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This issue of the Stormwater Runoff Water Quality Science/Engineering Newsletter is devoted to a review of the **Unreliability of Co-Occurrrence-Based Sediment Quality "Guidelines"** for evaluating the water quality impacts of sediment-associated chemicals.

Regulating Contaminated Sediments

One of the issues that is becoming of increasing concern is the water quality significance of chemical constituents that accumulate in aquatic sediments. As discussed in previous Newsletters (NL 1-1,1-5, 2-2, 3-4, 6-4, 7-2, 7-4 and 7-6/7), urban and highway stormwater runoff, as well as discharges/runoff from point sources and nonpoint sources (such as agricultural runoff) contain a variety of chemicals that tend to become associated with sediments and, therefore, can cause elevated concentrations of these chemicals in areas where the sediments accumulate (become bedded sediments). This situation has been recognized since the early 1960s; however, limited progress has been made in properly evaluating/regulating the water quality impacts of sediment-associated constituents. This is a topic area that the author (G. Fred Lee) has been involved in since the early 1960s. He and his associates have published extensively on this issue.

Corps of Engineers Dredged Material Research Program. There have been a number of approaches proposed for determining what constitutes an excessive concentration of a heavy metal, pesticide or some other potential pollutant in aquatic sediments. An area of particular concern has been that of regulating the disposal of contaminated dredged sediments as part of the US Army Corps of Engineers' (COE) Congressionally mandated responsibility of maintaining the navigation depth of US waterways. In the 1970s the US Congress made available to the US Army Corps of Engineers Waterways Experiment Station in Vicksburg, Mississippi, $30 million to conduct the Dredged Material Research Program (DMRP). The DMRP was a five-year effort focusing on evaluating and developing management approaches for the water quality impacts of dredged sediment disposal. The author was involved in helping to develop and conduct this program as an advisor to the COE. He also conducted about a million dollars in studies of the potential impacts of open-water disposal of contaminated dredged sediments.

The results of the DMRP demonstrated what was known in the early 1970s (at the time of its initiation) – namely, that the total concentration of a constituent(s) in a sediment is not a reliable indicator of the potential water quality impacts of that sediment on the beneficial uses of the waters in which the sediment is located. In the late 1970s this led the COE and the US EPA to develop biological effects-based dredged sediment water quality evaluation procedures. The COE and US EPA developed both freshwater and marine dredged sediment evaluation guidance

(US EPA/US ACOE, 1991, 1998) focusing on aquatic life toxicity testing and assessing the potential for excessive bioaccumulation of hazardous chemicals from sediments.

Attempts to Use Total Concentrations of Chemicals in Sediments. Over the years regulatory agencies and some investigators have measured the total concentration of a variety of potential pollutants in sediments. While it has been well-known since the early 1970s (and confirmed by the DMRP as well as other studies) that the total concentration of a contaminant in a sediment is not a reliable indicator of a potential water quality impact, some state regulatory agencies, environmental groups, some parts of the US EPA and others have been attempting to develop approaches that can utilize the total concentration data that have been developed, as part of contaminated sediment reconnaissance studies in regulating contaminated sediments. An example of this type of effort was the Long and Morgan (1990) development of co-occurrence-based sediment quality "guidelines."

Co-Occurrence-Based Sediment Quality Guidelines. The work of Long and Morgan (1990) and later of MacDonald (1992) has served as the basis for many of the co-occurrence evaluations made of sediment "quality." Those investigators reviewed literature on the concentrations of certain chemical constituents (primarily heavy metals and selected organics) in sediments and on assessments made of biological "impacts" that have been reported to be found associated with those sediments. For each of the selected chemicals that those investigators included in their evaluations, they developed a list of the concentration of that parameter in each of the sediments and an associated assessment of the "effect" of that sediment measured in any number of ways (e.g., benthic faunal analysis, toxicity tests), without consideration of what conditions or contaminants were causing or influencing the "effect." The sediments were listed in order based on concentration for that chemical, showing the co-occurrence of the concentration of the chemical and the reported "effect" of the chemical constituent in that sediment.

In regulatory applications, co-occurrence information has been used or proposed for use, albeit incorrectly, to establish various "effects threshold" values. That is, applying statistics to the ranked listing of co-occurrence information of a given chemical, it was determined for that data set the concentration of the chemical that has a given probability of co-occurring with an impact, or the lowest concentration with which "no effect" co-occurred for that set of sediments. Examples of these approaches are the "Apparent Effects Threshold" (AET), and numeric ER-L/ER-M values developed from Long and Morgan's (1990) data presentation, and "Probable Effects Levels" (PEL) values derived from MacDonald's (1992) co-occurrence compilations. If a sediment contains a chemical in concentrations above the AET, ER-L, ER-M, PEL, or similar value, (including NOAA "SQuiRT" values) the sediment is considered by some regulators or proposed regulations to be "polluted," and to require special consideration such as "remediation," alternate methods of dredged sediment disposal, or control of permitted discharges of a chemical to the waterbody that accumulates in the sediments.

Someone not familiar with aquatic chemistry, aquatic toxicology and water quality could conclude from the literature that the Long and Morgan, MacDonald and other co-occurrence-based "guidelines" have some technical validity and, therefore, are appropriate for screening sediments for potential water quality impacts, including establishing sediment remediation objectives. However, those who understand aquatic chemistry, aquatic toxicology and the

effects of chemicals on aquatic life recognize that the Long and Morgan, MacDonald and NOAA "SQuiRT" values are fundamentally flawed with respect to relating the concentrations of constituents in sediments to their potential impact on aquatic life. Dr. Jones-Lee and I have developed several peer-reviewed papers and reports on these issues, in which we have discussed our own experience in sediment quality evaluation, as well as the experience of others. Presented below is a summary of this information.

The co-occurrence-based approach is fundamentally flawed because it is based on the total concentrations of a limited number of constituents in the sediments. While some will claim that there is some validity to this approach and will even make the false statement that these have been adopted as NOAA values, in fact they are not NOAA values, and the Chief Scientist for NOAA Status and Trends program (Tom O'Connor) has repeatedly pointed out the unreliability of the approach with respect to whether a Long and Morgan sediment quality "guideline" is a reliable indicator of sediment toxicity. The facts are that, with a large database representing a variety of sites where chemical concentrations and sediment toxicity have been measured, the Long and Morgan and MacDonald "guideline" values are no more accurate in predicting sediment toxicity than flipping a coin.

Review of Selected Literature on Unreliability of Co-Occurrence-Based Approaches. In the mid-1990s Lee and Jones-Lee (1996) developed a comprehensive review of why co-occurrence-based approaches are not reliable for evaluating the potential water quality impacts of chemical constituents in aquatic sediments. Their review provides background information on the development of and problems with Long and Morgan ER-Ls/ER-Ms and MacDonald PELs. It contains a number of references to previous writings on this issue, which lead to the conclusion that co-occurrence-based values should not be used for any purpose, including the screening of sediments for potential water quality problems.

In 2002, through a contract issued by the California State Water Resources Control Board to CSU Fresno's California Water Institute, Drs. Lee and Jones-Lee (2002a) were asked to develop a comprehensive review on the occurrence and management of organochlorine legacy pesticides, PCBs and dioxins (collectively referred to as OCls) in California Central Valley fish. The section of the CSU Fresno OCl report devoted to the unreliability of co-occurrence-based values for evaluating sediment quality has been developed into a separate report (Lee and Jones-Lee, 2002b). Excessive bioaccumulation of the OCls is one of the (if not the) most important water quality problems in the Central Valley of California, since many waterbodies in the Central Valley contain edible fish with concentrations of OCls that have been determined by California EPA's Office of Environmental Health Hazard Assessment (OEHHA) to be a threat to cause cancer in people who eat these fish.

Since one of the issues of particular concern is the occurrence of OCls in sediments which serve as a source for the excessive bioaccumulation of these chemicals in edible aquatic life, a section of their report was devoted to a review of approaches for evaluating excessive concentrations of OCls in aquatic sediments. A detailed discussion was included in this section on the unreliability of co-occurrence-based approaches, such as Long and Morgan values, in predicting the water quality impact of the OCls on the beneficial uses of waterbodies. An issue of particular concern was the use of Long and Morgan or MacDonald values to determine excessive concentrations of

these chemicals in aquatic sediments. As Lee and Jones-Lee discuss, excessive concentrations of these chemicals should be based on evaluating whether the chemicals are toxic to aquatic life and whether the sediment-associated OCls are sources that lead to excessive bioaccumulation in fish and other aquatic life tissue.

Lee and Jones-Lee (2002a) point out that some regulatory agencies, including the US EPA Region 9 (US EPA, 2002), in connection with their development of a TMDL for control of excessive bioaccumulation of the OCls in edible fish in the Upper Newport Bay, Orange County, California, watershed and Bay, are inappropriately using the Long and Morgan values as TMDL cleanup goals. This is inappropriate, since the Long and Morgan values and MacDonald values are not based on bioaccumulation, but on sediment toxicity to aquatic life. Bioaccumulation of these chemicals to excessive levels in edible fish can occur at concentrations well below those that are toxic to benthic organisms associated with the sediments.

The US EPA Region 9's use of co-occurrence-based values for regulatory purposes is one of the examples that Lee and Jones-Lee (2002a) discuss as "horror stories" on an inappropriate approach for developing a regulatory program that can lead to the waste of public and private funds. They discuss a number of other situations where the public is being trapped into paying for multi-million-dollar sediment cleanup projects because of an exceedence of a co-occurrence-based sediment quality guideline(s), where the regulatory agencies ignore the literature on the unreliability of this approach and do not evaluate whether the guideline(s) has any validity for the particular situation to which it is being applied. Co-occurrence-based values should never be used to provide any inference on the potential for sediment-associated chemicals such as the OCls, mercury, etc., to bioaccumulate to excessive levels in edible aquatic life. The development of these values did not consider bioaccumulation as an impact of the sediment-associated constituents.

SQA5 Conference. In the fall of 2002 the International Aquatic Ecosystem Health and Management Society held a three-day conference in Chicago (Fifth International Conference on Sediment Quality Assessment - SQA5) where there were several presentations (including several invited keynote presentations) on sediment quality evaluation. Several of the leading authorities on sediment quality evaluation, including DiToro, Chapman and Burton, discussed the unreliability of co-occurrence-based approaches for evaluating sediment quality. DiToro, in his presentation at SQA5, characterized any so-called agreement between the results of co-occurrence-based values and observed sediment toxicity as a "coincidence," and certainly not cause and effect. While Long, MacDonald, and others claim that their co-occurrence-based values have predictive capability based on a particular dataset, a critical review of these datasets shows that they are not a reliable basis for evaluating the ability of co-occurrence-based values to predict sediment toxicity.

The focus of the SQA5 discussion by Chapman (2004) was on assessing bioavailable forms of contaminants in sediments, where he points to the unreliability of trying to assess bioavailability based on chemical measurements. As he pointed out in his presentation, co-occurrence-based sediment quality guidelines fail to reliably assess bioavailable forms.

O'Connor(2004), in his in-press paper, "The Sediment Quality Guideline, ERL, is not a Chemical Concentration at the Threshold of Sediment Toxicity," has provided additional information on the unreliability of using co-occurrence-based approaches for assessing sediment toxicity.

Lee and Jones-Lee (2004) presented a paper at the SQA5 conference entitled "Appropriate Incorporation of Chemical Information in a Best Professional Judgment 'Triad' Weight of Evidence Evaluation of Sediment Quality." Their paper contains an updated review of the unreliability of co-occurrence-based values for evaluating sediment quality. Particular emphasis in the paper is given to a discussion of how sediment quality evaluation should be conducted, involving a best professional judgment (BPJ) triad weight-of-evidence approach. This approach integrates information on aquatic toxicity and excessive bioaccumulation, altered organism assemblages relative to habitat characteristics, and chemical information. Lee and Jones-Lee discuss the inappropriateness of using total concentrations of a chemical or group of chemicals in a sediment to predict sediment toxicity and/or bioaccumulation. Of particular concern is the unreliability of using co-occurrence-based sediment quality "guidelines" in evaluating the potential for a sediment to be adverse to the beneficial uses of the waters in which the sediment is located. The approach that must be used for reliably incorporating chemical information into the BPJ triad weight-of-evidence approach involves conducting toxicity investigation evaluations (TIEs) or sediment bioavailability testing to determine the toxic available forms and their concentrations in sediments. Failure to use this type of chemical information, where exceedances of sediment quality guidelines are used instead, can lead to an erroneous BPJ weight-of-evidence conclusion on the role of chemicals in the sediments in affecting a waterbody's water quality.

BPJ Weight-of-Evidence Approach. Lee and Jones-Lee (2003a) have provided additional discussion on the unreliability of co-occurrence-based approaches in evaluating sediment quality. They point out that the frequently used approach of examining a sediment for the total concentrations of a selected group of chemicals relative to an exceedence of a co-occurrence-based sediment quality guideline is not a valid approach for assessing whether the sediments contain a chemical or chemicals that are altering the numbers, types and characteristics of aquatic life in the sediment and in the overlying waters associated with the sediment.

Failure to Consider Full Range of Potential Pollutants. The lack of technical validity in using the co-occurrence-based approach for evaluating sediment quality stems in part from the chronic problem that the sediment quality guidelines consider only a small number of the thousands of chemicals that can be present in sediments which can affect aquatic life. The failure to find any exceedances of an ER-M, ER-L, PEL or SQuiRT value in the sediments should never be assumed to be a reliable indication of a lack of impact of the sediment-associated chemicals on aquatic life. Lee and Jones-Lee (2003a) discuss the fact that one of the most common types of pesticides that is now widely used in agricultural and urban areas (pyrethroid-based pesticides) tend to accumulate in sediments. Weston et al. (2004) have reported finding aquatic sediments in the Central Valley with measurable toxicity and measurable concentrations of pyrethroid pesticides. Therefore, a sediment could be toxic to aquatic life and not exceed any co-occurrence-based sediment quality guideline, since these "guidelines" do not include values for the pyrethroid-based pesticides. A similar situation could occur with ammonia, hydrogen sulfide

and low dissolved oxygen in sediments, as discussed by Lee and Jones-Lee (1996). These chemicals/conditions are the most common cause of sediment toxicity, yet the co-occurrence-based sediment quality guidelines do not include guideline values for them. This is another fundamental flaw of the co-occurrence-based approach developed by Long and Morgan and MacDonald.

In the 1970s the author and his graduate students conducted about a million dollars of studies for the US Army Corps of Engineers devoted to developing dredged sediment disposal criteria. These studies involved taking sediments from about 100 sites across the US and determining the total concentrations of about 30 potential conventional pollutants, including heavy metals, organochlorine pesticides, PCBs, nutrients, etc. They also examined the amount of these chemicals that was released upon suspension of the sediments in water, and conducted sediment toxicity tests. This effort generated about 50,000 data points, which were published in two reports (Lee et al., 1978; Jones and Lee, 1978). A summary of these studies has been published by Lee and Jones-Lee (2000) in the Handbook of Dredging Engineering.

The work done in this project served as the basis for the US EPA and Corps of Engineers to develop criteria for open water disposal of contaminated dredged sediments. These studies clearly demonstrated that the total concentration of a particular chemical in sediments, such as a heavy metal or the sum of all heavy metals, bears no relationship to the toxicity of those sediments to aquatic life. It was clear that the toxicity of sediments was largely independent of the total concentrations of various conventional pollutants, such as heavy metals, pesticides, etc., as a result of sediment-binding detoxifying these potential pollutants. However, many of the sediments collected from near urban-industrial waterways were toxic to aquatic life. The cause of the toxicity was not identified.

Failure to Consider Ammonia, Hydrogen Sulfide and Low-Dissolved Oxygen. Subsequently, through followup studies that were conducted in the 1980s, Drs. R. A. Jones and G. F. Lee published a paper (Jones and Lee, 1988) in which they identified that the most common cause of sediment toxicity is ammonia. It is now well-recognized, based on studies conducted by numerous investigators, that ammonia is one of the (if not the) most common causes of sediment toxicity. This has particular relevance to co-occurrence-based sediment quality guidelines, since these guidelines do not include ammonia as a potential cause of sediment toxicity. It should be noted that Long and Morgan, in developing their original paper on co-occurrence, made use of the 1970s database that Dr. Lee and his graduate students had developed from about 100 sites across the US. This database included ammonia and hydrogen sulfide. However, Long and Morgan, while using the heavy metal, organochlorine pesticide and PCB data from the database, ignored the ammonia and hydrogen sulfide data. This makes their original and all subsequent co-occurrence-based sediment quality guideline evaluations fundamentally flawed. Any sediment quality evaluation concerned with assessing toxicity to aquatic life that does not consider ammonia as a potential toxicant can be highly unreliable.

Failure to Consider Additive and Synergistic Toxicity. Lee and Jones-Lee (2003a) have also discussed the fact that there is increasing evidence that the toxicity of pesticides and some other potentially toxic constituents, such as heavy metals, are additive and, in some cases, synergistic. This means that a sediment that does not exceed a co-occurrence-based sediment quality

guideline for a particular constituent could be causing sediment toxicity through additive or synergistic impacts with other chemicals for which there is not an exceedence of a sediment quality guideline or for which there is no sediment quality guideline. Therefore, any sediment evaluation that relies on exceedence of a co-occurrence-based sediment quality guideline can fail to detect additive and synergistic toxicity. It is for this reason that the only reliable way to assess whether sediments are toxic is through toxicity measurements. Toxicity cannot be assessed through chemical measurements.

Use of Co-Occurrence in Superfund Contaminated Sediment Investigation/Remediation

The US EPA Superfund management has been concerned for a number of years about the potential for using co-occurrence-based sediment quality guidelines as values upon which remediation decisions are made. The managers of US EPA Superfund have made it clear that this approach should not be followed, because of the unreliability of co-occurrence-based sediment quality guidelines. In April 2003 the US Army Corps of Engineers, US EPA Superfund and others held a national workshop, "Environmental Stability of Chemicals in Sediments," where the issues of appropriately regulating contaminated sediments were discussed. While there is no proceedings from this workshop, the PowerPoint slides from those making presentations are available at http://www.sediments.org/sedstab/agenda.pdf. Evison (2003) of the US EPA Office of Emergency and Remedial Response made a presentation, "Contaminated Sediment at Superfund Sites: What We Know So Far," in which a summary was presented on the magnitude of the problem of contaminated sediments at Superfund sites. Further, Ellis (2003), Sediments Team Leader with the US EPA Office of Emergency and Remedial Response, made a presentation, "Superfund Cleanup Issues at Contaminated Sediment Sites." According to Ellis, the US EPA Superfund program still supports the position that co-occurrence-based sediment quality guidelines are not appropriate for establishing the impacts of chemicals in sediments or to serve as the basis for sediment cleanup objectives.

Another example of an inappropriate use of co-occurrence-based sediment quality guidelines is occurring today in the University of California, Davis (UCD)/US Department of Energy LEHR national Superfund site Ecological Risk Assessment. UCD is attempting to use Long et al. (1995) and MacDonald et al. (2000) co-occurrence-based guidelines as a technical basis for conducting an ecological risk assessment for contaminated sediments associated with the Superfund site. However, as discussed by Lee (2004), this approach should not be allowed if this use could in any way influence the characterization of LEHR site sediments with respect to whether they represent a potential threat to aquatic life and, therefore, should or should not require remediation.

California Development of Sediment Quality Criteria

Lee and Jones-Lee (2003b) have reviewed the California State Water Resources Control Board's (SWRCB's) current effort to develop sediment quality criteria for regulating contaminated sediments in the state. They point out that there are potentially significant problems with the initial proposed approach, since the SWRCB staff propose to use co-occurrence-based sediment quality guidelines as one of the components of evaluating sediment quality. Further, one of the most significant problems is the attempt to use the existing sediment quality database that was developed as part of the Bay Protection and Toxic Cleanup Program (BPTCP) as a basis for developing sediment quality criteria. As discussed by Lee and Jones-Lee, that program did not

properly evaluate the role of measured contaminants in sediments relative to whether the contaminants were responsible for sediment toxicity and/or altered organism assemblages. The SWRCB organizers of the BPTCP did not include toxicity identification evaluation studies to develop cause-and-effect relationships that are essential to properly evaluating the impact of a chemical(s) on aquatic life.

More recently, the SWRCB staff have indicated that they are going to focus on using a weight-of-evidence approach for developing sediment quality criteria. At this time, the characteristics of this proposed weight-of-evidence approach have not been defined. However, Beegan (pers. comm., 2004), who heads up this effort for the SWRCB, has indicated that the weight-of-evidence approach would include the use of co-occurrence-based sediment quality guidelines as part of the chemical information used in the weight-of-evidence. As discussed by Lee and Jones-Lee (2004), this approach can readily lead to an erroneous weight-of-evidence evaluation of the significance of chemicals in sediments as they may impact the beneficial uses of the waters in which the sediments are located. Such an approach would fail to consider the full range of potential pollutants that can affect sediment quality, as well as the additive and synergistic effects of potential pollutants. It also fails to consider the significant detoxification ability of sediments that renders potential pollutants non-toxic/non-bioavailable. It remains to be seen whether the SWRCB's efforts will lead to development of sediment quality criteria that will properly evaluate whether a chemical or group of chemicals in the sediment is having a significant adverse impact on the beneficial uses of the water in which the sediments are located.

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