Summary of Issues Pertinent to Regulating Bioaccumulatable Chemicals

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From September 11-13, 1996 the US EPA held a National Sediment Bioaccumulation Conference in Bethesda, Maryland devoted to a selected review of the current state of knowledge on the regulation of chemical constituents present in aquatic sediments that tend to bioaccumulate to "excessive" amounts in aquatic organisms. The speakers at this conference were selected by the Agency.

The topic of bioaccumulation of chemicals from water and sediments is an area in which the senior author, Dr. G. Fred Lee, has worked since the mid-1960s. He has been particularly concerned about developing reliable approaches for regulating chemical constituents in sediments that could lead to excessive bioaccumulation of these constituents in higher trophic-level organisms that would impair the "water quality" of the waterbody in which the organisms and sediments are located. In the 1970s as part of the work that Dr. Lee's associates and he did on the Corps of Engineers Dredged Materials Research Program in developing dredged sediment disposal criteria, they specifically addressed the issue of how to regulate chlorinated hydrocarbon pesticides, PCBs and mercury in sediments that could be bioaccumulated directly from the sediments or through sediment water exchange from the water that would lead to excessive bioaccumulation in higher trophic-level organisms. At that time, it was concluded that there was no reliable way to predict the amount of bioaccumulation that would occur in higher trophic-level organisms based either on water or sediment concentrations of the bioaccumulatable chemicals.

A review of these issues and the authors' subsequent experience in this topic area has been published by Lee and Jones (1992) and Lee and Jones-Lee (1994). As discussed in these papers, since it is not possible to predict bioaccumulation that will occur in higher trophic-level aquatic organisms associated with a particular concentration of a potentially bioaccumulatable chemical in a waterbody's water or sediments, the authors recommend that the only way to reliably address this issue is to actually measure the bioaccumulation that occurs in order to determine whether there is, in fact, a water quality problem due to the excessive concentrations of chemical constituents in the aquatic sediments of a region.

The US EPA National Sediment Bioaccumulation Conference provided an opportunity to become familiar with the current state of knowledge on sediment bioaccumulation issues.

Presented herein is a summary of the key issues that were discussed at the US EPA National Sediment Bioaccumulation Conference that are pertinent to developing technically valid, cost-effective approaches for managing chemical constituents present in aquatic sediments that tend to bioaccumulate in higher trophic-level organisms, either impairing the organism populations or causing these organisms to be considered "hazardous" for use as food by humans and/or wildlife. This discussion presents a synopsis of information presented by various speakers at the conference as well as the authors' many years of experience working in this topic area.

This discussion has been prepared as a background document that can provide guidance to the approaches that should be used in developing the Sacramento River Watershed Toxics Control Program. Bioaccumulation of potentially hazardous chemicals has been selected by the stakeholders in this watershed-based water quality management program as one of the major areas of concern. The Toxics and Monitoring Subcommittees of this program are in the process of formulating programs designed to address "toxics" issues. Specific guidance is provided herein on how bioaccumulation should be incorporated into this program that is based on current knowledge of sediment and/or water higher trophic-level aquatic organism bioaccumulation issues. This guidance can also be used for many other waterbodies and their respective watersheds to develop programs that appropriately formulate approaches for determining whether excessive bioaccumulation is occurring and, where found, the development of control programs to control its occurrence.

Laboratory Measurement of Bioaccumulation

It is possible to measure using aquarium-type tests and contaminated sediments the amount of bioaccumulation that will occur in benthic organisms (worms). It is not possible, however, to translate the concentrations of contaminants in sediments or the concentrations in benthic organism tissue to the concentrations in fish and other higher trophic-level organisms in real world situations. The sediment bioaccumulation measurements tend to significantly over-estimate the real bioaccumulation that will occur in higher trophic-level organisms in ambient waters.

Bioaccumulation Factors

Bioaccumulation Factor (BAF) or Biota-to-Sediment Accumulation Factor (BSAF) are highly site-specific and cannot be reliably extrapolated from one site to another or even at one site upon significant changes in the characteristics of the sediments associated with sediment remediation programs. Bioaccumulation factors from water and/or sediments are gross over-simplifications of the real world situation. The typical bioaccumulation factors that were used in the US EPA water quality criteria development (1987 "Gold Book") tend at many sites to over-estimate, in some cases by orders of magnitude, the bioaccumulation that will occur in real world situations in higher trophic-level organisms.

Biokinetic (Food Web) Modeling of Bioaccumulation

While it is possible to develop (curve fit) biokinetic models that will track to some extent the bioaccumulation that occurs in a particular waterbody for a particular type of organism and chemical, these models have limited predictive capabilities with respect to determining the degree of bioaccumulation that will occur in higher trophic-level organisms after remediating sediments to a certain extent. While these models simulate more closely than a simple two-black box or three-black box bioaccumulation sediment accumulation factor, they still do not properly address to any significant degree the highly heterogenous nature of particles in sediments and the absolute as well as relative binding capacity of each major type of particle.

It should not be assumed that the highest concentrations of the constituent in sediments necessarily leads to the source of constituents that bioaccumulate. Those constituents that occur in highest concentrations in sediments may be more tightly bound to particles than those that occur on other types of particles with different types of organic carbon or other factors that tend to control the release of constituents from the sediment particles to the organism, either through release to the interstitial waters and exchange with the overlying waters or through bio-uptake by benthic and epibenthic organisms.

Water Quality Criteria for Protection Against Excessive Bioaccumulation

The US EPA's approach toward developing water quality criteria for chemicals that tend to bioaccumulate typically utilizes a bioaccumulation factor that represents a worst-case situation that was observed at the time the criteria were developed. For example, for PCBs, the water quality criterion was based on Lake Superior water situations where a certain concentration of PCBs in the water was found to co-occur with a certain concentration of PCBs in large predator fish, such as lake trout. It has been known for many years, however, that concentrations of PCBs in other waters do not result in the same bioaccumulation of PCBs in similar kinds of fish. The work of Dr. Lee's graduate students and Dr. Lee in the 1970s demonstrated this situation with respect to the bioaccumulation of PCBs in fish in the New York Harbor/Bight area. The American Fisheries Society's PCB subcommittee (Veith *et al.*, 1979) in their review of the US EPA "Red Book" criteria of 1976 cautioned against assuming that a bioaccumulation factor that was developed for PCBs in Lake Superior would be applicable to other waterbodies. With few exceptions, the actual amount of bioaccumulation that occurs for a given concentration of a chemical in water and/or sediments is highly site-specific and cannot be extrapolated to other situations. This makes the US EPA's bioaccumulation-based water quality criteria highly over-protective in most situations.

Based on the discussions at the US EPA's National Sediment Bioaccumulation Conference, the only reliable approach today for determining whether there is excessive bioaccumulation in a particular type of organism that is present in a particular waterbody during a certain time of the year is to actually measure the tissue residues in that organism. All other approaches, such as BAF, BASF, biokinetic models and laboratory-based bioaccumulation test

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results, that are being used to estimate potential bioaccumulation in higher trophic-level organisms are unreliable.

The basic problem with the various approaches that are being used to estimate bioaccumulation is that none of them properly incorporates the aquatic chemistry and transport fate information in estimating tissue residues in an aquatic organism based on either sediment and/or water concentrations of the chemical of concern.

Factors Influencing Bioaccumulation

Generally, it is found that for the chlorinated hydrocarbon pesticides and other highly hydrophobic chemicals that tend to bioaccumulate, greater bioaccumulation occurs in organisms with higher fat content. Any bioaccumulation measurements should also include measurement of fat content. Care must be exercised, however, to reliably determine fat content since there are problems with some of the procedures that are being used.

It should not be assumed that the areas with the highest concentrations of the chemical in water and/or sediments is the area from which the chemical leading to excessive bioaccumulation is derived. Aquatic life toxicity due to chemical constituents in water and sediments bioaccumulation is a function of available forms of constituents. Available forms cannot be predicted based on chemical concentrations. Such predictions must consider the mechanism of binding of the constituents in the sediments. This binding, in turn, determines the amount of constituents that is in equilibrium with interstitial (pore) water.

There is substantial evidence that for some chemicals the concentrations of binding materials, such as TOC for some organics and sulfides and iron hydroxide for metals, tend to reduce the availability of chemical constituents for bioaccumulation in aquatic organisms within the sediments and in the waterbody in which the sediments are located. It is also becoming more evident that total organic carbon normalization of sediment concentrations of potentially hazardous chemicals as is proposed to be used in the US EPA's proposed sediment quality criteria is not a constant value. The TOC toxics/bioaccumulatable chemical coupling is not a single factor, but can vary by a factor of 10 or more.

Relating Bioaccumulatable Chemical Concentration to Organism Toxicity-Ecological Effects

Over the past 30 years, there have been numerous attempts to try to relate tissue residues (organism body burden) to toxicological impacts on the organisms that have accumulated the residue. While considerable data exist on the amount of heavy metal or organics bioaccumulated in organism tissue that were found in organisms that have experienced toxicity due to the same chemical, there is limited ability today to relate organism toxicity to bioaccumulated residues (body burdens). At this time, there is no reliable relationship between accumulated residues and toxicities. This is the result of the fact that accumulated residues are typically in non-target organ areas, such as fish muscle. The toxicity, however, would be

specifically directed to a particular organ, such as through the gills, where the toxicity may not result in an accumulated residue.

A variety of other approaches are being used to try to estimate the excessive concentrations of chemicals in fish and other aquatic organism tissue that are harmful to the organism that has accumulated the residue or to higher trophic-level organisms. These range from so-called "NAS" criteria to various approaches that involve a comparison of the concentration in an organism tissue to some background (reference) concentration for organisms taken from another location. The California Water Resources Control Board staff made a significant error several years ago in interpretation of the reliability of the so-called NAS (National Academy of Sciences) tissue residue values. These values are not reliable values as used by the Board and regional boards. They are not recognized by the National Academy of Sciences as appropriate values for such use. The US EPA does not recognize them as valid values.

The senior author (Dr. Lee) was involved with the National Academies of Science and Engineering in the early 1970s as an invited peer reviewer of the "Blue Book of Water Quality Criteria" from which these values were derived. He has discussed this issue with Carlos Fetterolf, former Director of Aquatic Biology in the Department of Natural Resources for the state of Michigan and the coordinator for the "Blue Book" development, who was shocked that anyone was using these values as reliable values today for judging excessive bioaccumulation of chemicals in aquatic life.

It is very important to recognize that elevated concentrations of a chemical in aquatic organism tissue cannot and should not be interpreted to mean that the organism that has accumulated the residue or higher trophic-level organisms are being adversely impacted by the elevated concentrations. Many organism tissues, including man, accumulate residues of chemicals without apparent harm. There are, however, for some chemicals, concentrations of accumulated residues that represent significant threats to the use of these organisms as food by higher trophic-level organisms.

About all that can be said reliably at this time is that accumulated residues in an aquatic organism demonstrate an exposure of the organism to available forms of a constituent of concern. They cannot be used to reliably assess adverse impacts on the organism. The significance of an accumulated residue must be judged based on its threat to higher trophic-level organisms.

Human Health Effects

The primary focus of concern with respect to bioaccumulation of hazardous chemicals must be on those chemicals that bioaccumulate to a sufficient extent in animal organism tissue to cause the organism to be considered hazardous to those who use the organism as a source of food. While in the past, Food and Drug Administration (FDA) Action Levels were used to judge excessive bioaccumulation, there is increasing agreement today that the focus of assessing

what constitutes excessive bioaccumulation should be based on the US EPA's risk assessment approach in which the hazard of the chemical is evaluated based on its potential to cause cancer or, for non-carcinogens, toxicity in humans. This approach considers the cancer slope factor, the average amount of fish or other organisms consumed per day and the concentration of the hazardous chemical in the ingested food. It is becoming widely recognized that the US EPA's "Gold Book" fish consumption rates of 6.5 grams per day are low compared to the actual consumption that occurs by some populations (those whose diet is primarily fish from a local waterbody).

The FDA Action Levels are considered by many as too high an allowable concentration in an aquatic organism edible tissue of a potentially hazardous chemical. The differences between FDA and risk-based approach estimates of allowable edible organism tissue residues is thought to be due to the fact that the FDA incorporates economic and other factors into establishing an Action Level. It is important to point out, however, that there are, especially for mercury, significant differences between US EPA and FDA interpretation of the information that is available on the hazards of mercury to humans. It is the FDA's position that the US EPA is significantly over-estimating the hazard of mercury to humans in establishing their risk-based allowable tissue residues.

While the US EPA developed some wildlife-based bioaccumulation criteria as part of the Great Lakes Initiative, these criteria have limited reliability in predicting the bioaccumulation that will occur in other waterbodies for the same higher trophic-level organism as well as for other types of higher trophic-level organisms. It will likely be decades before reliable water quality criteria can be developed that can be used to regulate bioaccumulatable chemicals for the protection of wildlife. For now, it will have to be assumed that wildlife will be protected to some degree by human health-based criteria. Normally, except for those who utilize local fisheries as their primary source of food, this approach underestimates the hazard that chemicals represent to wildlife since some forms of wildlife will tend to utilize fish and other aquatic organisms as their primary source of food and thereby receive a higher exposure to hazardous chemicals that have bioaccumulated in the fish.

Deficiencies in Current US EPA Regulatory Programs for Bioaccumulatable Chemicals

Currently, the US EPA and other regulatory agencies are persisting with a highly inappropriate, technically invalid, regulatory approach of basing the assessment of the excessive concentrations of chemical constituents in water and/or sediments on a national bioaccumulation factor for a particular chemical that is applicable to all waters within the US. The Agency is using a convoluted approach for establishing water quality criteria for bioaccumulatable chemicals in which a bioaccumulation factor is developed based on an observed water concentration tissue concentration relationship that is developed for a particular organism in a particular waterbody. The bioaccumulation that has occurred is then developed into a BAF that is then used to develop a water quality criterion designed to keep the tissue residue in the organism below some critical level. In the past, the FDA Action Levels were used; today, there

is increasing use being made of risk-based concentrations in aquatic organism tissue that consider the hazard associated with the use of the organism as human food. It has been recognized for over 20 years that this approach is technically invalid. There were several papers presented at the US EPA National Sediment Bioaccumulation Conference which demonstrated that what was known 20 years ago in this area is applicable today.

The US EPA and others are following similar approaches for regulating chemical constituents in sediments. While there are no proposed national sediment criteria for bioaccumulatable chemicals, site-specific criteria are being developed as part of sediment remediation programs. Great caution must be exercised in the use of site-specific BAFs and BSAFs in predicting the impact of sediment remediation programs on the concentrations of hazardous chemicals that will occur in higher trophic-level organism tissue. Such extrapolations may prove to be highly unreliable.

At this time, only a small number of the potentially hazardous chemicals that tend to bioaccumulate in aquatic organism tissue are being regulated by the US EPA and other agencies. The basic problem is that there are about 75,000 chemicals in use in the US today. Only a few of these have been examined for their potential to bioaccumulate to excessive concentrations in aquatic organism tissue. It has been known since the early 1960's that gas chromatograms of extracts of aquatic organism tissue often show a large number of unidentified peaks of chemicals that are accumulating in fish tissue. Since the 1980's with the development of GCMS, it is possible to identify many of these chemicals. However, little regulatory attention is being given to determining what chemicals are bioaccumulating in fish tissue and the public health significance of this bioaccumulation. This problem arises out of the significant error that was made in the mid-1970s in formulating the Priority Pollutant list and the use of this list as the basis for regulating hazardous chemicals in the environment. There is an urgent need to significantly broaden the scope of the nation's water pollution control programs to more appropriately determine what chemicals are bioaccumulating in aquatic organism tissue, the potential public health and environmental significance of such bioaccumulation and, where significant, develop control programs for those chemicals which are not now regulated as bioaccumulatable chemicals.

Any study of bioaccumulation that is occurring in aquatic organisms of a region should examine the organisms for more than just the Priority Pollutants. If chemicals are found in aquatic organism tissue extracts by GC or GCMS, the presence of the unidentified as well as identified chemicals should be reported with the characteristics of the chemical identified to the extent possible. Such reporting could eventually lead to more appropriate focusing of resources on developing technically valid, cost-effective approaches for regulating hazardous chemicals that bioaccumulate in aquatic organism tissue.

Bioaccumulation of Mercury

Recently, Dr. Lee has given considerable attention to the mercury situation on what is known about mercury chemistry relative to being able to predict based on mercury

concentrations in water and/or sediments wheter excessive bioaccumulation of mercury will occur in higher trophic-level aquatic organisms. It is concluded that there is essentially no predictive capability for relating concentrations of mercury in water and/or sediments to the concentrations in fish or other higher trophic-level organisms. This is of particular importance in the Sacramento River watershed as well as a number of other waterbodies since there are several locations where mercury residues are contributing to elevated mercury concentrations in the Sacramento River watershed waters. It should be understood that there is an urgent need to better define how and to what extent mercury from a particular source area, such as Cache Creek, etc., contributes excessive mercury in a Sacramento River watershed waterbody or downstream thereof. The situation could develop where large amounts of public funds are spent trying to control mercury in mine tailings or some other source so that it does not enter the Cache Creek system only to find that the mercury in this creek is of little or no consequence in the Sacramento River system and downstream, such as San Francisco Bay, in leading to excessive bioaccumulation.

Bioaccumulation Studies in the Sacramento River Watershed Toxics Control Program

With respect to the Sacramento River Watershed Toxics Control monitoring Program, the focus should be on determining whether excessive bioaccumulation of the commonly found chemicals that cause bioaccumulation problems (health advisories) is occurring. This means that a substantial amount of funds should be made available early in the program to conduct a survey similar to the ambient water toxicity testing survey to define where in the Sacramento River watershed there are excessive concentrations of chlorinated hydrocarbon pesticides, PCBs, dioxins and mercury. The first phase of this program should be to develop a comprehensive review of the current Water Resources Control Board's Toxics Substances Monitoring Program data. This review would help define areas where there have been problems in the past as well as to find areas where there is need for further study to either determine whether excessive accumulation of these chemicals has occurred and/or is continuing to occur in a particular area.

Additional Information

A set of abstracts prepared by several of the presenters at the US EPA National Sediment Bioaccumulation Conference was made available to the conference attendees. The proceedings of the conference are expected to be available early next spring.

References

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