated sediments.

Toward the end of increasing the awareness and application of sound principles of aquatic chemistry in sediment quality management, this paper reviews the aqueous chemistry of iron as it relates to the controlling the release of potential pollutants from suspended sediments.

Overview Aqueous Environmental Chemistry of Iron

Iron can exist in aquatic systems (natural waters and their sediments) in several oxidation states: metallic iron (iron metal), ferrous iron (Fe II), and ferric iron (Fe III). The oxidation state in which iron exists in a particular aquatic system, and the redox reactions (chemical oxidation-reduction reactions) in which it participates, depends on the presence or absence of dissolved oxygen (DO).

The sediments of many, if not most, aquatic systems are anoxic (without oxygen) as a result of the bacterial oxidation of particulate organic matter. Sediment organic matter includes dead and decomposing aquatic plants, algae and other organisms that settle to and become part of the sediments. In some waters, anthropogenic oxygen-demanding material (particulate biochemical oxygen demand, such as from wastewater treatment plant effluents) also accumulates in sediments. In such an anoxic environment, iron exists in the sediment in the reduced form, ferrous iron (FeII). In that form, it is often associated with sulfide, as black, iron sulfide.

In the oxic (oxygen-containing) watercolumn, iron is in the oxidized, ferric form (FeIII), existing as particulate or colloidal ferric hydroxide (hydrous oxide). This form of iron is a scavenger of many types of chemicals including some heavy metals, organics, and phosphorus. Association with ferric hydroxide affects the bioavailability of these chemicals; associated with ferric hydroxide, they are largely unavailable or non-toxic to organisms.

In typical aquatic systems, anoxic sediments are juxtaposed with oxic overlying water. In a stratified water column with an anoxic hypolimnion, anoxic hypolimnetic water is juxtaposed with oxic overlying water. As these systems are disturbed by organism activity, mixing associated with wind, currents, watercraft, etc., reduced iron enters oxic areas and oxidized iron enters anoxic areas. Thus, the redox reactions of iron are always engaged in aquatic systems.

When reduced iron enters oxic waters, the iron is rapidly oxidized, creating an amorphous ferric hydroxide floc with the release of the associated sulfide which is rapidly oxidized to elemental sulfur or sulfate. Freshly precipitated ferric hydroxide is an effective scavenger of numerous other chemicals in the water, an association that renders them unavailable. The colloidal or particulate ferric hydroxide in the watercolumn can develop sufficient mass to settle and become part of the bedded sediments. In the anoxic sediment environment, the ferric hydroxide is reduced to ferrous iron which typically precipitates as an iron sulfide mineral. Some of the chemicals that had been associated with the ferric hydroxide are released to the watercolumn or sediment interstitial waters; other chemicals, especially metals, can be precipitated as metal sulfides.

In aquatic systems where undisturbed sediments are in contact with the oxic water column, the surface of the sediment can have a reddish brown color characteristic of oxidized, ferric hydroxide. This layer is underlain by the black ferrous sulfide/polysulfide of anoxic sediments. The black layer can be mistaken for “organics” if the aqueous environmental chemistry of iron is not understood.

Rates of Reaction

Stumm and Lee (1961) investigated the kinetics of ferrous iron oxidation by dissolved oxygen under conditions that simulate environmental conditions. The rate expression is presented in equation 1.

$$dFe(II)/dt = -k(Fe(II)(O_2)(OH)^{2} \qquad (1)$$

They found that this reaction is first order with respect to iron and oxygen concentrations and second order with respect to the hydroxyl ion concentration. This means that the rate of this reaction is highly dependent on pH; a 1 pH unit change causes a 100-fold change in the rate of oxidation of ferrous iron. Under the neutral pH conditions that typically exist in natural waters, the rate of the oxidation of ferrous iron is very fast. At pH 7, the reaction is complete in only a few minutes; the reaction is essentially instantaneous at higher pH values typical of aquatic systems.

Gardner and Lee (1965) studied the rate of oxidation of iron sulfides in sediments of Lake Mendota in Madison, WI by suspending reduced (black) lake sediment in oxic water and measuring dissolved oxygen consumption. They found an initially rapid consumption of DO followed by a long period of slower oxygen consumption. The rapid rate of DO consumption reflected the rapid oxidation of the iron on the surface of the ferrous sulfide particles. The rate of oxygen consumption slowed once the iron on the surface of the particles became oxidized. At that point, the rate of oxygen consumption became controlled by the rate of diffusion of oxygen through the ferric hydroxide coatings on the ferrous sulfide particles rather than by the rate of oxidation of the iron.

In contrast to the rapid exertion of the abiotic (chemical) oxygen demand of reduced iron and sulfide species in oxic aquatic systems, the exertion of biochemical oxygen demand (BOD) is slow; it occurs gradually over days to weeks. The rapid exertion of oxygen demand typical of the suspension of anoxic sediments into an oxic watercolumn is characteristic of the reaction of ferrous iron and ferrous sulfides with dissolved oxygen, rather than of the slow exertion of BOD. As part of their US Army Corps of Engineers Dredged Materials Research Program (DMRP) studies, Lee and Jones-Lee (1999) reviewed the oxygen demand of aquatic sediments and evaluated the oxygen demand of approximately 100 sediments taken from US navigation channels. They reported that when those sediments were suspended in oxygen-containing water, the first-hour oxygen demands ranged from 42 to 930 g $0_2/m^3$ wet sediment; typical values were on the order of 500 g $0_2/m^3$. That rate is in keeping with the rapid oxidation of the iron sulfides.

Scavenging by Ferric Hydroxide

As noted above, it has been recognized for more than four decades that the aqueous environmental chemistry of iron pays a significant, often controlling, role in the behavior and impact of chemical contaminants in aquatic systems (Stumm and Lee, 1960, 1961; Lee, 1970, 1975). That notwithstanding, the role of iron is often overlooked in the evaluation and management of chemical contaminants in aquatic systems, especially in association with sediments. Lee (1975) summarized the role of ferric hydroxide as a scavenger of dissolved trace chemicals in aquatic systems. Freshly precipitated ferric hydroxide is amorphous (floc) and has the ability to sorb (incorporate into the precipitate) heavy metals and many organics. In fact, this property of ferric hydroxide is used in several water and wastewater treatment processes such as for the removal of phosphate, selenium, and dissolved organic carbon. Gambrell et al. (1978) studied the role of the iron redox systems in controlling the release of metals from contaminated dredged sediments. Sridharan and Lee (1972) reviewed the literature on the coprecipitation of various types of organic compounds from sea water with iron. Prior to the development of more sensitive analytical methods, marine chemists would use iron-coprecipitation to concentrate certain trace elements and organics present in sea water, to raise their concentrations to measurable levels. They would add iron to a large volume of sea water, and trace elements and organics would become incorporated into the ferric hydroxide floc. This floc was allowed to settle, the water was decanted, and the floc was dissolved in acid releasing the associated chemicals. Sridharan and Lee (1972) investigated the use of this reaction and freshly precipitated ferric hydroxide as an analytical tool for concentrating trace chemicals from freshwater samples. They reported that phenol, and several other organics would similarly become incorporated into ferric hydroxide precipitate, although there were some organics of interest that were not coprecipitated by ferric hydroxide.

More recently, Martinez and McBride (2000) investigated the coprecipitation of several heavy metals with ferric hydroxide. They reported that Cu, Cd, Pb, and Zn were coprecipitated with ferric hydroxide and that the binding of the metal in the ferric hydroxide (as measured by extraction of the ferric hydroxide precipitate with citrate) depended on the type of metal and, for some metals, the age of the precipitate.

As discussed by Lee (1975), the high sorption tendency of ferric hydroxide exists primarily during its formation – during the oxidation of reduced iron to form the ferric hydroxide precipitate. Aged ferric hydroxide, such as that associated with oxidized sediments, has much lower sorption tendencies. In some waters, the precipitation of ferric hydroxide produces finely divided colloidal precipitates that can pass through the half-micron pore-size filter typically used to separate "dissolved" from "particulate" chemicals. While contaminants associated with that "colloidal" ferric hydroxide would be measured as "dissolved" and presumed available owing to the separation technique, they are likely non-toxic. Toxicity tests would be necessary to evaluate whether the chemicals apparently released are, in fact, available/toxic.

Demonstration of the Savaging by Ferric Hydroxide: Dredged Sediment Disposal

As part of the Corps of Engineers Dredged Material Research Program conducted in the 1970s, Lee and several of his graduate students conducted coordinated field and laboratory studies on the release and impact of chemical contaminants in dredged sediments under various laboratory conditions, as well as during their disposal in open water. More than 50 sediments from about 20 navigation channels throughout the US were subjected to a laboratory-based elutriation procedure in which one volume of sediment was mixed with four volumes of water for 30 minutes with compressed air, and allowed to settled for one hour. The settled elutriate was filtered, and the filtrate was analyzed for about 30 parameters including the suite of heavy metals, nutrients, organochlorine pesticides, and PCBs. The settled elutriates were also subjected to toxicity tests using grass shrimp (*Palaemonetes pugio*) for marine water and *Daphnia magna* for freshwater sediments. Variations of the elutriation procedure, including mixing under anoxic conditions, were evaluated for their impact on test results. At about 10 sites, the laboratory work was coordinated with field sampling of the watercolumn during open water disposal of the sediments tested. Overall, that study generated about 30,000 data points to characterize the release of chemicals to the watercolumn upon suspension of the sediments, in the laboratory and the field. The results were reported in a 1,500-page, two-part DMRP report by Lee et al. (1978) and Jones and Lee (1978). A summary of the results was published by Lee and Jones-Lee (2000).

The laboratory elutriate test results of Lee et al. (1978) and Jones and Lee (1978) showed that when anoxic conditions prevailed during elutriation, many of the chemicals of potential water quality concern were released to the water. However, when air was used to mix the sediment and water, typically only ammonia and manganese II were released to the dissolved phase; the other heavy metals, nutrients and organics studied were incorporated into the ferric hydroxide floc formed during aeration. Further, ferric hydroxide floc formation was visible in some of the filtered (0.5 µ pore-size) elutriates during storage.

The Lee et al. (1978) DMRP field studies included monitoring the release of the same suite of about 30 physical and chemical contaminants and characteristics in the down-current disposal site water during open water disposal of same sediments evaluated in the laboratory. In the hopper-dredge dredging process, dredged material is sucked up and discharged into hoppers within the hopper-dredge vessel for transport to the open-water disposal site. As illustrated in Figure 1, when the hopper-dredge reaches the designated disposal location, the hopper doors are opened and the sediment is released. Most of the sediment rapidly descends to the bottom as a fairly cohesive mass. The descent of the dredged sediment from the hopper to the bottom of the watercolumn forms a turbid cloud in the waters of the region.

To define the nature and extent of contaminant release, Lee et al. (1978) monitored the watercolumn downcurrent of the disposal at various depths before, during and after the disposal; for some sites the monitoring included upcurrent locations as well.

Figure 2 shows a characteristic pattern of turbidity over time in the watercolumn a few tens of meters downcurrent of the disposal site before, during, and after hopper-dredge disposal of dredged sediment. The turbidity persisted in the near-surface water at the sampling location for about 2 minutes; near the bottom at that location, the turbidity plume turbidity persisted for about 7 minutes. The plume of turbidity typically dispersed to levels indistinguishable from ambient turbidity of the disposal area within about one hour.

Lee et al. (1978) found that there was, in some instances, an increase in concentration of some chemical constituents in the turbid plume at the downcurrent sampling location, as well as some decrease in the dissolved oxygen (DO) concentration there, as is shown in

In the dredged sediment disposal site studies conducted by Lee et al. (1978), the only constituent of potential concern that was released was ammonia. The release of ammonia from two hopper-dredge dumps of contaminated sediments in open waters that took place about two hours apart, is shown in Figure 4. A release of ammonia of the type shown in Figure 4 would not cause a significant adverse impact on aquatic life unless the organisms were able to stay in the rapidly moving turbid plume for a considerable period of time and the plume persisted for a long period of time. Studies by Lee et al. (1978) at several locations showed that typically the turbid plume was no longer identifiable after about one hour following the dump. The concentration of released ammonia and the duration of exposure that organisms encounter associated with release are sufficiently short (minutes) so that no water quality problems due to ammonia release would be expected. Ammonia is a chemical that is not coprecipitated with ferric hydroxide.

Figure 1. Hopper-Dredge Disposal of Dredged Sediment (Lee and Jones-Lee, 2000)

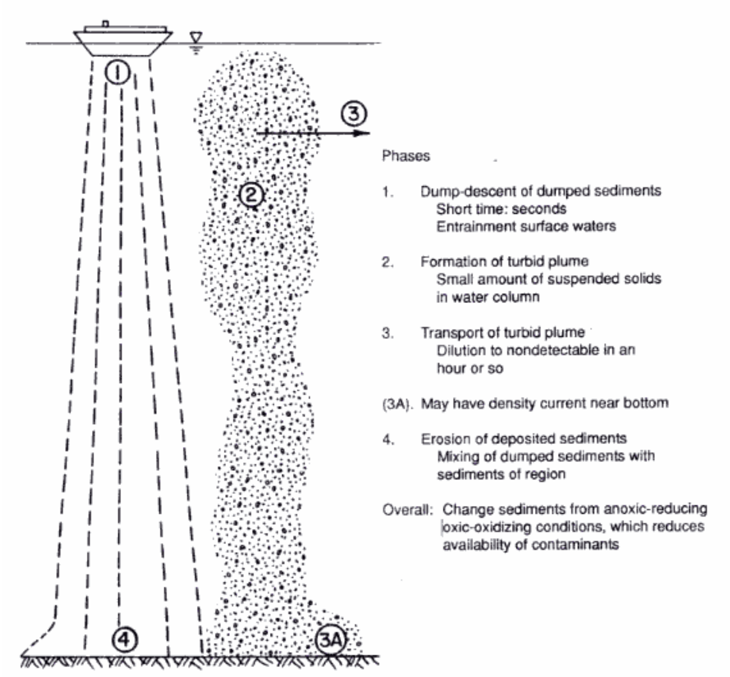


Figure 2. Percent Light Transmission with Depth during Passage of Turbid Plume from Open Water Disposal of Hopper-Dredged Sediment (Lee et al., 1978)

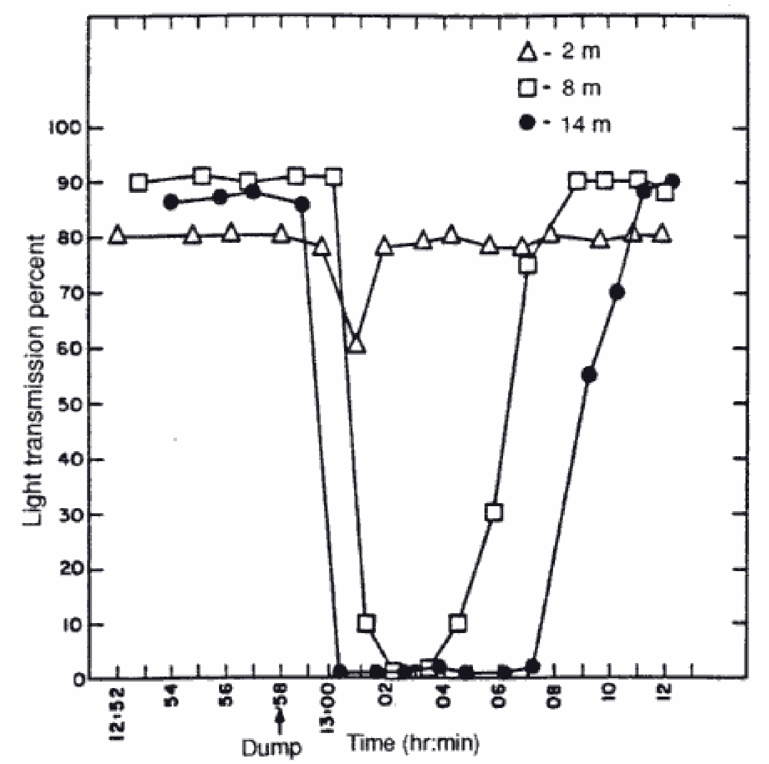


Figure 3. Dissolved Oxygen Concentration in Near-Surface Waters during Passage of Turbid Plume from Hopper-Dredge Disposal of Dredged Sediment (Lee et al., 1978)

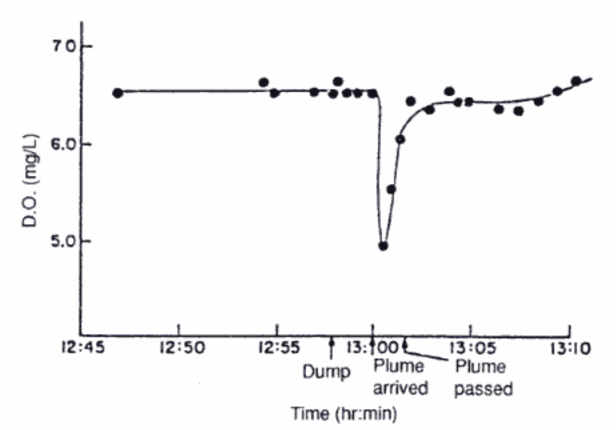
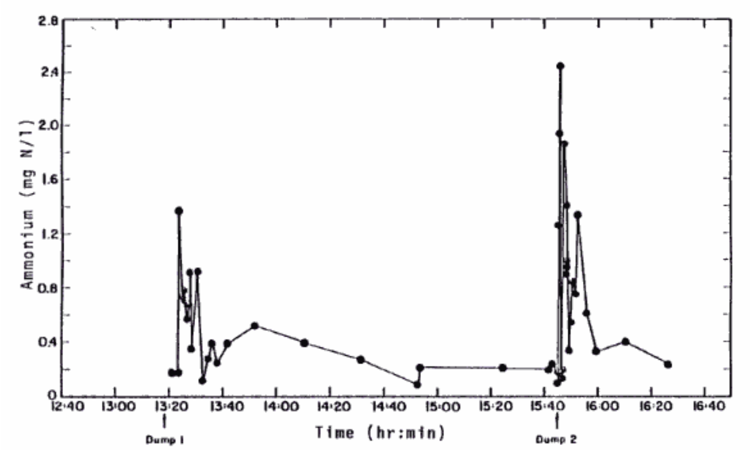


Figure 4. Concentration of Ammonia in Bottom Waters Downcurrent from Hopper-Dredge Disposal of Sediment in New York Bight (Lee et al., 1978)



It was concluded by Lee et al. (1978) and Jones and Lee (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 limited releases and the short exposures that aquatic organisms could experience from such releases. The limited releases that were noted were controlled by ferric hydroxide scavenging.

Consider Duration of Exposure

For many situations, the release of potential pollutants upon suspension of bedded sediments is limited by ferric hydroxide scavenging. For those constituents that are found to be released to the watercolumn, it is important to consider whether the released chemicals are present in the watercolumn in available forms for a sufficient period of time to adversely affect aquatic life through toxicity or bioaccumulation to higher trophic organisms. It should not be assumed that exceedance of US EPA worst-case water quality criterion represents a significant adverse to water quality. In making such assessments, it is important to conduct toxicity tests with appropriate durations of exposure that match the exposure that can be encountered in the area of sediment suspension and downcurrent.

Overall Conclusions

It is disconcerting, indeed alarming, to find the principles and understanding of aquatic chemistry disregarded in the development and implementation of water quality regulation. Of particular concern is the aqueous chemistry of iron and its role in controlling the release and availability of sediment-associated contaminants. The frequent assumption that the suspension of bedded sediments releases sediment-associated contaminants to the watercolumn where they can adversely affect water quality/aquatic life, substantially influences sediment quality assessment and regulation yet disregards the controlling role of iron.

It has been recognized for decades that freshly precipitated ferric hydroxide, formed upon resuspension of many bedded sediments, quickly scavenges many of the heavy metals, organics, and phosphorus that may concomitantly be released. This scavenging can limit the water quality impact of potential pollutants associated with bedded sediment. It should not be assumed that a chemical in a bedded sediment will be released to the watercolumn and thereby cause toxicity and or be available for bioaccumulation. Site-specific studies need to be conducted to determine whether there is release of pollutants to the watercolumn during resuspension of a magnitude and duration to adversely affect water quality. These studies need to incorporate appropriate toxicity tests and biological uptake studies, with reliable consideration of duration of exposure of the test organisms.

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