

Regulating Mercury in the Water Column and Sediments

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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.

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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 are in press. There is general agreement among experts in the field that a best professional judgment triad weight of evidence evaluation should be used for this purpose. A summary of this approach is presented in a subsequent section of this discussion.

Unreliability of Sediment Co-Occurrence-Based Approaches for Evaluating Aquatic Sediment Quality¹

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Beginning in the 1980s, several individuals ignored the then-well-established fact that the total concentration of a constituent in sediments is an unreliable predictor of aquatic life toxicity. The most notable of the inappropriate approaches that have been advocated for evaluating sediment quality is the co-occurrence-based approach first developed by Long and Morgan. Long and Morgan (1990) proposed co-occurrence-based sediment quality “guidelines” to predict the impact of sediment-associated chemicals on aquatic life living within or upon sediments. The co-occurrence-based approach as used by Long and Morgan and others such as MacDonald (1992) involves compiling sets of sediment data that contain some information on sediment biological characteristics, such as laboratory measured toxicity, or benthic organism assemblages (numbers and types of organisms) and the **total** concentration of potential pollutants. The potential pollutants are those that are typically considered in water quality assessments that have been found in some other non-sediment-related situations to be toxic to aquatic life. In the development of the Long and Morgan “guideline” values, the literature-reported concentrations are ranked according to increasing concentration. The sediment concentration which has a so-called “effect” is used to develop a co-occurrence between a sediment chemical concentration measured as a total concentration and a water quality “effect.”

Lee and Jones-Lee (1996a,b, 2002a) have provided a detailed discussion of the lack of technical validity of the co-occurrence-based approach for evaluating sediment quality. As they point out, this approach has a number of inherent, invalid assumptions.

¹ Excerpts from Lee and Jones-Lee (2002b). Updated in August 2003.

First, the approach presumes that there is a causal relationship between the concentration of each contaminant considered in sediment and the water quality impact of that sediment. Second, it presumes that the “effect” reported for each sediment was caused independently by each of the measured chemical contaminants in that sediment. Third, it presumes that no other chemical or condition not included in the database has any influence on the manifestation of the “effect” that co-occurs with the particular chemical of focus; ignored are several sediment-associated contaminants and conditions that are well-recognized to cause aquatic life toxicity, including ammonia, hydrogen sulfide, and low dissolved oxygen. Fourth, it presumes that the assessments made of “effects” of the sediments relate in some meaningful way to adverse impacts on beneficial uses of the waterbody in which the sediments are located.

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 values developed from Long and Morgan’s (1990) data presentation in the form of ER-L and ER-M values, 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, PEL, or similar value, 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 to the waterbody of a chemical that accumulates in the sediments.

As discussed by O’Connor (1999a,b, 2002), O’Connor and Paul (2000), O’Connor, *et al.* (1998), Engler (pers. comm.), Ditoro (2002), Chapman (2002), Burton (2002), Lee and Jones (1992), and Lee and Jones-Lee (1993; 1996a,b; 2000, 2002a), the co-occurrence approach is not a technically valid approach for assessing the potential impacts of chemical constituents in sediments. It has been well-known for over 30 years that the total concentration of a chemical constituent in sediments is not a valid measure of the toxic/available forms of constituents that can impact aquatic life through toxicity or cause other impacts. Further, and most important, co-occurrence is not a valid basis for simple systems with a limited number of constituents for evaluating the cause of a measured impact. Co-occurrence is obviously not valid for relating the concentrations of sediment-associated potential pollutants to observed laboratory-measured toxicity or altered organism assemblages in which the chemical constituent of concern is measured. In normal situations, there is no valid cause-and-effect relationship between the total concentration of a chemical constituent in a sediment and its responsibility for some measured “impact.”

As more and more data were accumulated that showed that the Long and Morgan and MacDonald guideline values were not reliable predictors of sediment toxicity and other impacts, Long and his associates tried to improve the reliability of the co-

occurrence-based approach by using the normalized summed quotients for several chemical constituents to establish the value for comparison with the biological characteristic of the sediments determined by their co-occurrence evaluation. While not discussed by Long and Morgan and others who advocate this approach, the magnitude of the normalized summed value depends on the constituents included in the data review. While for highly degraded areas there is some claimed success for the expanded approach, the expanded co-occurrence approach is also not valid to relate the concentration of a single chemical constituent or a group of constituents' impacts on sediment and overlying water quality/beneficial uses. DiToro (2002) has termed this claimed success of the expanded co-occurrence approach in predicting adverse impacts as a coincidence that has no cause-and-effect basis. The constituents responsible for the altered organism assemblages could be due to constituents not measured in the studies that served as the basis for establishing the coincidence. This is especially true since only a few of the many thousands of chemicals that are typically present in sediments receiving wastewater discharges from municipal, industrial and agricultural sources are measured in a sediment quality evaluation.

Even though it is well-recognized that the Long and Morgan (and, subsequently, MacDonald) co-occurrence approaches are not valid tools to evaluate the potential significance of a chemical constituent in a sediment, there is continuing use of the co-occurrence-based guideline values as regulatory goals upon which control programs, such as TMDLs, are based. This arises from a lack of knowledge and understanding of sediment chemistry and toxicology/biology by those who are responsible and/or interested in sediment quality management.

Those who advocate use of co-occurrence-based sediment guidelines frequently claim that there are insufficient funds available to conduct the needed biological-effects-based evaluation of sediment chemistry and toxicology/biology to properly evaluate the water quality significance of a constituent in sediments. Since total chemical concentration data are frequently available for sediments, and since co-occurrence approaches superficially seem to provide a way to use these data in sediment quality evaluation, the co-occurrence-based approach receives use by regulatory agencies in order to provide some "information" on sediment quality without having to spend any significant amount of additional funds in sediment quality evaluation. There is also a strong desire by some to do something in addressing sediment quality even if there is an inadequate technical information base to enable a reliable sediment quality evaluation to be made. Such an evaluation would require detailed study of the sediments' aquatic chemistry/toxicology/biology.

One of the most significant recent inappropriate uses of co-occurrence-based approaches for regulating sediment quality has been proposed by the US EPA (2002) Region 9. The Agency used the Buchman (1999) "NOAA Screening Quick Reference Tables (SQuiRTs)" to obtain TMDL targets for managing excessive bioaccumulation of organochlorine pesticides and PCBs in Upper Newport Bay, Orange County, CA, and its tributary San Diego Creek. The organochlorine chemicals of concern (for which there is excessive bioaccumulation in the Upper Newport Bay and its tributaries) are chlordane,

dieldrin, DDT, PCBs and toxaphene. In discussing numeric targets for organochlorine TMDLs, the US EPA (2002) states,

“As discussed in Section II, EPA evaluated the applicable water quality criteria and sediment and tissue screening levels to determine the appropriate numeric targets for these organochlorine TMDLs. We have prioritized sediment quality guidelines over tissue screening values and water column criteria. This decision is based on the following factors:

- 1) these pollutants are directly associated with sediments (i.e., fine particulate matter);*
- 2) sediments are the transport mechanism for these organochlorine compounds from freshwaters to salt waters;*
- 3) limited water column data are available to adequately describe the past or current conditions; and*
- 4) attainment of the sediment targets will be protective of the water column criteria and tissue screening values.”*

This approach and the reasoning in support of it are fundamentally flawed from several perspectives. First, the so-called “NOAA SQUIRT values” are co-occurrence-based values that evolved out of the Long and Morgan and MacDonald work. The biological effect used to establish these values did not consider bioaccumulation. The problem with these organochlorine chemicals in sediments is that they tend to bioaccumulate to excessive levels in edible fish tissue. Further, critical human health bioaccumulation concentrations in edible fish are frequently far below any concentration that is adverse to the host organism (fish). There is no relationship between the co-occurrence values of Long and Morgan and MacDonald and the potential for a chemical constituent in sediments to bioaccumulate to excessive levels in edible fish tissue.

With respect to the US EPA’s first and second justification listed above in support of this approach, the fact that a chemical tends to become associated with sediments is not justification for using co-occurrence to predict excessive bioaccumulation. As for the validity of the third justification, those familiar with bioaccumulation situations know that measurement of constituents of concern in the water column is not a reliable approach for predicting the bioaccumulation of organochlorine pesticides, PCBs, dioxins, etc. With respect to the fourth justification in support of this technically invalid approach, because of its fundamental unreliability, it is inappropriate to say that it is either under- or over-protective.

There is no reliable way to relate sediment concentrations of organochlorine pesticides and PCBs to excessive bioaccumulation of these chemicals in edible fish tissue except through site-specific studies. This issue is discussed in a subsequent section. The US EPA Region 9 has made a serious error in using the Buchman SQUIRT co-occurrence-based values. This approach should be immediately abandoned in favor of fish tissue target values developed by the CA Office of Environmental Health Hazard

Assessment. These values are appropriate TMDL goals for managing the excessive bioaccumulation of organochlorine pesticides and PCBs.

In April 2003 the US Army Corps of Engineers and the US EPA held a three-day international workshop on Environmental Stability of Chemicals in Sediments. This workshop focused on having experts in the field discuss the current state of knowledge of the water quality significance of chemicals in sediments. A number of the presentations dealt with sediment quality guidelines. None of the presenters supported the use of Long and Morgan co-occurrence-based approaches as regulatory guidelines for evaluating the water quality significance of chemicals in sediments. A number of the presenters discussed the unreliability of this approach. The PowerPoint presentations at this workshop are being posted at www.sediments.org.

In summary, co-occurrence-based so-called sediment quality guidelines should not be used for any purpose, including as screening values. For mercury, depending on the form of the mercury and the sediment characteristics, these values can underestimate or overestimate the water quality significance of mercury in sediments with respect to its potential to bioaccumulate to excessive levels in edible fish in the waterbody in which the sediments are located. The characteristics of the sediments influence the conversion of the various forms of mercury that can occur in sediments into methylmercury and its bioaccumulation in edible fish tissue to excessive concentrations. These issues can only reliably be addressed through site-specific investigations.

The issue of developing sediment quality guidelines is an issue that I have been concerned about since the early 1970s. During the 1970s I had over \$1 million in support from the Corps of Engineers to develop dredged sediment disposal criteria. A summary of our work on this effort has been published in

Lee, G. F. and Jones-Lee, A., "Water Quality Aspects of Dredging and Dredged Sediment Disposal," In: Handbook of Dredging Engineering, Second Edition, McGraw Hill, pp. 14-1 to 14-42 (2000).

This chapter in this handbook is available from <http://www.gfredlee.com/dredging.html> or directly from me at gfredlee@aol.com. As discussed, it is not possible to develop reliable numeric chemically-based sediment quality guidelines. The US EPA and Corps of Engineers in the 1970s adopted a dredged sediment regulatory approach based on chemical impacts, rather than concentrations.

The approach that should be followed in evaluating the water quality/sediment quality significance of a chemical constituent in sediments was defined by the US EPA and the Corps of Engineers in the 1970s for regulating contaminated dredged sediments. The US EPA/US ACOE (1991, 1998) developed dredged sediment quality evaluation manuals which provide detailed guidance on determining whether the management of a contaminated dredged sediment in a particular manner will impact water quality of the receiving waters where the management/disposal of the dredged sediment takes place.

These agencies used a biological-effects-based approach rather than a chemical-concentration-based approach.

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At the Chicago Aquatic Ecosystems and Public Health conference, Dr. Jones-Lee and I presented a paper, "Appropriate Use of Chemical Information in a Best Professional Judgment Triad Weight of Evidence Evaluation of Sediment Quality." This paper will be published in the proceedings of this conference. It discusses the approach that should be used to evaluate the water quality significance of chemical contaminants such as mercury in sediments. A preprint of our paper is presented below.

## **Appropriate Use of Chemical Information in a Best Professional Judgment Triad Weight of Evidence Evaluation of Sediment Quality<sup>2</sup>**

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### **Abstract**

There is increasing support for the use of a best professional judgment, non-numeric, triad weight of evidence approach for evaluating aquatic sediment quality. This approach is based on an integrated use of sediment toxicity/source of bioaccumulatable chemicals, organism assemblages and chemical information to determine the potential for constituents in sediments to be adverse to the beneficial uses of the waterbody in which the sediments are located. This triad approach is a far more reliable approach for evaluating whether a chemical constituent(s) associated with a sediment is adverse to sediment/water quality than a chemical-specific numeric sediment quality guideline. Significant problems occur, however, with the use of this approach by some in incorporating chemical information into the triad. The use of total concentrations of constituents and/or the exceedance of a co-occurrence-based so-called “sediment quality guideline” is technically invalid. Such an approach can distort the triad sediment quality evaluation because it incorporates information into the triad that is not related to the impact of the chemicals on aquatic-life-related beneficial uses. The chemical information that should be used in a triad evaluation includes the chemical forms and concentrations of the constituents of concern in the sediments that can be toxic to aquatic life or that can lead to bioaccumulation in higher-trophic-level organisms that are a threat to these organisms or those who use aquatic life as food. Sediment TIE information and information about the cause of toxicity or the amount of a bioaccumulatable chemical in a bioavailable form in the sediments should be used as the chemical component of a triad.

### **Introduction**

Increasing attention is being given to the use of a triad “weight of evidence” approach as a regulatory tool for water quality impact assessment and management. While there are a number of forms of weight of evidence, the approach that should be followed is a best professional judgment (BPJ) evaluation of aquatic life toxicity/bioaccumulation, aquatic organism assemblage information and chemical information. While there are some who attempt to develop numeric weight of evidence approaches in which arbitrary scale factors are assigned to each of the three components of the triad, such approaches are technically invalid, since the arbitrary scaling that is used for characterizing each of the parameters bears no relationship to the significance of

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<sup>2</sup> Published in part in the Proceedings of Sediment Quality Assessment (SQA5), Aquatic Ecosystem Health and Management Society, Chicago, IL (2002). Reference as: Lee, G. F. and Jones-Lee, A., “Appropriate Use of Chemical Information in a Best Professional Judgment Triad Weight of Evidence Evaluation of Sediment Quality,” Report of G. Fred Lee & Associates, El Macero, CA (2002).

the magnitude of each of these factors in relating the presence of a chemical constituent in a water or sediments to its impact on the water quality-beneficial uses of a waterbody.

Significant problems occur, however, with the use of the BPJ approach by some in incorporating chemical information into the triad. The use of total concentrations of constituents and/or the exceedance of a co-occurrence-based so-called “sediment quality guideline” is technically invalid. Such an approach can distort the triad sediment quality evaluation since it incorporates information into the triad that is not related to the impact of the chemicals on aquatic-life-related and other beneficial uses.

The BPJ weight of evidence approach should be based on the consensus of a panel of experts who, in a public, interactive, peer-review process, consider the information available, define what additional information is needed, and then render an opinion as to the integrated assessment of the information available on the significance of a particular chemical constituent in impacting the beneficial uses of a waterbody. The characteristics of the components of a BPJ weight of evidence approach which focuses on the appropriate use of chemical information are discussed in this paper.

### **Organism Assemblages**

Organism assemblage information on the numbers, types and characteristics of aquatic life and, as appropriate, terrestrial organisms such as fish-eating birds present at a potentially impacted site is a key component of the information base that needs to be obtained/critically reviewed in assessing the water quality impacts of chemicals on the beneficial uses of a waterbody. It should be understood, however, that a variety of physical (flow, temperature, sunlight, sediment, habitat alteration, etc.), non-potential-pollutant chemical (TDS, nutrients, organic constituents, hardness, alkalinity, etc.) and biological (reproductive cycles, disease, predation, etc.) factors other than chemical potential pollutants can affect the numbers, types and characteristics of aquatic life in a waterbody’s water column or sediments.

### **Toxicity/Bioaccumulation**

Aquatic life toxicity and/or bioaccumulation of potentially hazardous chemicals in aquatic organism tissue that is a threat to human health or higher-trophic-level organisms that use aquatic life as food are key components of a BPJ weight of evidence approach. However, as discussed by Lee and Jones-Lee (1996a), finding aquatic life toxicity in a water column or in sediments should not be interpreted to mean that this toxicity represents a significant impairment of the beneficial uses of the waterbody that are of concern to the public. It is not possible to relate laboratory-based sediment toxicity to water quality impairment. Many sediments have natural toxicity due to low dissolved oxygen, ammonia and hydrogen sulfide, yet have excellent fisheries and high water quality.

### **“Chemistry”**

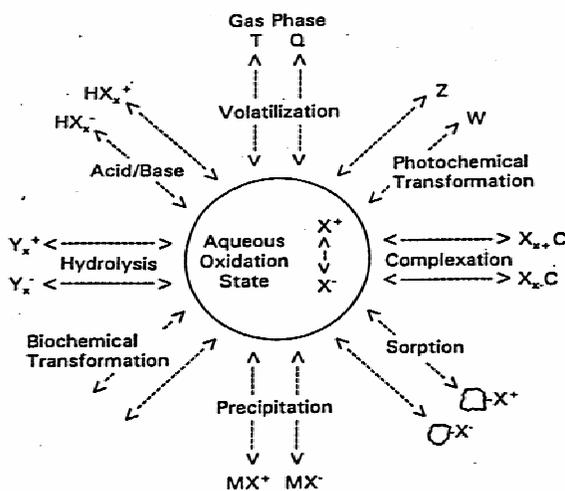
While chemical information is the third component of a water quality triad, there is considerable confusion and misinformation on the appropriate use of chemical information in a BPJ weight of evidence water quality evaluation. Because of a general

lack of understanding and appreciation of aquatic chemistry, the level of chemical information typically used in a weight of evidence evaluation is often based on a 1960s knowledge level of aquatic chemistry, where total concentrations of a few regulated constituents having water quality standards is the chemical information used. However, it has been well-known since the late 1960s that the total concentration of potentially toxic constituents in the water column and/or sediments is an unreliable basis for estimating the water quality impacts on the Clean Water Act designated beneficial uses of a waterbody.

**Aquatic Chemistry.** The reason that total concentrations of a selected chemical are unreliable in assessing water quality use impairments is that many chemical constituents exist in aquatic systems in a variety of chemical forms, only some of which are toxic/available. This relationship is shown in the aquatic chemistry “wheel” presented in Figure 1. The forms of a chemical, and therefore its impact on the beneficial uses of a waterbody, such as aquatic life propagation or wholesomeness of aquatic life used as food, depend on the concentrations of detoxification chemicals in the water or sediments. These types of chemicals, such as organic carbon, sulfides, carbonates, hydrous oxides, clay minerals, etc., react with potentially toxic forms of potential pollutants to detoxify or make unavailable the potentially toxic constituents.

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

Typically the water quality evaluation/management field operates at the “hub” of the wheel shown in Figure 1, where little or no consideration is given to the toxic/available forms of the chemical, which are controlled by the kinetics (rates) and thermodynamics (positions of equilibrium) of the reactions that lead to the chemical species that are present at the “rim.” Rarely is information available on the amounts of

the active forms of detoxification components of water and/or sediments and the characteristics of the reactions that occur with the potentially toxic/available forms. Because of this situation, it is not possible to predict, based on typical chemical analyses, the toxic/available forms of potential pollutants such as heavy metals, selected organics, nutrients, etc., that impact the beneficial uses of a waterbody which are of concern to the public.

Repeatedly, it has been found that when the significant technical deficiencies in the chemical information used in a weight of evidence evaluation are discussed with those who are proceeding to conduct the evaluation using unreliable or inadequate chemical information, such as total concentration of a chemical, those responsible claim that more appropriate chemical information is too complex to understand and difficult to obtain. The chemical total concentration approach can be characterized as an unreliable, “cheap” chemical investigation that, while providing some chemical information, is obviously unreliable for use in a weight of evidence approach.

***Chemical Composition versus Water Quality.*** A fundamental problem exists in the water quality field with many of its practitioners using chemical concentrations, as typically measured in US EPA or “Standard Methods” analytical procedures, as “water quality.” Water quality, by Clean Water Act requirements, is tied to the beneficial uses of a waterbody. Since it is not possible to translate chemical concentrations in either a discharge to a waterbody or within a waterbody to an impairment of beneficial uses, it is not appropriate to characterize a set of chemical analysis data as an assessment of water quality. Such data should be characterized as “water quality characteristics” that, when appropriately combined with other information, can provide inference on the relationship between a constituent(s) and the water quality characteristics of a waterbody which are of concern to the public.

A similar problem exists with respect to the term “chemistry” when referring to chemical data. Chemistry involves the evaluation of the thermodynamics and kinetics of the reactions that govern the distribution of chemical species in a waterbody (see Figure 1). A set of data on chemical concentrations is not “chemistry,” but provides information on the chemical characteristics of a waterbody.

Basically, the problem is that those who use total concentrations of a potentially toxic chemical, knowingly or through ignorance, use the presence of chemical constituents, regardless of impacts, as synonymous with pollutants -- i.e., constituents which adversely impact the beneficial use of waterbodies. This is an inappropriate approach which ignores the aquatic chemistry of constituents of concern, and can readily cause massive waste of public and private funds in unnecessary chemical constituent control. This approach is also a significant deterrent to obtaining the information needed for a reliable assessment of the beneficial use impacts of the unregulated constituents -- i.e., those without water quality criteria/standards -- since the focus is on chemical concentrations rather than chemical impacts.

***Association of Chemical Concentrations with Impacts.*** As long as regulatory agencies, environmental groups and others continue to use unreliable chemical information in a weight of evidence triad, such as total concentrations of a few chemicals, to “associate” the presence of a measured chemical constituent to a water quality impact (such as toxicity, bioaccumulatable chemicals, changes in organism assemblages, etc.), the BPJ weight of evidence approach is not a reliable tool, since one of the key components of the triad is fundamentally flawed. While toxicity and excessive bioaccumulation are readily measurable characteristics of an aquatic ecosystem, as are the numbers, types and characteristics of aquatic life in a particular system of concern, as well as the total concentrations of chemical constituents present in this system, the total concentration measurements often have no relationship to the impact of potential pollutants on beneficial uses.

***Unreliability of Co-Occurrence-Based Sediment Quality Guidelines.*** One of the most significant examples of inappropriate use of chemical information in a water quality assessment is the use of the Long and Morgan (1991), Long, *et al.* (1995), or Long and MacDonald (1998) co-occurrence-based so-called “sediment quality guidelines.” These “guidelines” are based on total concentrations of a few selected chemical constituents that co-occur with some type of biological impact/response. As discussed by Lee and Jones-Lee (1993), there is no cause-and-effect relationship established in the co-occurrence-based values. The fact that these co-occurrence-based approaches are based on total concentrations means that they are fundamentally flawed, and while there may be so-called “correlations” between toxicity and an exceedance of a sediment quality guideline, this is a coincidental situation that is an unreliable assessment of the cause of the biological impacts.

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 can readily be due to either a constituent(s) that is not measured or a combination of constituents that, while measured, do not exceed the “sediment quality guidelines.” Basically, in the co-occurrence-based approaches, “success” relies on the fact that chemical constituents derived from urban industrial areas, while having biological effects, often occur in the presence of other constituents which, while in non-toxic, non-available forms, are present in elevated concentrations. While the Long and Morgan, MacDonald, etc., “sediment quality guidelines” can, under some situations, indicate that there is potential for toxicity in sediments when several guideline values are significantly exceeded, under no circumstances should anyone assume that the exceedance of a guideline value represents a cause-and-effect relationship that can be used to determine the likely cause of a biological response.

As discussed by Lee and Jones-Lee (1996b), co-occurrence-based sediment quality guidelines are a cheap “chemistry” approach that gives those who have little or no understanding of aquatic chemistry and water quality issues a means of incorporating so-called “chemical information” into a weight of evidence approach without having to become knowledgeable in aquatic chemistry and toxicology relationships that are

fundamental to any proper water quality assessment with respect to the cause of a water quality problem.

The state of California Water Resources Control Board (WRCB, 1998) adopted the Bay Protection and Toxic Cleanup Program (BPTCP) Water Quality Control Policy for Guidance on Development of Regional Toxic Hot Spot Cleanup Plans, which allows the Regional Water Boards to use elevated concentrations of constituents in sediments as a basis for identifying Principal Responsible Parties (PRPs) for a sediment “Superfund” (“Aquafund”) to pay for clean-up of contaminated sediments that are designated as a “toxic hot spot.” Further, this same “association” approach is supported under the WRCB BPTCP Policy to allow the Regional Water Boards to amend NPDES wastewater discharge permits for dischargers to limit the concentrations of a constituent that is present in elevated concentrations in the sediment or water column without investigating whether the elevated concentrations of the constituent are, in fact, causing adverse impacts to the beneficial uses of a waterbody.

Lee (1998a,b) and Lee and Jones-Lee (1998) have provided detailed discussions on the technically invalid approaches that the WRCB adopted in the BPTCP policy. They point out that this policy can readily lead to inappropriate designation of “toxic hot spots” and PRPs and inappropriate modifications of NPDES permits that can cause large-scale unnecessary expenditure of public and private funds in the name of water pollution control that will have little or no impact on the beneficial uses of the waterbodies in which the sediments of concern are located.

There have been a number of notable examples of inappropriate approaches that have developed from the inappropriate application of co-occurrence-based sediment quality guidelines. One of the most notorious of these is the Santa Monica Bay Restoration Project, where the regulatory agencies from the local LA Regional Water Board, through the US EPA, endorsed having the public in the LA region spend \$42 million over five years to control, on a mass-emission strategy basis, the concentrations of heavy metals and other constituents commonly present in urban area and highway stormwater runoff. This policy was justified based on finding lead in Santa Monica Bay sediments at concentrations above a co-occurrence-based sediment quality guideline.

It was suggested to these regulatory agencies (Lee and Jones-Lee, 1994), prior to the adoption of the Bay Restoration Plan, that the lead in the Santa Monica Bay sediments may be in an inert, non-toxic form, as frequently occurs in marine sediments. It was further suggested that before any restoration plan of this type is adopted (one that causes the public to make such a massive expenditure in the name of water pollution control and Santa Monica Bay restoration), toxicity testing should be done on the sediments to determine whether the lead present at elevated concentrations is in a toxic/available form and, if it is, whether it is a significant cause of impairment of the beneficial uses of Santa Monica Bay. These recommended approaches were ignored by the regulatory agencies, including the US EPA, and these agencies and environmental groups blindly accepted the exceedance of a single co-occurrence-based sediment quality guideline as sufficient reason to cause the public to spend \$42 million over five years in

controlling the input of 22 constituents of concern to stormwater runoff in the Los Angeles region.

US EPA Region 9 (2002) has proposed to use co-occurrence-based sediment quality guidelines as the basis for establishing organochlorine pesticide and PCB excessive bioaccumulation TMDL targets for controlling excessive bioaccumulation in edible fish taken from the Upper Newport Bay in Orange County, California. However, as discussed by Lee and Jones-Lee (2002), this approach is technically invalid for a variety of reasons, including the fact that there is no relationship between the total concentrations of DDT, chlordane and PCBs in a sediment and the bioaccumulation of these chemicals in lower- and upper-trophic-level forms of aquatic life. Further the so-called “biological effects” which are used in the co-occurrence relationships were not based on bioaccumulation. US EPA Region 9’s approach for controlling excessive bioaccumulation of organochlorine pesticides and PCBs in Upper Newport Bay fish is obviously technically invalid and should be abandoned.

As discussed by O’Connor (1999a,b, 2002), O’Connor and Paul (2000), O’Connor, *et al.* (1998), Engler (pers. comm.), Ditoro (2002), Chapman (2002), Burton (2002), Lee and Jones (1992), and Lee and Jones-Lee (1993; 1996a,c; 2000, 2002), the co-occurrence approaches are technically invalid and unreliable for assessing cause and effect which can be used as the basis for a regulatory program. O’Connor, in an assessment based on the NOAA Status and Trends, as well as US EPA EMAP databases, stated that,

*“All these criteria are better than random selections in identifying toxic sediment but they are not reliable. They are all more often wrong than right and should not be used, by themselves, to imply anything about biological significance of chemical data.”*

Co-occurrence-based approaches for estimating sediment toxicity provide a method by which total concentration chemical data can be used by those who are either unknowledgeable or unwilling to admit their technical deficiencies in aquatic chemistry and toxicology as applied to water quality evaluation and management. They should not be used in sediment quality evaluation or in a BPJ weight of evidence evaluation.

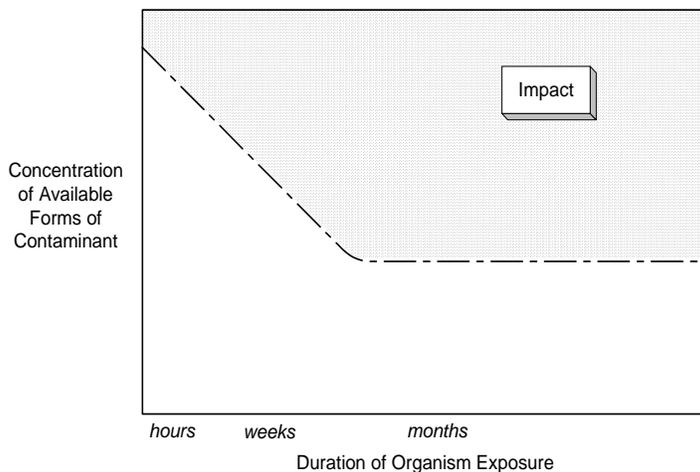
### **Recommended Approach for Incorporation of Chemical Information into a BPJ Weight of Evidence Water Quality Evaluation**

The recommended approach for the use of chemical information in a BPJ weight of evidence evaluation on the cause of a water quality impairment involves reliably defining the water quality/use impairment that is of concern. Basically, adopting this approach requires that the emphasis in water pollution control programs be shifted from focusing on chemical concentrations that exceed worst-case-based standards/guidelines to reliably assessing chemical impacts on the beneficial uses of a waterbody. Rather than measuring copper, lead, zinc and cadmium that typically occur in street and highway stormwater runoff at concentrations above US EPA worst-case-based water quality criteria and state water quality standards based on these criteria, the chemical impact

evaluation approach determines whether the water or sediment of concern is toxic. If it is toxic, then, through toxicity identification evaluations (TIEs), an assessment is made as to the cause of this toxicity. Jones-Lee and Lee (1998) describe an Evaluation Monitoring approach that has been developed to focus on chemical impacts rather than chemical concentrations.

If toxicity is found, then an assessment should be made as to whether this toxicity is significantly adverse to the waterbody's beneficial uses. It should not be assumed that toxicity measured in a standard toxicity test necessarily translates to toxicity that is significantly altering the numbers, types and characteristics of desirable forms of aquatic life in a waterbody. This is especially true for situations such as urban area and highway stormwater runoff, where there can be short-term pulses of toxicity associated with a runoff event that are not of sufficient magnitude and duration to exceed the critical magnitude and duration needed to be adverse to important forms of aquatic life in a waterbody. Figure 2 shows the relationship between duration of exposure and toxicity that typically occurs, where high concentrations of standard laboratory-measured toxicity can be tolerated by some forms of aquatic life, provided that the duration of exposure of this toxicity is short, compared to the critical toxicity/duration of exposure relationships that exist in ambient waters for aquatic life.

**Figure 2**  
**Critical Concentration/Duration of Exposure Relationship**



Under the total concentration “association” approach, the elevated copper, zinc, lead and sometimes cadmium in urban area and highway stormwater runoff above US EPA worst-case-based water quality criteria/standards is assumed to be toxic, and it is also assumed that this toxicity is significantly adverse to the beneficial uses of the waterbody. This “association”-based identification of copper, zinc, lead and cadmium as significant “pollutants” derived from urban area and highway stormwater runoff could cost the public large amounts of funds in treating the runoff waters to remove these

metals so that their concentrations do not exceed worst-case-based water quality criteria/standards by any amount more than once every three years.

As an example of the high costs of eliminating exceedances of worst-case-based water quality criteria/standards, it is estimated that to control the concentrations of these heavy metals in urban area street and highway stormwater runoff in the Los Angeles area so that they do not cause exceedances of water quality standards, it will cost the public in excess of \$50 billion for collection and treatment works. This expenditure would be made under conditions where studies in the San Francisco Bay region, Sacramento, Stockton and Orange County, California, have shown that the heavy metals in urban area street and highway stormwater runoff are in non-toxic forms (Lee and Taylor, 1999). While urban street and highway stormwater runoff in these areas is toxic to *Ceriodaphnia* (a freshwater zooplankton), this toxicity is due to the organophosphate pesticides diazinon and chlorpyrifos, which are not regulated based on water quality standards. The adoption of Evaluation Monitoring, which makes use of a BPJ weight of evidence approach, can be highly effective in focusing water quality evaluation and management resources on real, significant water quality problems.

The approach that should be followed in using chemical information to assess the potential for a particular chemical to cause a water quality impact involves the appropriate use of TIEs to define whether a particular constituent that occurs at concentrations above a water quality standard is in a toxic/available form, and/or to determine the chemical(s) that cause the toxicity in water or sediments. This approach requires the allocation of sufficient funds to determine the characteristics of the constituents/conditions of concern, with particular emphasis on properly defining toxicity and water quality cause-and-effect relationships. Those with limited aquatic chemistry/toxicology expertise and experience sometimes comment that, since there are no “standard” TIE procedures for determining the cause of toxicity in sediments, it is not possible to identify the cause of toxicity in sediments. Identification of the cause of toxicity in sediments requires that individuals knowledgeable in aquatic chemistry, aquatic toxicology and water quality provide guidance on and appropriate interpretation of the kinds of chemical and toxicity studies that are needed to appropriately incorporate chemical information into assessing the water quality significance of chemical constituents in impacting the beneficial uses of a waterbody.

### **Addressing Conflicting Technical Information**

As discussed above, the BPJ weight of evidence approach should be conducted by a panel of experts knowledgeable in the topic areas. If disagreements arise among panel members or between the panel and others, then a full, public interactive peer review should be conducted of the issues in disagreement. Lee (1999) has presented a recommended approach for addressing conflicts on interpretation of information on water quality issues. Adoption of the public, interactive peer review process recommended by Lee (1999) would be a major advance over the typical adversarial approach in incorporating technically reliable science into public policy development.

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## **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