

Stormwater Runoff Water Quality Science/Engineering Newsletter
Devoted to Urban/Rural Stormwater Runoff
Water Quality Management Issues

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This issue of the Stormwater Runoff Water Quality Science/Engineering Newsletter (NL) is devoted to a review of **regulating the water quality impacts of urban stormwater runoff** to ports and harbors. This NL contains a reprint of a paper by Lee and Jones-Lee, "Regulating Water Quality Impacts of Port and Harbor Stormwater Runoff," that was presented at the International Symposium on Prevention of Pollution from Ships, Shipyards, Drydocks, Ports, and Harbors held in November 2003 in New Orleans, LA. This paper covers both surface water and sediment water quality issues.

The regulation of sediment-associated chemicals derived from urban and rural/agricultural stormwater runoff as well as other sources is receiving increasing attention. As discussed in the paper, some of the approaches being used to regulate sediment-associated potential pollutants, such as total concentrations of constituents in sediments and co-occurrence-based so-called "sediment quality guidelines," are technically invalid. While the focus of the paper is ports and harbors it is applicable to many urban and rural stormwater runoff water quality management issues. The proceedings of the symposium is scheduled to be available on CD ROM from www.ATRP.com in March. Information on this symposium was presented in NL 6-10.

US EPA Proposed Criteria for Copper

One of the topics of particular concern at the New Orleans symposium was the regulation of copper derived from its use as an antifoulant on boat hulls. This use leads to an accumulation of copper in the receiving waters and, especially, their sediments. Ports and harbors located in urban areas also receive copper from street and highway stormwater runoff, which accumulates in sediments. As a result, there is considerable interest by port and harbor managers and urban stormwater managers in properly regulating copper in ports and harbors and areas receiving stormwater runoff. At the New Orleans symposium, Charles Delos of the US EPA Office of Water, Washington, D.C., made a presentation, "Preview of U.S. EPA's not yet released Draft Saltwater Criterion for Copper." According to Delos,

"A new draft copper criteria document was announced in late December. Technical views are requested from the public. Comments are requested by March 1. However, this is not a regulation, and consequently, the March 1 date has no formal significance.

The project team will probably begin working through the comments some time in March, with an initial target of attempting publication of the completed document in February 2005. Additional comments submitted within the first few months of the

revision cycle are the most useful. For practical reasons, comments received late in the revision cycle are much less useful.

*The URL for obtaining the document is:
<http://www.epa.gov/waterscience/criteria/copper/>*

The freshwater criterion is expressed in terms of the Biotic Ligand Model. A version of the model is available from the web site. Certain information on how to get the model to calculate the freshwater criterion was inadvertently omitted from the download package. Contact me for e-mail directions on model inputs for obtaining a calculated criterion. The download package will be fixed shortly, but I don't know the target date.

The saltwater criterion is a conventional value unadjusted for site water quality parameters such as DOC or salinity. The draft value is noticeably lower than the previous criterion. I think it fair to assume that if states adopted the draft value, then places like New York Harbor and San Francisco Bay would retain their site-specific Water-Effect Ratio, but that ratio would then be applied to the newly adopted statewide criterion to obtain a new site criterion. Thus, the draft criterion has relevance to such localities.

It is important to note that EPA does not endorse its draft criteria. The purpose of publishing the draft is to air whatever new data EPA has found and show its implications on the criteria concentrations. Now is the time for the public to show us any additional data we did not have, or to present possible improvements in the interpretation of the available data.”

A copy of Delos' PowerPoint presentation at the New Orleans symposium on this issue will be available on the CD ROM symposium proceedings. A copy of this presentation can be made available upon request from gfredlee@aol.com.

Regulating Water Quality Impacts of Port and Harbor Stormwater Runoff¹

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Abstract

The waters of ports and harbors are subject to a variety of potential pollutant sources including boat and ship antifoulants, boat hull cleaning, and other releases and discharges from boats, wastewater discharges from municipalities and industrial facilities, stormwater runoff from municipal, industrial (including shipyards) and agricultural activities, groundwater and the atmosphere. These sources of potential pollutants can degrade the water quality-beneficial uses of the waters through causing aquatic life toxicity and excessive food web bioaccumulation, as well as causing other impairments of the waterbody's beneficial uses. For some ports and

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harbors municipal stormwater runoff is one of the most important, if not the most important, sources of a variety of potential pollutants in the water column and waterbody sediments. There is considerable confusion and unreliability in regulating stormwater runoff water quality impacts. Typical US EPA water quality criteria and state water quality standards tend to overregulate stormwater runoff-associated constituents for which there are water quality criteria/standards. There is underregulation of potential pollutants for which there are no criteria/standards. The regulation of potential pollutants that accumulate in sediments is even more unreliable since there is no relationship between the total concentration of a constituent in sediments and water quality impacts. This paper discusses the problems in current regulatory approaches for urban stormwater runoff water quality impacts and recommends regulatory approaches that will provide for technically valid, cost-effective regulation of stormwater runoff-associated pollutants. These include the development of “wet weather” water quality standards for regulating water column impacts. For sediments a non-numeric Best Professional Judgment Weight of Evidence Triad approach implemented through an expert panel in a public peer review process should be used. The triad is to be based on aquatic life toxicity, sources of chemicals that bioaccumulate to excessive levels in the higher trophic food web, benthic organism assemblages, and appropriate chemical evaluation of the cause of toxicity (TIEs).

Keywords: stormwater runoff, water quality impacts, water quality criteria/standards, contaminated sediments

Introduction

Managers of ports and harbors face the problem of input of pollutants from port or harbor activities, such as antifoulant releases from painted boat hulls, boat hull cleaning, as well as stormwater runoff to the port or harbor from the port/harbor property and the surrounding urban and industrial, and sometimes agricultural areas. This paper reviews a number of the problems that exist today in properly regulating stormwater runoff water quality impacts on the beneficial uses of port and harbor waters. The paper is divided into two parts. The first part is concerned with regulation of water column water quality impacts and suggested approaches for managing real, significant water quality problems due to stormwater runoff-associated constituents. The second part is devoted to regulating port/harbor contaminated sediments that derive their potential pollutants from stormwater runoff and other sources of constituents that accumulate in port/harbor sediments.

The authors have developed an email-based Stormwater Runoff Water Quality Science/Engineering Newsletter. This Newsletter is devoted to presentation of information on the problems with current approaches for regulating urban area and highway stormwater runoff, and recommendations on approaches that should be considered in addressing these problems. Many of the issues summarized in this paper have been discussed in more detail and in references provided in the Newsletter articles. Past issues of the Newsletter are available from www.gfredlee.com.

While the focus of this paper is on ports and harbors, it is equally applicable to other urban, highway, agricultural and rural stormwater runoff situations.

Water Column Impacts

It has been known for many years (since the 1960s) that urban area and highway stormwater runoff contains potential pollutants, such as heavy metals (copper, lead, zinc, cadmium), a variety of organics (PAHs, oil and grease), and pathogen-indicator organisms (fecal coliforms), whose concentrations frequently exceed water quality standards in the stormwater runoff from urban areas. In 1990 the US EPA (1990) established the current regulatory requirements for urban area and highway stormwater runoff. It requires that pollution caused by the runoff be controlled with best management practices (BMPs) to the “maximum extent practicable” (MEP). The Agency still has not defined which BMPs to use, or what is meant by MEP. This situation has led to considerable confusion about the current regulatory requirements.

The regulation of stormwater runoff-associated potential pollutants in ports and harbors is generally governed by the regulations governing municipal stormwater runoff. The exception to this is for industrial properties, where the current regulatory approach is to require that the concentrations of potential pollutants not exceed the water quality standard at the edge of the property line. For urban stormwater runoff, the US Congress established that it is to be regulated under an NPDES permit; however, it does not require (as it does for wastewater discharges) that the concentrations of potential pollutants in the discharge not cause exceedances of water quality standards, either at the point of discharge or, if a mixing zone is allowed, at the edge of the mixing zone, by any amount more than once every three years. Violations of water quality standards in the receiving waters for wastewater discharges can cause regulatory agencies to fine the NPDES-permitted wastewater discharger, and require that it control the violations of the water quality standard in future discharges.

While the US EPA municipal/urban stormwater runoff water quality regulations will ultimately require compliance with water quality standards at the point of discharge or at the edge of a mixing zone, the compliance date has not been established. Instead, because of the very high cost of trying to treat urban area and highway stormwater runoff to achieve compliance with water quality standards, a best management practices (BMP) ratcheting-down process has been developed, in which the regulatory agency and the stormwater discharger work together to implement ever-more-effective best management practices to ultimately achieve water quality standards in the runoff.

While the effectiveness of conventional BMPs is an issue that has been under considerable discussion, it is now generally recognized (Jones-Lee and Lee, 1998) that conventional BMPs, such as grassy swales, detention basins, etc., do not treat urban area and highway stormwater runoff sufficiently to control the concentrations of potential pollutants in the runoff so that they do not cause violations of water quality standards. This leads to an impossible situation of trying to achieve water quality standards, yet knowing that the conventional BMPs cannot achieve compliance with water quality standards.

There is also the problem, with the current regulatory approach, of the extremely high cost of trying to retrofit even conventional BMPs into developed areas. It is estimated that the purchase of the land associated with installing conventional BMPs into a developed area will cost urban dwellers served by the storm sewer system from one to three dollars per person per day. To treat urban stormwater runoff to achieve NPDES-permitted water quality standards will

cost an estimated five to ten dollars per person per day for the population served by the storm sewer system. It is obvious that the current regulatory approach for urban area and highway stormwater runoff cannot be fully implemented in developed areas to achieve water quality standards. This situation is of importance to managers of water quality in ports and harbors, since they will likely continue to face violations of water quality standards in the port and harbor waters associated with the discharge of stormwater from urban areas and highways.

Generally what is being done today by regulatory agencies is to require that new urban developments include grassy swales, detention basins, etc., which will help control potential pollutants in stormwater runoff under low flow conditions. These systems, however, are not effective, especially under high flow, for reducing the concentrations of potential pollutants in stormwater runoff to comply with water quality standards at the point of discharge.

Environmental groups (US Ninth Circuit Court of Appeals, 1999) have filed suit against the US EPA for the purpose of trying to force the Agency to implement full compliance with water quality standards in urban area and highway stormwater runoff. The Ninth Circuit Court determined that, under the current regulatory requirements, the US EPA must require the use of BMPs to work toward achieving water quality standards, but does not have to specify a date by which compliance with water quality standards must be achieved. The US EPA Inspector General (US EPA, 2002a) determined that the selection of BMPs for use in the BMP ratcheting-down process should be conducted in such a way as to achieve ever-more-effective control of violations of water quality standards in stormwater runoff. At some time in the future, through the BMP ratcheting-down process, NPDES-permitted stormwater discharges will have to achieve or come close to achieving compliance with water quality standards in urban stormwater runoff under the conditions where the next round of BMPs will be too costly to implement. It is clear that there is need for an alternative approach for regulating the water column impacts for potential pollutants in urban area and highway stormwater runoff as they may affect any water, including ports and harbors.

Background to Properly Regulating Urban Area Stormwater Runoff Water Column Impacts.

There are several issues that should be considered in developing technically valid, cost-effective regulation of urban area and highway stormwater runoff water quality impacts. The senior author was part of the US EPA invited peer review panel for development of the 1986 US EPA water quality criteria development approach (US EPA, 1987). This approach is still being used today. He also served on several of the US EPA peer review panels for specific water quality criteria adopted in 1986. In accord with the 1972 federal "Clean Water Act," these criteria are designed to be protective of the aquatic life-related beneficial uses of waterbodies. As a result, the US EPA national water quality criteria are "worst case" with respect to assuming that the potential pollutants are in the most toxic, available forms and that the organisms are exposed to them for extended periods of time. It is the authors' finding that mechanical application of the US EPA national criteria to stormwater runoff-associated constituents in a manner similar to that which has been used to regulate domestic and industrial wastewaters will lead to significant overregulation of urban area and highway stormwater runoff-associated potential pollutants for those constituents for which there are water quality criteria that have been adopted as state water quality standards. It will also lead to underregulation of stormwater runoff for constituents for which there are no water quality criteria/standards.

In developing the worst-case (most protective) criteria the US EPA independently developed an implementation approach for the use of the US EPA criteria as NPDES-permitted discharges, which are largely inappropriate for regulating stormwater runoff-associated potential pollutants. The inappropriateness stems from the fact that water quality standards based on these criteria tend to significantly overregulate urban area and highway stormwater runoff. Some of the most important of the implementation problems include the definition of acute criteria as a one-hour average and the chronic criteria as a four-day average concentration. The acute criteria are, in general, of particular significance to regulating urban and highway stormwater runoff-associated constituents since it is rare that urban and highway stormwater runoff events will last for more than a day or so. Therefore, it is rare that the four-day average chronic criteria would be applicable to an urban stormwater runoff event. As those familiar with short-term toxicity of chemicals to aquatic life know, some constituents in urban and highway stormwater runoff that are regulated potential pollutants can be present well in excess of the acute criterion without toxicity to aquatic life.

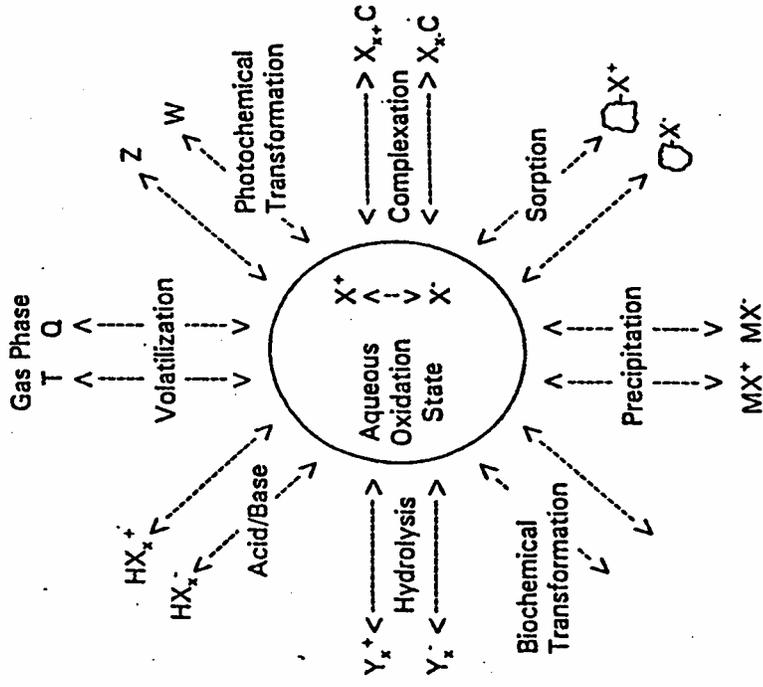
Another factor to consider in regulating urban stormwater runoff is that many of the constituents in urban and highway stormwater runoff are in non-toxic, non-available forms. The US EPA (1995), finally, after it was well known for 20 years, adopted regulation of potentially toxic heavy metals (Cu, Zn, Pb, Ni, Cd) for aquatic life toxicity as the ambient water “dissolved” forms. Currently the Agency does not regulate particulate metals in ambient waters in the water column and bedded sediments. The problems of regulating bedded sediment-associated potential pollutants are discussed below. It is known that, with respect to water column impacts, particulate forms of organics are often in non-toxic, non-available forms and, therefore, should also be regulated based on dissolved forms for those constituents where the concern is toxicity to water column aquatic life.

Figure 1 presents the aquatic chemistry “wheel” which shows the types of chemical reactions that can influence impact of a chemical on aquatic life through toxicity or excessive bioaccumulation. There are eight types of reactions that can influence whether a particular potential pollutant remains in a waterbody in a toxic available form or converts to this form in the receiving waters for stormwater runoff. The “hub” of the wheel contains the unreacted chemical species that are potentially present in stormwater runoff and in the receiving waters. For example, copper can be present in stormwater runoff as metallic copper, copper-1 (cupric), and copper-2 (cuprous). Each of these oxidation states of copper enters into the eight types of reactions shown, to varying degrees. The forms of a chemical, as represented by the products of the reactions at the “rim” of the wheel, are controlled by the reaction’s kinetics (rates) and thermodynamics (positions of equilibrium). One of the more important types of reactions of concern to those responsible for managing water quality of ports and harbors is complexation. Complexation of a metal, such as copper, can form a soluble or particulate chemical. Strongly “complexed” metals are generally non-toxic.

Throughout this paper the term “potential pollutant” is used. This term refers to regulated constituents (those for which there are water quality criteria) that are present at concentrations above the water quality criterion. It reflects the fact that many chemical constituents exist in a variety of chemical forms, only some of which are toxic/available. For many situations there is need to incorporate the aqueous environmental chemistry of the

Figure 1

Aquatic Chemistry of Chemical Constituents

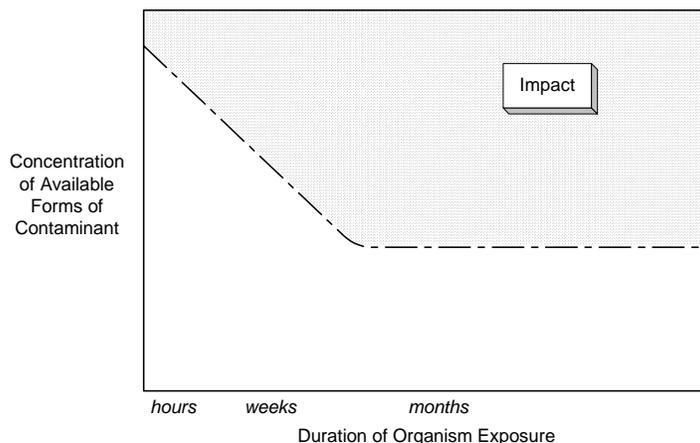


- Distribution among Species Depends on Kinetics & Thermodynamics of Reactions in the Particular Aquatic System
- Each Chemical Species Has Its Own Toxicity Characteristics
 - Many Forms Are Non-Toxic

constituent of concern into evaluating the potential impact of a chemical on the beneficial uses of a waterbody. The US EPA national water quality criteria are designed to be adjusted for site-specific conditions that properly consider the aquatic chemistry of the constituents of concern. The US EPA (1994a) in its Water Quality Standards Handbook has provided guidance on making site-specific adjustments of the national criteria to address site-specific conditions. The US EPA guidance for adjustment of the national water quality criteria for site-specific conditions adjusts for some of the aquatic chemistry issues. There are other issues that are not adequately addressed. Of particular concern is the form of the constituent in the runoff. Some forms of constituents do not participate in equilibrium reactions, such as those shown in Figure 1, that impact the toxicity of a potential pollutant.

Another important aspect of evaluating the impact of potential pollutants in stormwater runoff is the duration of exposure that an organism can receive during and following a stormwater runoff event. Figure 2 shows the relationship between the duration of exposure and toxicity for toxic chemicals. If the duration of exposure concentration of a toxic available form is above the “no impact” line – i.e., in the stippled area – then there will be an adverse impact on aquatic life. This impact can range from acute toxicity, leading to death of the organism in a short period of time, to chronic toxicity, where there is impairment of reproduction, abnormal growth, greater susceptibility to disease, predation, etc. As shown, much higher concentrations of a toxicant can be present if the duration of exposure is short. This is why the acute criterion is typically a factor of two to ten times higher than the chronic criterion. This has important implications for evaluation of stormwater runoff water quality impacts. Those runoff situations which only show elevated concentrations near the point of stormwater discharge during the discharge event could have much higher concentrations in the discharge without adverse impacts.

Figure 2
Concentration Duration of Exposure Relationship



The US EPA water quality criteria are implemented as acute (one-hour average) and chronic (four-day average). Typically, stormwater runoff lasts a day or two and is regulated by the acute criteria/standards. However, the US EPA averaging periods for the acute and chronic criteria were somewhat arbitrarily developed. Concentrations well above the acute criterion can be present for considerable lengths of time without adverse impacts on aquatic life. Similarly, there are situations where concentrations above the chronic criterion (four-day average) occur without adverse impacts to aquatic life.

Recently the US EPA (2003) has indicated, as part of its announced “Strategy for Water Quality Standards,” that it plans work on developing “wet weather” standards. The concept of wet weather standards has been discussed since the early 1990s as an approach to more appropriately regulating urban and highway stormwater runoff water quality impacts. Lee and Jones-Lee (2000a) have discussed the need for approaches for developing wet weather standards. There are several potential approaches for developing wet weather standards, including a short-term wet weather variance from compliance with the water quality standards during and immediately following a runoff event. The wet weather standards should incorporate the duration of exposure in the water column during and following a stormwater runoff event, as well as the toxicity and bioavailability of the potential pollutant.

Water Column Aquatic Life Toxicity in Stormwater Runoff. Studies by various investigators in California and Texas have found that urban stormwater runoff is toxic to the zooplankter *Ceriodaphnia dubia*. This organism is the US EPA standard freshwater zooplankton test organism (US EPA 2002c,d,e). Lee, et al. (1999, 2001) conducted comprehensive studies of stormwater runoff from urban and rural areas in the Upper Newport Bay, Orange County, California, watershed during the mid- to late 1990s. They found that all stormwater runoff from urban areas was toxic to *Ceriodaphnia* and to *Mysidopsis bahia* (the marine zooplankton test organism). This toxicity, however, was not due to heavy metals, but due to pesticides used in urban and rural areas. The pesticides of greatest concern were the organophosphorus (OP) pesticides diazinon and chlorpyrifos.

Recommended Approaches for Regulating Water Quality. In connection with developing best management practices for a new 22-mile toll road in Orange County, California (the Eastern Transportation Corridor), the authors, working with Scott Taylor of RBF, Inc. of Irvine CA, have published several papers and reports discussing the development of an alternative approach to evaluating the water quality impacts of stormwater runoff from urban areas and highways. This approach is called “Evaluation Monitoring.” Jones-Lee and Lee (1998) have provided a review of the Evaluation Monitoring approach. It focuses on using the monitoring funds available to examine the receiving waters for the stormwater runoff, associated with and following a runoff event, for water quality beneficial use impacts. For example, for aquatic life toxicity, rather than measuring copper or some other potentially toxic heavy metal in the runoff waters and then trying to extrapolate to the conditions that exist in the receiving waters with respect to predicting toxicity, Evaluation Monitoring measures toxicity in the runoff waters and in the receiving waters, to determine whether the runoff waters are toxic and, if toxic, the magnitude, areal extent and duration of the toxicity.

As another example, rather than measuring a potentially bioaccumulatable chemical, such as mercury or PCBs, in runoff, appropriate fish in the receiving waters in the vicinity of the discharge are analyzed for excessive bioaccumulation of the chemicals of concern. Further, if there is potential for beach closures associated with a runoff event, the actual beach closures then become the assessment of concern. Once a potential problem has been identified, then it is appropriate to determine if the constituents responsible are derived from stormwater runoff. In the case of toxicity, the cause of the toxicity is determined through toxicity identification evaluations (TIEs). If the toxic constituent (such as copper) is derived from stormwater runoff, then it is appropriate to explore how to develop source control management approaches, since it will not be economically feasible to treat stormwater runoff to control real pollutants in the stormwater.

Basically, the Evaluation Monitoring approach is part of an effort to define the real pollutants in the stormwater runoff that are having a significant adverse impact on the beneficial uses of the receiving waters for the runoff. In the case of the Eastern Transportation Corridor, rather than simply throwing various conventional BMPs at stormwater runoff from the Corridor, a focused program of evaluation was conducted to determine whether there were constituents in the runoff that were potentially adverse to the beneficial uses of the receiving waters for the runoff. None were found. The authors have published several papers and reports on the Evaluation Monitoring approach, which are available on their website, www.gfredlee.com.

Regulating Sediment-Associated Potential Pollutants

Many of the constituents in urban area and highway stormwater runoff, such as copper, lead, zinc, cadmium, nickel and various high-molecular-weight organics, are in particulate form, which tend to accumulate in sediments. Further, some of the biocides used as antifoulants on boat hulls also accumulate in sediments. Elevated concentrations of heavy metals and various organics, which are potential pollutants, create concerns as to whether the potential pollutants in sediments are having an adverse impact on the beneficial uses of the waterbody in which the sediments are located. It has been known since the late 1960s/early 1970s that there is no relationship between the total concentration of a constituent in sediments and its potential impacts on aquatic life or other beneficial uses of a waterbody. As with the water column, but even more pronounced in sediments, chemical constituents exist in a variety of chemical forms, only a small part of which, for a particular potential pollutant, is toxic/available. Most of the forms of many potential pollutants in sediments are inert – i.e., non-pollutants.

One of the issues that needs to be understood about evaluating the water quality significance of contaminants in sediments is that sediment concentrations of a potential pollutant are not analogous to constituent concentrations in the water column. The concentrations of constituents in the water column, including particulate materials, are assessed based on a mass per volume – typically a liter of water. A liter of water is 55 moles (gram molecular weights) of water. It is of constant composition. However, in sediments, the concentration units are mass of potential pollutant per kilogram (mass) of sediments. The sediment matrix that makes up the bulk composition of the sediments is of variable composition, depending on the erosion from the watershed, the precipitation that occurs in the waterbody, as well as any accumulation of aquatic plants and other vegetative material in the sediments. This situation is extremely important, since each of the major types of sediment matrices, such as clays, calcium carbonate precipitates,

sulfide precipitates, organics, iron oxides, quartzite sand, detrital carbonates, etc., have different binding capacities for various types of pollutants. For example, large hydrophobic organic molecules, like DDT, PCBs, some PAHs, etc., tend to bind strongly to the total organic carbon content of the sediments. They also bind to any iron oxides that are present, and to clays.

Further, it is known that it is not just the bulk TOC that is the key to binding. Different types of TOC, depending on its origin and characteristics, bind differently. Carbonates in sediments tend to bind some heavy metals, such as copper. Clays tend to bind metals and organics. However, quartzite particles, such as sand, which do not have iron oxide coatings, tend to do very little binding of anything. It has become clear over the years, through the large amount of research that has been done by various investigators, that in order to determine whether a constituent, such as a heavy metal, in sediments is responsible for toxicity, it is mandatory that toxicity investigation evaluations (TIEs) be used to determine if the sediment copper, lead, or some other constituent is in a toxic form. Similarly, for organics that tend to bioaccumulate through the food web, it is necessary that benthic organism sediment accumulation tests, of the type prescribed by the US EPA (2000a,b) be used, where the organism then becomes the assay tool to determine whether the constituents in the sediments are bioavailable.

After years of trying to prove otherwise, it is now found that it is not possible to predict bioavailability in sediments based on total concentrations of a particular constituent. It is even difficult to try to do this based on normalized concentrations, such as by the TOC content of the sediments. Further, the typical approach that is being used by the US EPA to establish water quality criteria for bioaccumulatable substances, of a generic bioaccumulation factor for a constituent in all types of sediments and waterbodies, is not technically valid. The US EPA is now abandoning this approach in favor of regulating bioaccumulatable substances based on an edible tissue residue of the substance that represents a threat to human health for those who eat the fish. The tissue residue-based water quality criterion/standard is then translated on a site-specific basis to an allowable water/sediment concentration. This issue is discussed in Lee and Jones-Lee (1996, 2002a). The US EPA (2000a,b) has also developed guidance on toxicity testing of sediments, using *Hyalella azteca* as the test organism.

Some individuals from the regulated community and regulators try to regulate chemicals that are potential pollutants in sediments with chemical-concentration-based sediment quality criteria or guidelines. It is well established that chemical-concentration-based approaches, such as the Long and Morgan (1990) “ERM” or “ERL” or the MacDonald (1992) “PEL” co-occurrence-based guidelines, are not technically valid, and any semblance of predictive capabilities from these approaches is simply a coincidence that does not have a reliable cause-and-effect relationship.

The chemical-concentration approach, based on a single numeric concentration of a constituent, violates one of the fundamental tenets of sediment quality evaluation – namely, that there is no relationship between the total concentration of a contaminant in sediments and its impact on aquatic life and other beneficial uses of the waterbody in which the sediments are located.

In the 1970s the US Army Corps of Engineers conducted the Dredged Material Research Program (DMRP). The primary thrust of this program was to examine the potential adverse impacts of the Corps' practice of dredging contaminated sediments in order to fulfill their obligation to maintain a waterway's navigation depth, and then disposing of these dredged sediments in deeper open waters. G. F. Lee (senior author of this paper) and his colleagues conducted over a million dollars in research, as part of the DMRP, specifically devoted to developing open water dredged sediment disposal criteria. Sediments from about 100 sites across the US were examined for their potential to release constituents to the water column upon their suspension in the water. Also, toxicity tests and, in some situations, bioaccumulation evaluations were made on the sediments. Thirty chemical parameters were measured on each of the samples, including the suite of heavy metals, organochlorine pesticides, PCBs, nutrients, ammonia, etc. This generated a database of about 30,000 data points. An updated summary of the results of these studies is provided by Lee and Jones-Lee (2000b). These studies confirmed what was known at the time this work was initiated in the early 1970s, that there is no relationship between the total concentration of a constituent in the sediments and its release to the water column or to toxicity. This is related to the binding capacity of the sediments discussed above.

Based on these and other studies, the US EPA and the US Army Corps of Engineers developed dredged sediment disposal criteria, which focused on biological-effects-based approaches, rather than chemical-concentration-based approaches. Such effects parameters as toxicity and bioaccumulation serve as the basis for this regulatory approach. It was originally adopted in the late 1970s and has been successfully used over the past 25 years. The Corps and the US EPA have manuals for freshwater (1998) and for marine waters (1991), which provide detailed guidance on its implementation.

Equilibrium Partitioning. Beginning in the mid-1980s through the late 1990s, the US EPA (1993, 2002b) attempted to develop equilibrium-partitioning-based approaches for developing sediment quality criteria. The focus of this effort was on organics, which tend to partition with particulate total organic carbon in sediments. As was suggested (Lee and Jones, 1992) when the US EPA first started this effort, equilibrium partitioning, in which a simple partitioning is made between particulate TOC on the surface of sediment particles and the interstitial water, has been found to be unreliable in predicting water quality impacts. In addition to variable-composition TOC, which affects binding capacity and strength, there are also other types of surfaces that tend to bind organics.

Acid Volatile Sulfides. With respect to heavy metals, it has been found that heavy metals in sediments tend to form highly insoluble precipitates with sulfides. Since many sediments are anoxic (i.e., do not contain oxygen), this leads to sulfate being reduced to sulfide resulting in metal sulfides being common in many sediments. A procedure has been developed (US EPA, 1994b) called "acid volatile sulfide (AVS) extraction," whereby it is possible to determine whether on a molar basis, there are excess sulfides in the sediments to precipitate the non-iron heavy metals that are simultaneously extracted in the AVS test. If the molar sum of sulfides is in excess of the non-iron heavy metals, the heavy metals have been found to be non-toxic. However, if the heavy metals exceed the sulfides, there is a potential for metal toxicity to benthic organisms. While the metals are not fully bound as metal sulfide precipitates, the metals can be

bound (detoxified) by organics, carbonates, clays, etc. As Lee and Jones (1992) discussed, the use of AVS screening of sediments is a useful tool as part of toxicity identification evaluation (TIE). It is not, however, a reliable basis for developing sediment quality criteria.

Co-occurrence Based Approaches. In the late 1980s, Long and Morgan (1990) developed co-occurrence-based sediment quality guidelines (SQGs). MacDonald (1992) subsequently developed his own version of sediment quality guidelines. These so-called “guideline” values are based on examination of the total concentration of a constituent in a variety of sediments, relative to what some investigator found with respect to toxicity or organism assemblages, or some other so-called “response parameter.” The same endpoint was used for a sediment for all parameters that were included in the guidelines development. The sediment chemical concentrations for each element considered were then ranked from low to high, and an effects level was determined. This approach is obviously technically invalid, since it is based on total concentrations of constituents in sediments. There is no attempt to relate the “effect,” through a cause-and-effect examination, to the concentration of a particular constituent. At best, as DiToro (2002) pointed out, it is a “coincidence” approach that has nothing to do with sediment chemistry, toxicology or other scientific issues. The co-occurrence-based approach ignores the substantial literature, which was available to Long and Morgan and MacDonald at the time they proposed their values, on the lack of relationship between the total concentration of a constituent and its impacts. O’Connor of NOAA (1999a,b) has found, based on a review of US EPA and NOAA databases, that flipping a coin is more reliable in predicting sediment toxicity than exceedance of the guideline values. Lee and Jones-Lee (2002a) have provided a detailed critique of the co-occurrence-based approach.

In an effort to improve the reliability of co-occurrence-based approaches, Long has developed a summed quotient approach, in which the concentration of a constituent in sediments is divided by the guideline value, and these values are then summed, and a new guideline value is developed for potential adverse impacts. Again, this is nothing other than a coincidence if there is a relationship between high summed quotient values and effects, such as toxicity. Basically, it shows that in areas where there are a variety of chemical constituents in the sediments at elevated concentrations (typically in urban or industrial areas), there tends to be toxicity in the sediments. This does not mean, however, that there is any relationship between the concentration of a single constituent, or the sum of the constituents that were included in the evaluation, and the toxicity found. The toxicity found could readily have been due to some unmeasured constituent, or several constituents, through additive toxicity, which are each below the individual guideline value. The summed quotient approach depends on the number of constituents, such as the number of PAHs, that are included in the evaluation.

There are a number of attempts to use Long and Morgan sediment quality guideline values (ERMs, ERLs) as “screening” values, in which it is assumed that, if the concentrations of the various constituents that are considered in the evaluation are below guideline values, the sediments do not represent a threat to water quality, and that concentrations above the guideline value are typically associated with a constituent in sediments causing adverse impacts. The use of Long and Morgan co-occurrence-based values for sediment screening is technically invalid. The fundamental problem with this approach is that there are constituents in the sediments that are toxic to aquatic life, yet are not included in the evaluation. This is one of the fundamental

flaws of the Long and Morgan original approach, in that they used a considerable part of the authors' 1970s Corps of Engineers data in developing the original guideline values, but they did not use ammonia, low dissolved oxygen or sulfide, for which data were available in the database.

It is well established that the most common cause of sediment toxicity and adverse impacts on organisms is low dissolved oxygen, the presence of sulfides and/or ammonia. Ammonia is present in many sediments at concentrations that are toxic to aquatic life. To ignore ammonia toxicity in making a sediment quality evaluation is technically invalid and shortsighted in terms of the purpose of sediment quality guidelines – namely, to make an evaluation of the potential significance of a particular contaminant in sediments. To a benthic organism it makes little difference whether it is killed by a heavy metal that is in a toxic/available form or by ammonia. It is still dead. Therefore, any sediment evaluation that ignores ammonia toxicity is inappropriate.

The origin of the low dissolved oxygen (DO), elevated sulfide and ammonia in sediments is related to the trophic status of the waterbody. Waterbodies with elevated algal content (higher degrees of eutrophication) tend to deposit more algae in sediments, which, when they decompose, use up the oxygen present in the sediments. This leads to sulfate reduction to sulfide and an accumulation of ammonia associated with the minimization of organic nitrogen in the algal and other plant material that accumulates in the sediments. Therefore, the ammonia/sulfide/low-DO toxicity is typically related to the input of nitrogen and phosphorus to the waterbody that stimulates algal growth.

Pesticide-Caused Toxicity. As Lee, et al. (1999) and Lee and Taylor (2003) reported, urban area stormwater runoff in California and many other areas contains elevated concentrations of the organophosphorus pesticides diazinon and chlorpyrifos. This is a result of the use of these pesticides by the public on their property to control ants, termites and other home and garden pests. The organophosphorus pesticides are highly toxic to certain zooplankton, such as *Ceriodaphnia*. They are not especially toxic to fish. The US EPA has determined that these pesticides represent a threat to the health of children, and chlorpyrifos has been banned from further sale in urban areas. Diazinon is being phased out, so that by December 2004 it will no longer be sold in urban areas for residential use.

The pyrethroid pesticides, however, are being sold in large amounts as replacements for the organophosphorus pesticides. Pyrethroid pesticides are as toxic, if not more toxic, to zooplankton and fish. One of the differences between the organophosphorus pesticides and the pyrethroid-based pesticides is that pyrethroids tend to sorb strongly on sediments. Weston (2003) has reported finding that sorbed pyrethroid-based pesticides are bioavailable to at least some benthic organisms (i.e., can be taken up from the benthic organism's intestinal tract). Further, Weston found that these same sediments are toxic to some benthic organisms. It is not clear from the work that has been done thus far whether the toxicity is due to the pyrethroid pesticides. There is no doubt that, in areas where pyrethroid pesticides are sold over the counter for residential use, which is many areas of the US, pyrethroid-based pesticides will be present in stormwater runoff from the areas where they are used, and they will accumulate in the receiving water sediments. Any attempt to screen these sediments for potential adverse impacts due to heavy metals or other constituents for which Long and Morgan or MacDonald have developed a

guideline value, will miss the potential for the pyrethroid-based pesticides in the sediments to be adverse to sediment quality.

Pyrethroid pesticides are not the only chemicals of this type. There are many chemicals that can be present in sediments, which are not part of the co-occurrence-based sediment quality guideline evaluation, which can be adverse to sediment quality and not be properly “screened” by the use of co-occurrence-based approaches. It will be extremely important that port and harbor water quality managers not assume that toxicity in stormwater runoff or sediments is due to heavy metals, since it is unlikely that this will be the case, even though the heavy metal concentrations found exceed the US EPA water quality criteria. It will be important to use toxicity identification evaluations (TIEs) to identify the cause of toxicity in stormwater runoff and in the receiving waters for this runoff and their sediments in order to properly identify the cause of toxicity.

The opposite type of problem is commonly occurring, in which regulatory agencies and others use a co-occurrence-based guideline value as a regulatory limit, which, if exceeded, trips the need to take remedial action. The use of Long and Morgan so-called “guidelines” as screening values for measured constituents would tend to overestimate their significance. It would be indeed rare that the total concentration of a constituent in sediments, which is the basis for the Long and Morgan values, would be a proper assessment of potential adverse impacts. This situation has led to overregulation of nonpollutants.

However, the use of Long and Morgan or MacDonald guideline values does occur, especially by those who just want a number of some type, so that they can proceed with their project, or so that they can claim that they are regulating sediment-associated constituents. These values give a false sense of reliability to those who want a number, in order to proceed with their project.

In the past few years Long has frequently stated that his so-called “guideline” values should not be used for regulatory purposes, yet they are being used for projects in which tens of millions of dollars of public funds are being spent because of exceedance of a Long and Morgan value. Some of the “horror” stories that the authors are familiar with include the exceedance of a Long and Morgan lead concentration value in Santa Monica Bay sediments causing those in the stormwater runoff watershed for Santa Monica Bay to spend \$42 million controlling lead and other heavy metals in urban area and highway stormwater runoff. This approach (the Santa Monica Bay Restoration Project) was shepherded by a State Water Resources Control Board staff member, and had the approval of the Los Angeles Regional Water Quality Control Board, the State Water Resources Control Board and the US EPA Region 9. However, it was obviously technically invalid, since anyone who understands even the most elementary aspects of lead chemistry in marine environments knows that lead is not a pollutant in a marine environment. Its chemistry is such that it is rendered inert and does not impact the aquatic-life-related beneficial uses of marine waters and sediments. Lead can be present in marine sediments well above Long and Morgan guideline values without adverse impacts. Flegal (2003) has presented a review on this issue.

When the Santa Monica Bay Restoration Project approach was first proposed, the authors (Lee and Jones-Lee, 1994; Lee, 1995) suggested to the Santa Monica Bay Restoration Project management that, before they adopted a restoration program costing the public \$42 million, which was based on exceedance of a Long and Morgan lead concentration in Santa Monica Bay sediments which predicted that the lead could be toxic, they ought to measure sediment toxicity. The Regional Board, the State Board and the US EPA Region 9 did not follow this suggestion. Instead, they simply assumed that exceedance of a Long and Morgan co-occurrence-based lead guideline demonstrated that there was such a significant adverse effect on Santa Monica Bay by lead in stormwater runoff, so as to cause the public to spend \$42 million trying to control it.

Another equally technically invalid approach occurred when the US EPA developed the TMDL to control the organochlorine “legacy” pesticides (such as DDT) and PCBs that are entering Upper Newport Bay (Orange County, California) and become incorporated into Bay sediments. The organochlorine compounds that were bioaccumulating to excessive levels were derived from stormwater from both agricultural and urban sources. It should have been obvious, through the most elementary review of how the Long and Morgan guideline values are developed for the organochlorines, that the guideline value does not consider in any way the potential for the constituent to bioaccumulate to excessive levels in fish, which would render the fish hazardous to those who consume the fish as food. Bioaccumulation to excessive levels in edible organisms was not, and still is not, an endpoint that is used in evaluating the coincidence (co-occurrence) between a concentration of a constituent in sediments and its bioaccumulation in aquatic organisms. These issues are further discussed in Lee and Jones-Lee (2002a).

Another recent example of the gross unreliability of Long and Morgan co-occurrence-based values that contributes to another “horror” story on their use is with the California Department of Fish and Game (DFG). DFG staff are attempting to improve anadromous fish spawning habitat in California Sierra rivers through the addition of gravel to the rivers. The gravel source that is being used is the dredger tailings from the former gold recovery operations in the terrestrial areas near existing rivers. These areas, through former erosion, have transported appreciable gold concentrations into the surficial sediments. Miners dredged these sediments and extracted some of the gold from them, using mercury to bind the gold. This approach has left substantial amounts of mercury in the dredged tailings. DFG staff have been using the Long and Morgan guideline value for mercury as a criterion to determine whether the dredger tailings contain excessive mercury. Again, this is obviously a technically invalid approach when an elementary review is conducted of the basis by which Long and Morgan developed their mercury guideline value. Mercury is of concern because, in certain aquatic sediment environments, it is converted to methylmercury, which then can bioaccumulate through the food web to excessive levels in fish, so that the fish become hazardous for use as food by humans and some fish-eating birds. The Long and Morgan guideline value for mercury does not in any way consider this issue.

Even though it is well recognized that the Long and Morgan and MacDonald co-occurrence (coincidence) values are unreliable and should not be used for any purpose, including screening, regulatory agency staff and others still use them. It is the authors’ experience that there are some individuals, including some in the regulatory community, that just want a number so that they can regulate or be regulated. They do not want to be confused with such issues as

the aquatic chemistry and toxicological reliability of the value that they are using. While there are some individuals, such as the authors (Lee and Jones, 1992), Dr. Robert Engler of the Corps of Engineers Waterways Experiment Station, and Dr. Tom Wright formerly of the Corps of Engineers Waterways Experiment Station, who have been discussing the unreliability of the Long and Morgan and MacDonald co-occurrence-based guideline values for over 10 years, recently there has been increasing recognition of the inappropriateness of using these values for any purpose.

In the fall 2002, the Aquatic Ecosystems Health and Management Society held an international conference entitled “Aquatic Ecosystems and Public Health: Linking Chemical, Nutrient, Habitat and Pathogen Issues.” A number of the leading authorities on sediment quality evaluation, such as Dr. Alan Burton, Dr. Peter Chapman, Dr. Dominic DiToro, as well as others at other conferences (US COE, US EPA 2003), including Dr. Robert Engler, Dr. Todd Bridges and Richard Wenning, have all discussed in the last year or so the unreliability of Long and Morgan and MacDonald so-called “sediment quality guidelines.” These guidelines should not be used for any purpose. It is a serious mistake by Long and Morgan to have ever developed them. They have done and will continue to do significant harm to properly regulating contaminants in sediments, especially those associated with stormwater runoff situations.

How Should Sediment-Associated Contaminants be Regulated?

It is clear, as was found by the authors’ and other studies in the 1970s, that chemically based approaches are unreliable and should not be used for regulating sediment-associated constituents. Instead, biological-effects-based approaches should be used. There is growing recognition that the approach for regulating constituents in sediments that are potential pollutants – i.e., under some conditions, the constituent can be adverse to the beneficial uses of a waterbody – should be based on a non-numeric, best professional judgment (BPJ) triad weight-of-evidence approach. This approach integrates reliable information on sediment toxicity to a suite of sensitive organisms, organism assemblage information in the area where the constituents of concern are located relative to similar unimpacted habitats, and chemical information. In addition, information on the potential for chemicals present in the sediments to be incorporated into the aquatic food web through bioaccumulation in aquatic life to levels that are hazardous to their use by higher trophic level organisms (including humans) as food needs to be included in the sediment quality evaluation. The US EPA (2000a,b) procedures should be used to assess the bioaccumulability of potentially hazardous chemicals, such as the organochlorine legacy pesticides, PCBs and dioxins. The aquatic organism assemblage assessment should include appropriate reference site information and gradient analysis from a hot spot or source of pollutants, to see if the organisms are potentially responding to the constituents of concern. Burton, et al. (2002a,b), and Chapman, et al. (2002, 1992), have provided comprehensive reviews of the approach that should be used in implementing the weight-of-evidence approach for sediment quality evaluation.

There is an aspect of the weight-of-evidence approach that is not well understood with respect to how to reliably incorporate chemical information into the triad. A number of investigators attempt to use total concentrations of constituents in sediments as the weight-of-evidence chemical information. This approach is obviously technically invalid. High concentrations of inert forms of contaminants, such as routinely occur in many sediments, can

skew the weight-of-evidence evaluation so that it becomes unreliable. Lee and Jones-Lee (2002b) discuss this issue, and point out that the chemical component of a triad weight-of-evidence approach must be based on toxic/available forms, evaluated through a TIE, and not based on total concentrations. While many individuals, especially those with limited chemistry backgrounds, attempt to shortcut or circumvent the complexity of the aquatic chemistry of constituents in aquatic sediments, there is no reliable shortcut. Properly developed and implemented chemical tools should be used.

As discussed by Lee and Jones-Lee (2002b), the weight-of-evidence approach should be implemented as a non-numeric best professional judgment by an expert panel in a public interactive peer-review process. This approach would eliminate many of the biases that become involved in scientific evaluation by individuals who either do not understand the issues or want to support their client's or agency's position on issues, irrespective of the technical information available.

Conclusions

The current approach for regulating the water quality impacts in the water column and sediments caused by urban stormwater runoff-associated constituents is not technically valid and leads to significant overregulation of the regulated constituents. To avoid this problem, there is need to develop wet-weather-based standards for regulating water column stormwater-derived constituents, and a non-numeric triad best professional judgment weight-of-evidence approach for regulating chemical constituents in sediments. Those interested in or responsible for managing water quality associated with ports and harbors will need to conduct detailed investigations of the role of urban area and highway stormwater runoff-associated constituents as they may impact water quality in the port or harbor. Failure to conduct these studies in a reliable manner could readily result in an inappropriate assessment of the role of port and harbor activities – including the release of some biocides, such as copper and diuron, used as antifoulants – on water quality in the port and harbor.

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