

**Comments on the CA Bay Delta Authority
Dredge tailings issue paper:
DRAFT 1/14/05
Mercury in Dredge Tailings: Considerations for Restoration
Prepared by D. Podger**

Comments prepared by
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Overall this draft paper covers many of the issues that need to be considered in evaluating the use of gold dredge tailings as a source of gravel for fish streambed habitat spawning area improvement. There are several areas that need attention, these are discussed below.

Regulating Mercury

The sections on regulating mercury have several deficiencies that need attention.

“Mercury regulations: Water:”

With regard to the discussion of the 50 ng/L US EPA CTR water quality criterion, the paper should discuss the approach that the US EPA used in establishing the 50 ng/L CTR criterion. As discussed by Lee (2003) “Regulating Mercury in the Water Column and Sediments,” that was prepared in response to early discussions of the potential use of dredged tailings from gold recovery operations for streambed gravel enhancement by the Dredge Tailings Workgroup, the 50 ng/L criterion is not based on the finding that concentrations of mercury below this amount will not bioaccumulate to excessive levels in fish. The previous US EPA 12 ng/L “Goldbook” criterion was raised to 50 ng/L as an interim value as a result of the US EPA changing the approach used to develop this type of water quality criteria. As indicated in the Lee (2003) discussion, P. Wood, who heads the US EPA Region 9 water quality criteria section, has indicated that Hg concentrations as low as about 5 ng/L can in some situations bioaccumulate to excessive levels in fish.

It would be inappropriate for those conducting gravel enhancement projects as well as those who regulate these projects to assume that waters with mercury concentrations below 50 ng/L do not represent a threat to bioaccumulate mercury to excessive concentrations in fish tissue. Any water with total concentration of mercury above about a few ng/L is a threat to cause excessive bioaccumulation of mercury. Excerpts from the Lee (2003) review is attached.

Mercury regulations: Sediment:

The current draft report suggests at several locations that the Long and Morgan type cooccurrence based sediment quality guidelines can be used to evaluate whether mercury contaminated dredged sediments can be safely used in streambed gravel restoration projects. When I learned at one of the early Dredge Tailings Workgroup meeting that

Long and Morgan so-called sediment quality guidelines (“NOAA No Effects Level”) were being used by CA Department of Fish and Games staff to determine if a particular gravel contained excessive mercury, I commented that this is a technically invalid approach and not necessarily protective from excessive bioaccumulation of mercury in areas where gavel containing gravel with mercury less than the Long and Morgan et al. guidelines is used in streambed gravel restoration. This situation caused me to prepare the Lee (2003) write up on this issue.

It is obvious to those who understand aquatic chemistry and review how these guidelines were developed, that these so-called sediment quality guidelines should not be used for any purpose. They are well known to be unreliable to assess aquatic life toxicity and have no applicability to addressing bioaccumulation of mercury. Bioaccumulation was not considered in developing these guidelines. In the Lee (2003) I enclosed a write up on this issue. Recently, Jones-Lee and Lee (2004) have prepared an updated review of this issue. This update is currently in press in a national referred journal, a preprint is attached.

Mercury regulations: Tissue:

This discussion should indicate that the implementation of the US EPA proposed tissue based mercury criterion requires a site specific evaluation of mercury concentrations/loads that can occur without excessive bioaccumulation in fish. The aqueous environmental chemistry of mercury is such that there is no simple way to make this evaluation except by study of the area of interest.

The discussion should also indicate that based on comments on the Cache Creek TMDL for Hg by the US Fish and Wildlife Service staff, the 0.3 mg/kg concentration that is proposed for protection of human health at a certain level of fish consumption may not be protective of fish eating bird populations. See CVRWQCB website comment,

“Based on guidance provided by the US Fish and Wildlife Service, the numeric targets for concentrations of methylmercury in fish have been lowered. This change resulted in a lowering of the aqueous methylmercury concentration goal for Cache and Bear Creeks and revision of the methylmercury load allocations”

For more information, please contact Janis Cooke (jcooke@waterboards.ca.gov) or Patrick Morris (pmorris@waterboards.ca.gov).

Evaluating the material for contamination:

.The statement,

“Although there are no sediment criteria to compare concentrations with, you can compare to background or ERL and ERM values as a general comparison for elevated mercury levels.”

These criteria cannot be used to reliably determine the elevated concentrations of mercury in sediments.

Oxygen in Water Column/Sediments

At several locations mention is made that the absence of dissolved oxygen in the water column is a key parameter in the conversion of mercury to methyl mercury. For example, "*The floodplain should be designed to minimize the amount of time that water is "standing", so that the water does not become warm and anoxic.*" It should be mentioned that methyl mercury is formed in waterbodies with dissolved oxygen in the water column. The key issue is the absence of DO in the sediments.

Estimating MeHg Production

At several locations comments about trying to estimate methyl mercury based on the concentration of various forms of mercury in gravel/sediments. This approach is suggested to be used instead of measuring methyl mercury since such measurements are expensive. These measurements are essential if reliable determinations are to be made.

References

Lee, G. F., "Regulating Mercury in the Water Column and Sediments," Report to Dredge Tailings Workgroup, by G. Fred Lee & Associates, El Macero, CA (2003).

<http://www.gfredlee.com/TotalMercuryandDissolvedMercuryStandards-rev.pdf>

Jones-Lee, A. and Lee, G. F., "Unreliability of Co-Occurrence-Based Sediment Quality Guidelines for Contaminated Sediment Quality Evaluation at Superfund/Hazardous Chemical Sites," In Press (2004).

<http://www.members.aol.com/annejlee/SQGSuperfund2.pdf>

**Excerpts from
Regulating Mercury in the Water Column and Sediments**

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August 8, 2003

At the March 27, 2003, and July 9, 2003, meetings of the Dredge Tailings Workgroup, questions were raised regarding the regulation of mercury in the water column and sediments. With respect to the water quality standard (objective) for regulating mercury in the water column, about a year ago Dr. Anne Jones-Lee and I were subcontractors to a firm developing an SEIR for Cache Creek in-channel projects. In connection with this effort we developed the Water Quality chapter of the Yolo County Department of Public Works SEIR. This effort involved reviewing the water quality data that are available on Cache Creek that had been collected from the mid-1990s to date for the Cache Creek Improvement Project area – i.e., Capay Dam to I-5. Our review included a presentation and discussion of all of the data that the County and others had collected in this area during this period. Further, we reviewed the regulatory requirements governing water quality in Cache Creek that are applicable to the project area. Our chapter was included in the SEIR which was certified by the County Board of Supervisors.

In order to make this information available to others(i.e., to not have it buried in an SEIR which has limited availability), we developed a separate report on the Cache Creek water quality issues that we covered, which does not include the SEIR issues, but does include the water quality data and regulatory limits. This report,

Lee, G. F. and Jones-Lee, A., “Review of Yolo County Lower Cache Creek Water Quality,” Report of G. Fred Lee & Associates, El Macero, CA, September (2002),

is available from our website at www.gfredlee.com/CacheCreekwatqualrpt.pdf. Presented below are excerpts from this report that cover the mercury water quality criteria/standards/objectives issues that were discussed at Dredge Tailings Workgroup meetings.

**Excerpts from
G. Fred Lee and Anne Jones-Lee, “Review of Yolo County Lower Cache Creek
Water Quality,” Report of G. Fred Lee & Associates, El Macero, CA,
September (2002)**

Total Mercury and Dissolved Mercury: Mercury is one of the most important water quality parameters for Cache Creek. This importance arises from the fact that mercury can convert to methylmercury, which then bioaccumulates in fish tissue. Methylmercury

is highly toxic to fetuses and young children, causing neurological damage. The CA DHS has established a mercury drinking water MCL of 0.002 mg/L.

The CVRWQCB does not have a water quality objective for mercury; however, the US EPA (1987) developed a water quality criterion for total recoverable mercury of 12 ng/L. The US EPA (2000c), as part of developing the California Toxics Rule, subsequently raised this criterion to 50 ng/L. The US EPA (Woods, 2000) has indicated, however, that this change does not represent a change in the level of significance of mercury in water, but a change related to how the Agency determines critical concentrations of mercury. Woods (2000) has indicated that the mercury criterion could be lowered to about 5 ng/L total recoverable mercury within a few years. This concentration represents a “worst case” situation for bioaccumulation of mercury in fish tissue. By “worst case” it is meant that the mercury in the water column is in a bioavailable form that can be bioaccumulated by the trophic food web in the area that could lead to excessive mercury in edible fish tissue.

Mercury Special Studies

To date, the US EPA has been regulating mercury in water based on water concentrations of total recoverable mercury. This approach has proven to be unreliable, since there are a wide variety of factors that influence the conversion of total mercury in water and/or sediments to methylmercury in water and fish tissue. The US EPA (1999c,d; 2001b,c) is recommending a change in the approach for regulating mercury, which would be based on fish tissue residues. The US EPA (2001c) states,

“To assess health risks, EPA developed a reference dose that is a scientifically justifiable maximum level of exposure to protect public health from all toxic effects. EPA based the methylmercury criterion on a new reference dose that protects all exposed populations. EPA also updated the exposure assessment and relative source contribution following the recently published 2000 Human Health Methodology. The resulting criterion of 0.3 mg methylmercury/kg in fish tissue should not be exceeded to protect the health of consumers of noncommercial freshwater/estuarine fish.”

This is a much more reliable approach for regulating mercury. It will require that a Cache Creek-specific translation factor between methylmercury in water and methylmercury in fish tissue, be established. Slotton (pers. comm., 2001) has indicated that he is developing such a relationship for Cache Creek.

Woods (2001) has indicated that the US EPA is also developing guidance for implementing the methylmercury tissue-based criterion. A draft of this guidance was scheduled to be available in 2002; however, recent events have caused the US EPA to shift the personnel working in this area to other activities related to terrorism.

References

U.S. Environmental Protection Agency. May 1987. Quality Criteria for Water 1986, US Environmental Protection Agency, Office of Water Regulations and Standards, US EPA 440/5-86-001, Washington, D.C.

U.S. Environmental Protection Agency. 1999c. Mercury Update: Impact on Fish Advisories, US Environmental Protection Agency, Office of Water, US EPA-823-F-99-016, Washington, D.C.

U.S. Environmental Protection Agency. 1999d. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Vol. II, Risk Assessment and Fish Consumption Limits, Second Edition, US EPA 823-B-97-004, US Environmental Protection Agency, Office of water, Washington D.C.

U.S. Environmental Protection Agency. 2000a. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule, US Environmental Protection Agency, Region 9, *Federal Register* 40 CFR Part 131, Vol. 65, No. 97, [FRL-6587-9], RIN 2040-AC44, San Francisco, CA.

U.S. Environmental Protection Agency. 2001b. Water Quality Criteria for the Protection of Human Health: Methylmercury, US Environmental Protection Agency, Office of Water, US EPA-833-F-01-001, Washington, D.C.

U.S. Environmental Protection Agency. 2001c. Water Quality Criteria: Notice of Availability of Water Quality Criterion for the Protection of Human Health: Methylmercury, US Environmental Protection Agency, *Federal Register*, 66(5):1344-1359, Washington, D.C.

Woods, P. 2000. pers. comm., US Environmental Protection Agency, Region 9, San Francisco, CA.

Woods, P. 2001. pers. comm., US Environmental Protection Agency, Region 9, San Francisco, CA.

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Recently Phil Woods of the US EPA Region 9 has provided the following information with respect to future regulation of mercury:

Phil Woods  
US EPA Region 9  
San Francisco, CA

Phil,

Recently I have been comparing the US EPA CTR criteria for California against the US EPA National Recommended Water Quality Criteria 2002, which was published in November of last year. In some cases I am finding that there are significant differences. Is the US EPA updating

the CTR criteria for California to reflect the 2002 Recommended Criteria? What is the status of the Recommended Criteria with respect to states having to adopt them? Any guidance you can provide on these issues would be appreciated.

Fred

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Fred,

The 2002 criteria are the current national 304(a) criteria guidance. As such, states should use this guidance as they carry out WQS reviews. A few entities in Region 9 are in that process, and we expect that others will gradually join in that effort. Also, this criteria guidance can be applied currently in quantifying narrative WQS requirements in implementing various individual planning and regulatory requirements.

EPA (Region 9 with HQ) began preparing revisions to the CTR for Hg and Cd before the 2002 criteria were published based on their individual criteria publications. As part of the national Hg criteria publication, EPA made a commitment to develop implementation guidance to go with the tissue based criterion. That process has been delayed, and, therefore, the CTR amendment has not moved to FR proposal yet. We expect that Hg will move "soon"; however, I think you know what "soon" means as well as I do.

In general, there is intent to update existing promulgations (such as the CTR) as national 304(a) criteria guidance becomes available/is published. Under current circumstances, we expect that most individual states will be able to act more quickly than the federal government can. (Note also that some of the 1999 criteria were so significantly changed that EPA solicited public comment. As I recall, these were all human health criteria changes based on the 2000 human health methodology. I have not heard how significant the public comments were. In any case, responses will be developed, and these additional criteria revisions will be added to the revisions you have observed in the 2002 publication before anyone even considers updating existing promulgations.)

Phil

Water Quality Standards for Mercury in Bedded Sediments

During Dredge Tailings Workgroup meetings, several references were made to standards for mercury in sediments. It was indicated that the “NOAA No Effects Level” was being used to judge excessive mercury in DFG anadromous fish habitat restoration projects. Also, several project reports were circulated at a meeting, in which the authors had used these values to judge excessive mercury in sediments. At the end of that meeting I mentioned that this approach is obviously technically invalid and unreliable, based on a critical review of how these so-called “NOAA” values were developed. First, these values should not be called “NOAA” values. As discussed below, they were developed by NOAA staff. They have never been adopted by NOAA as reliable values. Further, there is substantial NOAA literature that shows that these values are unreliable for use for any purpose – much less, to regulate projects involving mercury. The proper terminology that should be used in connection with these values is “co-occurrence-based values.”

During the past year, Dr. Jones-Lee and I have developed a report for the State Water Resources Control Board and Central Valley Regional Water Quality Control Board on managing excessive bioaccumulation of the organochlorine pesticides, PCBs and dioxins in Central Valley waterbody fish and other aquatic life. This report,

Lee, G. F. and Jones-Lee, A., “Organochlorine Pesticide, PCB and Dioxin/Furan Excessive Bioaccumulation Management Guidance,” California Water Institute Report TP 02-06 to the California Water Resources Control Board/Central Valley Regional Water Quality Control Board, 170 pp, California State University Fresno, Fresno, CA, December (2002),
<http://www.gfredlee.com/OCITMDLRpt12-11-02.pdf>

is available from the URL listed above or directly from me, at gfredlee@aol.com.

The report contains a major section on the unreliability of co-occurrence-based approaches for evaluating aquatic sediment quality. This section is based on my approximately 40 years of work on evaluating the water quality significance of chemical contaminants in aquatic sediments. The section of our report devoted to unreliability of co-occurrence-based so-called sediment quality guidelines is presented below. While this section focuses on the organochlorine pesticides, PCBs and dioxins, it is equally applicable to mercury.

The fundamental problem with co-occurrence based values is that they are based on total concentrations versus some biological effect, such as aquatic life toxicity, altered benthic organism assemblages, etc. Bioaccumulation to excessive levels was not used in their development for those constituents such as mercury, where the concern is excessive bioaccumulation in edible organism tissue. This in itself should be the clue that these values should never be used to regulate a constituent that is of concern because of excessive bioaccumulation. Further, it has been well known since the 1960s that the total concentration of a chemical in sediments is not a reliable indicator of its potential impacts

on water quality. It has been well known now for over 30 years that chemical constituents exist in aquatic sediments in a variety of forms, only some of which are bioavailable.

Last October the Aquatic Ecosystem Health and Management Society held a several-day conference in Chicago devoted to Aquatic Ecosystems and Public Health. As discussed below, a number of internationally recognized experts were invited to make presentations on the co-occurrence-based approach for evaluating sediment quality. There was unanimous agreement that this approach is obviously unreliable and should not be used. The proceedings of this conference have been published and this paper is available as,

Lee, G. F. and Jones-Lee, A., "Appropriate Incorporation of Chemical Information in a Best Professional Judgment 'Triad' Weight of Evidence Evaluation of Sediment Quality," Presented at the 2002 Fifth International Symposium on Sediment Quality Assessment (SQA5), In: Munawar, M. (Ed.), *Aquatic Ecosystem Health and Management* 7(3):351-356 (2004). <http://www.gfredlee.com/BPJWOEpaper-pdf>

Recommendations for Dredge Tailings Workgroup Activities

It is my recommendation that the Dredge Tailings Workgroup should work toward acquiring funding that can be used to develop recommended approaches for evaluating the water quality significance of mercury in bedded sediments. There is an urgent need for this type of information to reliably evaluate the potential for mercury in gold recovery dredged sediments to lead to excessive bioaccumulation or other human health effects, in connection with the use of these sediments as aggregate, for stream restoration projects, and for the protection of waterbodies that receive the dredged sediments in stormwater runoff. To the extent that there is interest, and especially if there is support, Dr. Jones-Lee and I could become active participants in this activity.

If there are questions about these comments, please contact me.

G. Fred Lee, PhD, DEE

Unreliability of Co-Occurrence-Based Sediment Quality Guidelines for Contaminated Sediment Quality Evaluation at Superfund/Hazardous Chemical Sites

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ABSTRACT

Many Superfund/hazardous chemical sites include waterbodies whose sediments contain hazardous chemicals. With the need to assess, rank, and remediate contaminated sediments at such sites, as well as in other waterways, regulators seek a simple, quantitative assessment approach that feeds easily into a decision-making scheme. Numeric, co-occurrence-based “sediment quality guidelines” have emerged with the appearance of administrative simplicity. However, the very foundation of the co-occurrence approach, based on the total concentrations of a chemical(s) in sediment, is technically invalid; its application relies on additional technically invalid presumptions. Use of technically invalid evaluation approaches renders any assessment of the significance of sediment contamination, unreliable. This paper reviews the technical roots and assumptions of the co-occurrence-based SQGs, the fundamental flaws in the rationale behind their development and application, and their mis-application for sediment quality evaluation. It also reviews concepts and approaches for the more reliable evaluation, ranking, and clean-up assessment of contaminated sediments at Superfund sites and elsewhere.

INTRODUCTION

Many Superfund/hazardous chemical sites include waterbodies with sediments that have been contaminated by hazardous or otherwise deleterious chemicals associated with the site. The complexity of the remediation of these sites is compounded by the fact that the evaluation of the impacts of sediment-associated contaminants is, itself, complicated and not amenable to simple appraisal. With the need to assess, rank, and remediate contaminated sediments, an almost reflexive approach to the evaluation and management of “contaminated sediment” has been the quantification of the concentration of selected contaminants in the sediment. While chemical analysis is simple, renders numeric data for comparison, and lends itself to easy decision-making, it has been long-understood that there is no relationship between the total concentrations of chemical contaminants in sediments and toxicity, bioaccumulation, or other adverse impact.

Nevertheless, in an attempt to make simple chemical analysis useful, some have developed and advanced the use of co-occurrence-based “sediment quality guidelines” (SQGs). These are being adopted by state and other regulatory agencies for any number of purposes including sediment hot-spot identification and remediation, as well as

Superfund site remediation. This is a source of mounting concern, however, because of the inherent unreliability and technical invalidity of this approach. Use of technically invalid evaluation approaches renders any assessment of the significance of contamination, invalid. It also renders invalid conclusions regarding the necessity for, specification of the type of, and assessment of the sufficiency of any proposed or undertaken “remediation.”

This paper reviews the fundamental technical failings of the chemical concentration-based and co-occurrence-based sediment quality guideline approaches for assessing potential impact of sediment-associated contaminants. It also reviews an approach that can be followed to make more technically valid, cost-effective assessments for identification, ranking, remediation, and management of sediment-associated contaminants. While the focus is largely on the misapplication of this approach for evaluating sediment-associated contaminants at federal and state “Superfund” sites, the information presented is equally applicable to the evaluation, regulation, and remediation of sediment-associated contaminants in any situation.

WIDESPREAD PROBLEM

L. Evison of the US EPA Office of Emergency and Remedial Response summarized the magnitude of the problem of contaminated sediments at Superfund sites in a presentation entitled, “Contaminated Sediment at Superfund Sites: What We Know So Far,” at a US EPA and US Army Corps of Engineers (US ACOE) national contaminated sediment workshop (Evison, 2003). Also at that workshop, the Sediments Team Leader at the US EPA Office of Emergency and Remedial Response presented a discussion entitled, “Superfund Cleanup Issues at Contaminated Sediment Sites,” highlighting the breadth of the problem (Ellis, 2003). In his recent summary of the scope of the contaminated sediment problem, Bridges et al. (2004) noted that in 1997 the US EPA concluded that there were 1.2 billion cubic yards of surface sediments in the US that “pose potential risks.” They also indicated that there are approximately 350 contaminated sediment sites within Superfund, about 30 of which are “megsites” (>\$50 M). The megasites include Hudson River, NY (\$460 M); New Bedford Harbor, MA (\$361 M); Bayou Bonfouca, LA (\$90 M); Marathon Battery, NY (\$84 M); Triana/Tennessee River, AL (\$80 M); Fox River, WI (\$361 M); Silver Bow Creek, MT (\$97 M); Commencement Bay, WA (\$197 M); Bunker Hill (Coeur d’Alene Basin) and Housatonic, MA. According to Bridges et al. (2004), others sites are expected to be identified as investigation continues.

The US EPA Superfund program has established a “Contaminated Sediments in Superfund” website, <http://www.epa.gov/superfund/resources/sediment/> that contains additional information on the magnitude of the contaminated sediment issue at Superfund sites. The US EPA has also established a Superfund Sediment Resource Center (SSRC) where information is available on various technical aspects of managing contaminated sediments. Information on the SSRC and links to other website information sources (such US EPA programs, US ACOE, NOAA, academia, and consultants) are available at http://www.epa.gov/superfund/resources/sediment/ssrc_resources.htm.

Given the magnitude and extent of Superfund-associated and non-Superfund sediment contamination in the US and the costs associated with their “remediation,” it is imperative that technically valid assessments be made in the screening of sediments for determining

- the comparative urgency of attention,
- the environmental significance of the sediment-associated contaminants
- the effectiveness of remediation alternatives, and
- the sufficiency of remediation accomplished at Superfund and other sites.

“CO-OCCURRENCE”- BASED SQGs

As noted above, it has been understood for decades that there is no relationship between the total concentrations of chemical contaminants in sediments and toxicity, bioaccumulation, or other adverse impact that may be caused by those contaminants. Such impacts are controlled by the aqueous environmental chemistry of chemicals in the aquatic sediments, which, in turn, is controlled by the physical, chemical and biological character of the particular sediment/water environment. There is no simple protocol for making a reliable determination of the potential water/environmental quality significance of contaminants associated with a sediment; as discussed in a subsequent section, protocols that have proven reliable require site-specific assessment of the release, behavior, and availability of the sediment-associated contaminants. However, legislative and regulatory imperatives for identifying and ranking contaminated sediment areas and ordering them for remedial attention, as well as for remediation of Superfund sites, beg for a simple, quantitative assessment approach that feeds easily into a decision-making scheme. An illusion of an easy comparative quantitation of sediment contamination has been offered by numeric, co-occurrence-based “sediment quality guidelines.” Because of its simplicity and ease of application, that approach has been embraced and advanced by some for evaluation and regulation of sediment-associated contaminants, without regard to its foundation and presumptions that render it technically invalid for the evaluation or regulation of contaminants in sediments.

Basically, the “co-occurrence”-based sediment quality guidelines were developed by examining a group of sediments for biological impact or “effect” as measured any number of ways without consideration of what conditions or constituents were causing or influencing the “effect.” The concentrations of a few selected contaminants in those sediments were also measured. For each contaminant considered, the sediments were ordered by concentration, along with their associated assessments of their “effects.” In this ranked order, the lowest concentration of the contaminant in a sediment that had been identified as having an “effect” was noted; the concentration of that contaminant being considered became the basis for a “sediment quality guideline” and presumed to be a cause for concern in that, as well as any other, sediment. Fundamental but refutable presumptions made are

- that there is a causal relationship between the concentration of each constituent considered in a sediment and the water quality “effect” of that sediment,
- that the “effect” reported for each sediment was caused independently by each of the measured chemical constituents in that sediment, and

- that no other condition(s) or chemical(s) influenced the “effect.”

Tables of such “co-occurrences” of chemicals at a given concentration and an “effect” developed by Long and Morgan (1990), Long et al. (1995, 1998), and MacDonald et al. (1992, 2002) have formed the foundation of what are termed “co-occurrence” approaches for sediment quality evaluation.

In regulatory applications, “co-occurrence” information has been used, albeit incorrectly, to establish various “effects threshold” values based on statistical manipulation. Examples of co-occurrence applications are the “Apparent Effects Threshold” (AET), the ER-L and ER-M values developed from Long and Morgan's (1990) data presentation, the “Probable Effects Level” (PEL) values derived from MacDonald's et al. (1992, 2002) co-occurrence compilations, and “NOAA” “SQiRT” values. If a sediment contains a chemical in concentrations above the AET, ER-M, PEL, or similar value, the sediment is considered by some regulators or in proposed regulations to be polluted, triggering special consideration such as “remediation,” alternative methods of dredged sediment disposal, or additional control of discharges to the waterbody of the chemical that can accumulate in sediments.

SUMMARY OF TECHNICAL DEFICIENCIES

Failure to Consider Cause and Effect.

As discussed by Lee and Jones-Lee (1993, 1996b, 2004), in the development of co-occurrence-based SQGs, no consideration has been given to the actual cause of the “effect” reported for any particular sediment. Independent of the cause of the biological response, the same degree of response was attributed to (“co-occurred” with) the concentration of each individual chemical constituents measured in the sediment. Further, no consideration was given to the fact that total concentration is not related to impact. No consideration was given to many of the common chemicals and conditions that are, in fact, well-understood to cause sediment toxicity. No consideration was given to sediments that contain concentrations of the contaminant higher than the “effects”-associated concentration without exhibiting adverse impacts. The only basis for the so-called “guideline” concentration was the “co-occurrence” of that concentration of the contaminant in a sediment and the exhibiting by that sediment of some biological impact.

While there may be statistical manipulations to create “correlations” between toxicity and an exceedance of a sediment quality guideline, such relationships are not demonstrations of cause and effect, but rather are coincidental and thus unreliable for assessing of the cause of the biological impacts. It is entirely expected that sediments in urban/industrial areas contain chemical constituents that cause biological effects, along with elevated concentrations of what under some circumstances could be toxic chemicals, which are in non-toxic, unavailable forms. The fact that a chemical constituent exceeds a particular “sediment quality guideline” does not mean that that constituent is in any way related to biological effects, such as toxicity, bioaccumulation and/or changes in organism assemblages. The actual cause of the biological response seen could readily be another measured constituent, a constituent or constituents that was not measured or not

considered in the scheme, or a combination of constituents that, while measured, do not, individually or summed, exceed the “sediment quality guidelines.” Thus, without a cause-and-effect relationship, there can be no expectation that funds spent to achieve “sediment quality guideline” values will result in any improvement in sediment/water quality or that sediments targeted by the exceedance of guideline values are, in fact, of the greatest concern.

Failure to Consider Full Range of Potential Pollutants.

The failure to find any exceedances of an ER-M, ER-L, PEL or SQuiRT value in a sediment should never be assumed to be a reliable indication of a lack of impact of sediment-associated chemicals on aquatic life. Aside from the fundamental fatal defect in the basic premise of the approach, the co-occurrence-based sediment quality guidelines consider only a small number of the thousands of chemicals that can be present in sediments and can affect aquatic life. For example, Lee and Jones-Lee (2003a) discussed the fact that pyrethroid-based pesticides, one of the most common types of pesticides now used widely in agricultural and urban areas, tends to accumulate in sediments. Weston et al. (2004) reported finding aquatic sediments in the Central Valley of California with measurable toxicity and measurable concentrations of pyrethroid pesticides. The sediment quality “guidelines” do not include pyrethroid-based pesticides or other similar chemicals.

Failure to Consider Ammonia, Hydrogen Sulfide or Low-Dissolved Oxygen.

As discussed by Lee and Jones-Lee (1996a), ammonia, hydrogen sulfide and low dissolved oxygen are, by far, the most common causes of sediment toxicity. However, none of these common causes was included in the co-occurrence-based sediment quality guidelines. In their extensive laboratory and field studies of the release of contaminants from sediment discussed subsequently, Jones and Lee (1988) found that the most common cause of sediment toxicity in their sediments was ammonia. Numerous other investigators have found this, as well, making ammonia one of the most common causes of sediment toxicity. Co-occurrence-based sediment quality guidelines do not include consideration of ammonia as a potential cause of sediment toxicity, despite the fact that Long and Morgan made use of the authors’ sediment database. While they used the heavy metal, organochlorine pesticide and PCB data from the database, Long and Morgan ignored the ammonia and hydrogen sulfide data. 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 toxicities 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 any co-occurrence-based sediment quality guideline could be causing or contributing to sediment toxicity through additive or synergistic impacts with other chemicals for which there may or may not be an SQG. This type of chemical

interaction intensifies the importance of assessing the potential for sediment impacts through toxicity testing.

Failure to Consider Bioaccumulation as an Effect.

Bioaccumulation of chemicals to excessive levels in fish to cause them to be a threat to those who eat them, can occur at concentrations well-below those that are toxic to benthic organisms. Lee and Jones-Lee (2002a) reviewed approaches for evaluating excessive concentrations of organochlorine (OC) pesticides in aquatic sediments. They, also, discussed the unreliability of co-occurrence-based approaches, such as Long and Morgan or MacDonald values, for predicting the water quality impact of the OCs in sediments on the beneficial uses of waterbodies. Evaluation of sediments for these chemicals should be based on the toxicity of the sediment-associated chemicals to aquatic life and whether the sediment-associated OCs contribute to excessive bioaccumulation in fish and other aquatic life tissue.

Use of Co-Occurrence for “Screening”.

Some try to skirt the fundamental technical flaws in the co-occurrence-based SQG approach by limiting its use to “screening” sediments. However, using a patently unreliable “screening” tool can do nothing but provide patently unreliable results, which will serve to misdirect concern, responsibility, and funds for remediation, and leave real problem areas unaddressed. While sediments that exceed one or more “sediment quality guidelines” may, in fact, merit further investigation or remediation, the guideline values are meaningless for making that assessment. Under no circumstances should anyone assume that the exceedance of a guideline value implicates a sediment as a potential, or actual, cause of problems, much less rank sediments for attention. Further it cannot be assumed that not exceeding an SQG indicates that the sediment should be of diminished water quality concern. A reliable evaluation and regulatory program must be based on reliable assessments of the adverse effect and its cause.

Recent Reviews of the Unreliability Chemical Concentration-Based SQGs

As the need for sediment evaluation tools broadens and intensifies, SQGs have received wider audience and been embraced by regulatory bodies looking for an easily implementable approach. This has made the technical community more vocal on the unreliability of SQGs. Presented below is a summary of several presentations made at recent conferences that provide additional information on the applicability of SQGs.

SETAC 2004 Conference. Grapentine et al. (2004) reported on the results of a large study on the relationship between SQGs and sediment toxicity in selected nearshore sediment of the US-Canadian Great Lakes. They found that exceedance of co-occurrence-based sediment quality guidelines was a poor predictor of sediment toxicity.

Bay et al. (2004) reported that exceedance of co-occurrence-based SQGs was a poor predictor of sediment toxicity in southern California coastal bays and nearshore marine sediments, even when applied to limited areas.

MacDonald et al. (2004) presented a paper comparing sediment toxicity with SQG values in a number of areas including the Grand Calumet River in Northern Indiana. That presentation could leave the mistaken impression those SQG values had some validity for assessing the potential impact of sediment-associated contaminants in those sediments. Lee (2004b) discussed the unreliability of using MacDonald's co-occurrence-based SQGs to predict toxicity in Grand Calumet River sediments.

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) at which several presentations were made (including several invited keynote presentations) on sediment quality evaluation. A number 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. In his presentation, DiToro (2002) characterized any so-called agreement between the results of co-occurrence-based values and observed sediment toxicity as a "coincidence," and certainly not indicative of a cause-and-effect relationship. 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 do not form a reliable basis for evaluating the ability of co-occurrence-based values to predict sediment toxicity, and certainly not anything that can be extrapolated to sediments outside the dataset upon which they were based.

The focus of Chapman's SQA5 discussion (Chapman, 2004) was the assessment of bioavailable forms of contaminants in sediments. He pointed out the unreliability of trying to assess bioavailability based on chemical measurements, noting specifically that co-occurrence-based sediment quality guidelines fail to reliably assess bioavailable forms of contaminants.

As discussed by O'Connor (1999a,b; 2002), O'Connor and Paul (2000), O'Connor et al. (1998), Engler (2004), DiToro (2002), Chapman (2004), Burton (2004), Lee and Jones-Lee (1993; 1996a,b,c; 2004), the co-occurrence approaches are obviously technically invalid and unreliable for assessing cause-and-effect. From these assessments, it may be concluded that flipping a coin is a more reliable method of predicting sediment toxicity than exceedance of the guideline values.

Some, out of unawareness or obdurate advocacy, have claimed that co-occurrence-based SQGs are NOAA generated or supported values. Those values and approaches are not NOAA values. In fact, the Chief Scientist for NOAA Status and Trends program (T. O'Connor) has repeatedly pointed out the unreliability of a Long and Morgan sediment quality "guideline" as an indicator of sediment toxicity. In his paper entitled, "The Sediment Quality Guideline, ERL, Is Not a Chemical Concentration at the Threshold of Sediment Toxicity," O'Connor (2004) has provided additional information on the unreliability of using co-occurrence-based approaches for assessing sediment toxicity. He stated in his abstract, "*While it is being used as such, the sediment quality guideline ERL (effects range low) is not a threshold of any chemical concentration in sediment at*

which the probability of toxicity shows an abrupt increase. Similarly, while it has been done, there is no basis for assuming that multiple concentrations above an ERL increase the probability of toxicity.”

Long (2004) recently commented that it is possible to predict the broad scope of relationships between sediment chemical concentrations and toxicity. However, the error bars are very large, making such predictions worthless for site- or area-specific assessments. He concluded, “*The presumption that you can predict benthic impacts with sediment chemistry data alone is very weak.*”

EXAMPLES OF MISUSE OF CO-OCCURRENCE-BASED APPROACHES

Lee and Jones-Lee (2002b) summarized several examples of egregious misuse of co-occurrence-based SQGs in contaminated sediment remediation. The US EPA (2002) Region 9 is using co-occurrence based SQGs as cleanup objectives for organochlorine legacy pesticides in contaminated sediments in a TMDL program. The inappropriateness of this application is compounded by the fact that, as discussed above, the Long and Morgan and MacDonald “effects” did not include bioaccumulation as an effects measure, but rather focused on toxicity to aquatic life.

Even though there is substantial literature that shows that this approach is fundamentally unreliable, some state regulatory agencies, environmental groups, some parts of the US EPA and others have been attempting to develop approaches that utilize the total concentration data that have been developed as part of contaminated sediment reconnaissance studies, in regulating contaminated sediments.

State of California’s Attempts to Develop Sediment Quality Objectives

The California State Water Resources Control Board (SWRCB) is now trying to use a concentration-based approach for developing sediment quality objectives (SQOs)(standards) in its regulatory program. As discussed by Lee and Jones-Lee (2003b), the SWRCB is under a court decree to develop SQOs that can be used in a sediment quality regulatory program by August 2005. The goal is to identify, evaluate, and rank sediments in need of cleanup; NPDES permits from public and private wastewater dischargers and stormwater management agencies could then be altered to reduce the concentrations of constituents that exceed the SQOs.

In the late 1980s the California legislature adopted the Bay Protection and Toxic Cleanup Program (BPTCP) that required that the SWRCB developed SQOs that could be used to regulate polluted sediments. SWRCB staff adopted an approach for the use of the available funds that failed to focus on developing the information needed to be developed with the result that the SWRCB failed to develop SQOs. This led to litigation by an environmental group. The litigation settlement led to the current effort by the SWRCB to try again to develop SQOs.

The renewed effort is now in its 18 month. While the work plans for developing the SQOs have only recently been released, it appears that the SWRCB staff is making many of the same errors in attempting to develop SQOs as occurred in the BPTCP. Those who developed the work plans assert that the SQOs will be based on a weight-of-evidence approach involving developing numeric ranking of organism assemblage, sediment toxicity, and “chemistry” information. However, the approach for using the chemical concentration information is based on total concentration of chemicals relative to some co-occurrence-based sediment quality guideline. SWRCB staff states that the some yet-to-be-developed total concentration-based value is to be used as a “threshold” to indicate when the regulatory agency needs to take action. As discussed herein, this approach is not technically valid; its inclusion invalidates the results of the weight-of-evidence assessment.

This approach ignores the substantial literature that exists on the lack of a relationship between the total concentration of a chemical in sediments and its water quality impacts. As discussed above, O’Connor (2004) of NOAA, Chapman (2004), DiToro (2002) and Lee and Jones-Lee (2003a, b) have recently published information on the unreliability of total concentrations of a chemical as an indicator of sediment toxicity. The State Water Board staff and its selected “Science Team” (many members of which had been part of the failed BPTCP SQO development effort) have determined that the regional water boards’ staffs who will be implementing the SQOs into regulatory programs, do not have sufficient technical expertise to use aquatic chemistry, toxicology, and water quality information properly in evaluating sediment quality. They have deemed that therefore, the SQOs need to include “scaling factors” that would enable the regional board staff to use total concentrations chemical information without having to understand the unreliability of their use in evaluating the water quality/beneficial use impacts of the chemical. For the SWRCB staff to now propose total chemical concentration-based “scaling factors” for a chemical or chemicals in sediment, and presume that they are in some way related to sediment quality impacts as measured by aquatic life toxicity reflects a lack of understanding of, or disregard for, the basic principles of aquatic chemistry/toxicology. As discussed by Lee and Jones-Lee (2003a), the appropriate use of chemical information must be based on toxic/available forms of chemicals and not on the total concentration of a chemical or group of chemicals. As summarized by Lee and Jones-Lee (2004) (SQA5) several international recognized authorities have warned against trying to use numeric scaling in weight of evidence evaluation of sediment quality.

In order for the SQOs to be scientifically defensible they must not contain arbitrary components that can be easily shown to be technically invalid, such as the total concentration of a chemical when it is known that much, if not all, of the chemical is in a non-toxic form. It is important to consider the scrutiny that the SQOs will face in the regulatory process and the costs associated with their challenge. Regulatory boards and the courts are not likely to support the use of SQOs that can be shown to be based on invalid premises such as arbitrary scaling factors, inert-non-toxic chemical concentrations’ influencing the ranking of the pollutional characteristics of the sediment, etc. Technically weak or invalid SQOs will rightfully be challenged by dischargers or

others who could become responsible for paying for sediment cleanup. While not included in the literature cited in support of the currently proposed SWRCB SQO workplans, there is a substantial literature that shows that the exceedance of a co-occurrence-based SQG is a technically invalid tool for assessing the impact of sediment-associated contaminants. This makes any SQO that uses an SQG as a trigger value unreliable for regulating or screening sediments. All of these issues were brought to the attention of the SWRCB staff and Board prior to their beginning to develop SQOs.

Application of Co-Occurrence SQGS to NPL Superfund Sites

Notwithstanding the extensive literature demonstrating the unreliability of the co-occurrence SQG approach for evaluating the potential impact of chemicals in sediments, the site investigators at two different NPL Superfund sites at which the authors are US EPA TAG advisors to the public have proposed to use and/or have used chemical concentration-based SQGs as pass/fail values in an ecological risk assessment for the pollutants in the sites' aquatic sediments. One of these locations is the University of California, Davis (UCD)/US Department of Energy LEHR national Superfund site. 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 that Superfund site. However, as discussed by Lee (2004a), that approach can not be relied upon for characterization of LEHR site sediments with respect to their potential threat to aquatic life and, therefore, whether or not they should require remediation. A similar approach had been initiated at the Lava Cap Mine Superfund site near Nevada City, CA; the US EPA contractor had proposed to use co-occurrence-based SQGs in an ecological risk assessment for the site. Following on Lee's (2001) critique of the proposed approach, the US EPA changed the ecological risk assessment approach to focus on toxicity assessment rather than numeric SQGs.

The US EPA Superfund Program national headquarters' management has been concerned for a number of years about the potential for using co-occurrence-based sediment quality guidelines as a foundation for remediation decisions. The managers of US EPA Superfund have made it clear that that approach should not be followed, because of the unreliability of co-occurrence-based sediment quality guidelines. According to Ellis (2003), the US EPA Superfund Program 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.

BACKGROUND TO DEVELOPING SEDIMENT QUALITY EVALUATION

Numerous approaches have been proposed over the years for determining what constitutes an excessive level of a heavy metal, pesticide or some other potential pollutant in aquatic sediments. One of the earliest, and the most comprehensive efforts to develop and evaluate protocols for this purpose was undertaken by the US Army Corps of Engineers (US ACOE), which has been mandated by Congress to maintain the navigation depth of US waterways. With only unreliable bulk sediment guidelines for a few parameters available, an understanding that contaminant release and impact could not be determined based on sediment concentrations, and increasing awareness of the

environmental impacts of chemical contaminants often associated with sediment, US ACOE recognized the need for developing an expedient, technically sound approach to assessing the potential impact of sediment-associated contaminants.

In the 1970s the US Congress authorized and funded the US Army Corps of Engineers Waterways Experiment Station in Vicksburg, Mississippi, to investigate the water quality impacts of dredged sediment disposal. This \$30 million, five-year Dredged Material Research Program (DMRP) focused on evaluating and developing management approaches for the water quality impacts of dredged sediment disposal. The author G. F. Lee, served as an advisor to the US ACOE to help develop that program, and directed about a million dollars worth of the studies of the potential impacts of open-water disposal of contaminated dredged sediments.

In his DMRP studies, Lee and his graduate students evaluated the total concentrations of about 30 potential conventional pollutants, including heavy metals, organochlorine pesticides, PCBs, and nutrients in sediments from about 100 sites across the US. They also examined the behavior of those chemicals in many of those sediments as they were suspended in the watercolumn during the open water disposal; disposal sites were extensively monitored for total and soluble contaminants and physical characteristics before, during and following disposal operations. In addition, in conjunction with the field assessments, they worked with the US ACOE to develop and evaluate laboratory protocols to assess the release and potential toxicity of sediment-associated contaminants disposed of in open water. This effort generated about 50,000 data points; the findings were published in two reports (Lee et al., 1978; Jones and Lee, 1978). A summary of those studies has also been published by Lee and Jones-Lee (2000) in the **Handbook of Dredging Engineering**.

The work done in the DMRP served as the basis for the US EPA and Corps of Engineers to develop criteria for open water disposal of contaminated dredged sediments. The results clearly demonstrated that the total concentration of a particular chemical in a sediment, such as a heavy metal or the sum of all heavy metals, bears no relationship to the amount of that contaminant released to the watercolumn during disposal or to the toxicity of that sediment to aquatic life. Many of the sediments collected from urban/industrial waterways caused toxicity to aquatic life in laboratory tests. This toxicity, however, was largely independent of the total concentrations of various conventional pollutants, such as heavy metals and pesticides, as a result of their sediment-binding characteristics. While the identification of the cause of laboratory toxicity was beyond the scope of the studies, in subsequent work, the authors (Jones and Lee 1988) found a link between toxicity and ammonia released that was consistent with the known toxicity of ammonia. As noted above, ammonia was not even considered in the co-occurrence-based SQGs.

Thus, the results of the DMRP substantiated what was known at the outset of the studies – namely, that the total concentration of a constituent(s) in a sediment is not a reliable indicator of the potential impacts of that sediment on the beneficial uses of the waters in which the sediment is located. The results also led the US ACOE and the US EPA to

develop, in the late 1970's, biological effects-based dredged sediment water quality evaluation procedures for both freshwater and marine dredged systems (currently US EPA/US ACOE, 1991; 1998). Those protocols focused on aquatic life toxicity testing and assessing the potential for excessive bioaccumulation of hazardous chemicals from sediments. The dredging of contaminated "Superfund" and other sediments and their disposal requires attention to the same water quality/environmental quality and contaminant availability, transport, and impact issues that are considered in dredging and disposal of contaminated sediment associated with channel depth maintenance.

BPJ WEIGHT-OF-EVIDENCE APPROACH

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." In addition to updating the review of the unreliability of co-occurrence-based values for evaluating sediment quality, they gave particular attention to how technically valid sediment quality evaluations should be conducted. As they described, a best professional judgment (BPJ) triad weight-of-evidence approach that integrates information on aquatic toxicity and excessive bioaccumulation, alteration in organism assemblages relative to habitat characteristics, and chemicals as a cause of toxicity/bioavailability, should be used. Chemical information is incorporated into the approach through toxicity identification evaluations (TIEs) and sediment bioavailability testing to determine the toxicity/availability of the forms and mixtures of contaminants and characteristics in the sediment.

CONCLUSION

It will be important that other regulatory agencies not follow the California SWRCB and others in regulating sediment-associated chemicals based on SQGs and SQOs developed through, or influenced by, chemical concentration/co-occurrence approaches. Regulatory agencies should adopt the technically sound approaches of the US EPA Superfund, US Army Corps of Engineers; they advocate making sediment quality evaluations through effects-based approaches using aquatic chemistry, aquatic life toxicity, and excessive bioaccumulation of hazardous chemicals in higher trophic-level organisms. Chemical concentration information should focus on the availability/toxicity of the chemical in a TIE framework. Numeric scaling factors should not be used in sediment quality evaluation. Scaling schemes are arbitrary and can readily lead to a technically invalid assessment of sediment quality. The focus of the SQOs should be the use effect-based assessment of aquatic toxicity to several types of sensitive aquatic life and whether there is excessive bioaccumulation of hazardous chemicals edible aquatic life. Chemical studies should be used to identify the constituent(s) responsible for the toxicity through toxicity identification evaluation and the concentration of toxic/available constituents in the sediments. It should be combined with toxicity in forensic studies to identify the source of the toxic constituent(s). Where excessive bioaccumulation is found in edible fish and other aquatic life, the source of the bioaccumulatable chemicals should be

determined and sediment uptake studies be conducted to define the availability of the chemical in the sediments.

Adoption of this effects-based approach will led to a technically valid regulatory approach for defining the sediments that are having adverse impact on the beneficial uses of waterbody.

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