Measuring Bioavailability of Sediment-Associated Contaminants

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Introduction

There is frequently a need to assess the risk that contaminated sediments pose to aquatic biota, and for this purpose the concept of bioavailability is crucial. While the need to measure the bioavailable contaminant fraction is apparent, doing so in practice has proven to be quite difficult. However, a new technique designed to mimic digestive processes is under development that provides a straight-forward means to measure bioavailability in a wide variety of risk assessment scenarios and to study the basic mechanisms of how organisms accumulate contaminants from sediments.

Chemical methods of extraction are generally designed to recover the total, rather than the bioavailable, contaminant. There have been some selective extractions proposed (e.g., a weak acid extraction for trace metals) that purport to quantify the bioavailable fraction, but none of these have been generally accepted or broadly adopted. Biological methods such as toxicity or bioaccumulation testing are currently used widely to measure bioavailability, yet interpretation of results can be confounded by other factors unrelated to bioavailability. Toxicity can be a function of the organisms prior acclimation or adaptation, not bioavailability alone. Bioaccumulation as a measure of bioavailability is confounded by behaviors affecting exposure (e.g., feeding and respiration rates) as well as metabolism of the contaminant of interest.

We are currently developing in vitro digestive fluid extraction as a technique to measure sediment-bound contaminant bioavailability (Mayer et al. 1996; Weston and Mayer 1998a,1998b). When a deposit-feeding organism ingests sediment, the chemistry of the gut environment determines if the associated contaminants can be desorbed from the particles and are available for dietary absorption. We mimic this process in vitro, by incubating the sediments of concern in digestive fluid and expressing bioavailability as the percentage of contaminant that has been solubilized in those fluids. The approach presumes that the contaminant extractable by digestive fluid is implicitly a far better indicator of the bioavailable fraction than that extractable by the strong acids or exotic organic solvents typically used in a chemical analysis. Our approach is essentially a chemical extraction, but with a biologically relevant extractant.

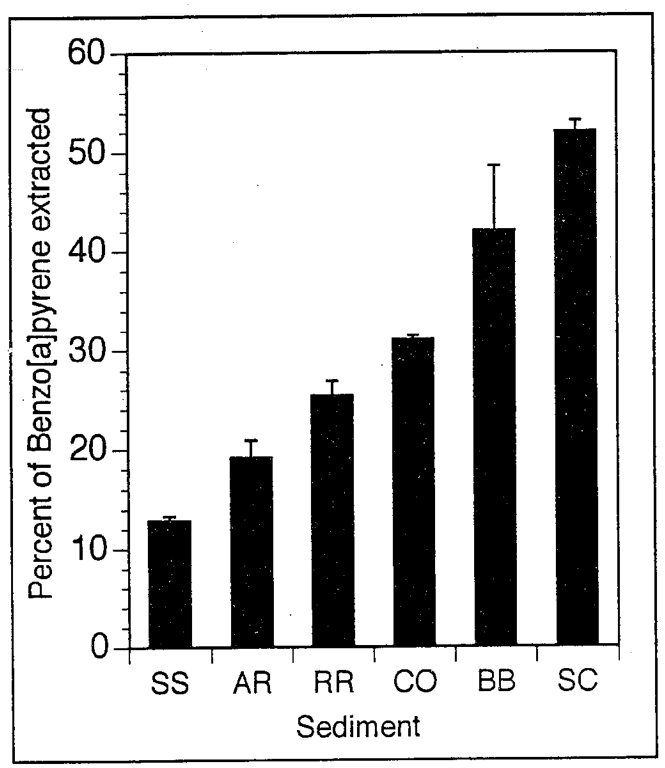

Figure 1
Proportion of sediment-associated benzo[a]pyrene extractable by digestive fluid of *Arenicola brasiliensis*. Each of the six sediments tested is denoted by an arbitrary two-letter designation.

Results

The polychaete *Arenicola brasiliensis* has been a source of digestive fluid for most of the work to date simply because of its large size and the amount of digestive fluid that can be recovered. We have used this fluid to extract sediments from throughout California contaminated with either polycyclic aromatic hydrocarbons (PAH), PCBs, or trace metals. Results have included the following observations:

- Gut fluid pH of a wide variety of invertebrates is near neutral, questioning the biological relevance of the strong acid extractions used in traditional chemical analyses for metals.
- Much of the contaminant that is extractable by traditional chemical means is not extractable in digestive fluid. When six California sediments were spiked with PAH, only 12 to 50% of the PAH were solubilized in an in vitro digestive fluid extraction (Figure 1). Thus, any assessment based on total PAH would have over-estimated the risk posed by these sediments by a factor of 2-8 times.
- In vitro contaminant extraction is similar to that obtained in vivo. Allowing intact *A. brasiliensis* to feed on contaminated sediments and then analyzing the PAH content of their gut fluids produced very similar results to dissecting digestive fluid from unexposed *A. brasiliensis* and doing the extractions in vitro.
- Digestive fluid extraction gives results similar to other traditional bioavailability measures using whole animal exposures.
- The extractability of PAH in digestive fluid is highly dependent upon the organic carbon content of the sediment. Organic carbon is widely recognized as an important determinant of bioavailability, thus it is encouraging that its influence is apparent in in vitro extractions as well.
- Extraction efficiency is concentration dependent. The more contaminated a sediment is, the greater the proportion of contaminant that is bioavailable. This result that is not unexpected, but has never been tested by other bioavailability studies.
- We have extended our work to include 20 species representing seven phyla in order to establish if results could be generalized to deposit-feeders as a group. The results clearly show that bioavailability is a concept that depends upon the exposed species (Figure 2). The digestive fluid of some species is capable of extracting an order-of-magnitude more contaminant from ingested sediment than the fluid from other species.
- Echinoderm digestive fluid is extremely ineffective at solubilizing PAH or zinc, suggesting that echinoderms are likely to bioaccumulate much less of these contaminants from a given amount of ingested sediment than are many other taxa.
- The approach can be used to test the effect of sediment holding time or conditions (e.g., freezing) on bioavailability of sediment-bound contaminants. For example, when a sediment was spiked with PAH and immediately extracted by digestive fluid, 70% of the PAH was solubilized. Holding the sediment for three weeks decreased the extractable proportion to 35%. Sediment aging has been shown to decrease bioavailability in a number of other bioaccumulation and microbial degradation studies as well.

Summary and Future Activities

The in vitro digestive fluid extraction technique provides an intuitively attractive method to quantify contaminant bioavailability to aquatic organisms. It has obvious utility in any application where quantification of the bioavailable, rather than total, contaminant is desirable and when ingestion of contaminated sediments is a potential route of contaminant bioaccumulation. The approach has the ecological relevance of biologically-based methods to measure bioavailability such as bioaccumulation testing, but without some of the complications such as metabolism of the compound of interest. Since the technique does not require exposure of whole animals, sediments can be evaluated even when conditions are unsuitable for long-term animal exposure (e.g., anaerobic conditions, hypersaline environments). The approach holds great promise in studying the fundamental mechanisms of bioaccumulation, in estab-

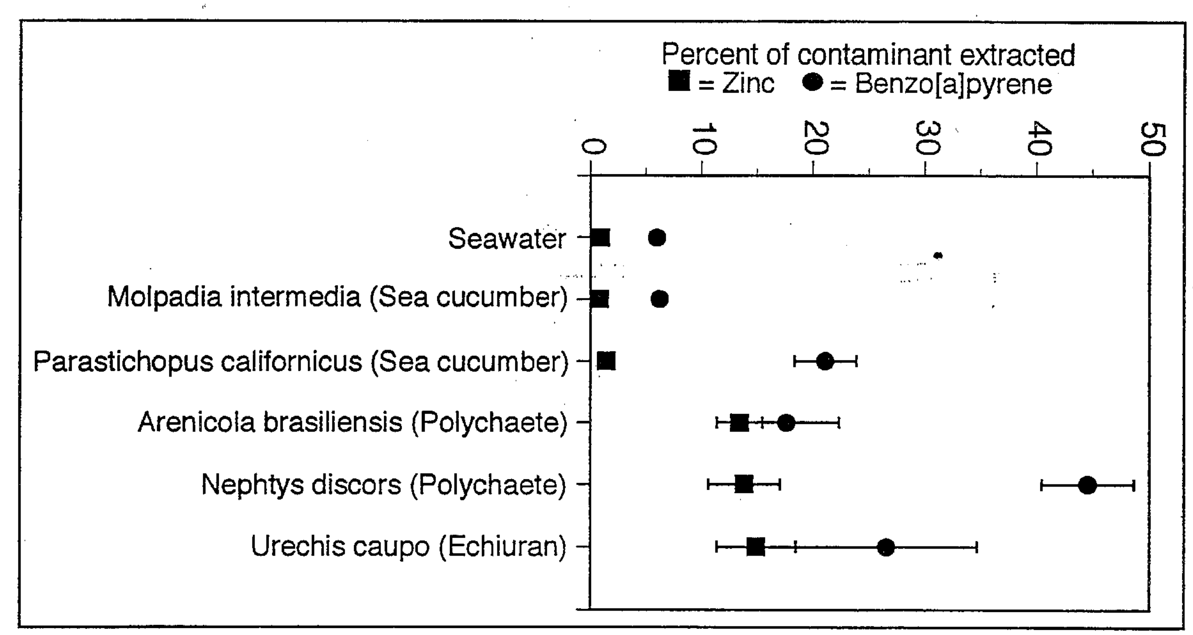

Figure 2
Proportion of zinc and benzo[a]pyrene extractable from a single sediment using the digestive fluids of five invertebrate species. A seawater extraction is shown for comparison.

lishing the effect of laboratory manipulations of sediment on bioavailability, and in ecological risk assessment of contaminated aquatic sediments.

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The Case for a Mechanistic Model for Aquatic Ecosystems of the Bay/Delta

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In recent weeks there has been considerable discussion of the merits, whys, and wherefores of integrative ecosystem models for the Bay/Delta. Some of this has taken place in the Estuary Ecological Teams meetings, some on the EET email reflector, and some at a panel discussion during the recent annual IEP meeting at Asilomar. The panel discussion followed Dr. Daniel Pauly's presentation on the results of his food web-based approach to analysis of resource status in a number of the world's marine fishery systems.

I've been a consistent advocate of the value of a mechanistic ecosystem model as a research tool in the Bay/Delta and I'd like to clarify, as concisely as possible, what kind of tool I am advocating and what I think will be its value. I should make clear in the beginning that, in spite of the terminology used above, this is not really *a* model, in the sense of a single computer program which is all things to all ecologists, but rather a computerized, theoretical framework or model system which has the capability to be configured to study a very broad variety of aquatic ecological circumstances.

I'm thinking about a computerized mathematical tool which projects a time series of its state variables from an initial starting point (just like the hydrodynamic models) and has the following characteristics.

1. Variable spatial resolution which can focus on a single area regarded as homogenous (e.g., Suisun Bay) or on multiple areas each with unique characteristics and which communicate materials and biota.

2. Strong interface to existing hydrodynamic models which are currently in use for water management decision making (but not necessarily tied to a single such model or version) and which can provide certain essential environmental driving variables (temperature, salinity, DO, current, etc.).

3. Broad temporal dynamic range, i.e., intraseasonal, multi-seasonal, multi-year, or long-term (e.g., 50 years), depending upon configuration.

4. State variables of the system as (meta-)population densities (numbers/area) and biomass (grams carbon) indexed (variably) by age, species, and geographic location, and carbon (detrital) densities indexed by size. (Optionally, additional state variables may include various body constituents of organisms, such as trace isotopes or contaminants, and other non-living ecosystem constituents besides carbon—N, PCBs.)

5. Incorporation of the known ecological mechanisms and their interrelations which are operational in animal populations (e.g., feeding, growth, reproduction, mortality and other processes related to viability and death), configured according to the most appropriate sources of information and/or hypotheses under investigation.

6. Mechanisms are responsive to physical (e.g., temperature, salinity, turbidity) and biological (e.g., predator and food density, space for attachment), environmental variables as provided by the hydrodynamic driver and other mechanisms of the system, configured according to the most appropriate sources of information and/or hypotheses under investigation.

If such a research tool were to be undertaken, a guiding principle would be to build upon existing information about the ecosystem. The model system would be capable of both building upon this knowledge as well as testing it. This seeming paradox is possible because the model system in any given configuration is regarded as a complex hypothesis. Its projections may immediately contradict known information, in which case parts of the hypothesis (once logical errors are ruled out) are suspect—knowledge has been tested. Otherwise, its projections are subject to direct or indirect verification through the usual empirical methods—knowledge has been used to design research. Finally, if enough confidence exists in a desirable projection of the system (i.e., the model is validated) then the management actions to bring about that result might be proposed—research results in practical application. This is a gross simplification but should illustrate the main idea.

Here are a few sources of existing information which should be incorporated in any early configurations:

1. The existing suite of known or suspected X2 relations among the environment and organisms (Interagency Technical Report 52, Jassby et al. 1995);
2. The relationships of the Food Web Conceptual Model (Interagency Technical Report 42, Estuarine Ecology Team 1995);
3. The feeding relations identified among zooplankters (Interagency Technical Report 41, Orsi 1995);
4. The information concerning historic salinity preferences and abundances of aquatic animals (Interagency Technical Reports, as updated by more recent surveys).

In cases where there are neither existing known or suspected mechanisms (e.g., larvae of certain species have never been collected) it is necessary to make a plausible, consistent assumption (perhaps several alternative assumptions) about what is happening and incorporate it into the model configuration. A strong statement about that assumption in the configuration documentation should be made. After all, the entire model is a hypothesis. While this may limit some applications of the model projections, it may equally turn out to be irrelevant or it might even shed light on what is actually happening in the system or direct research appropriately. In any event, the objective is to gain a projection of probable future dynamics of the system as a whole; it is important to not allow small details to obstruct that goal.

A common objection to this research approach is that there are "too many unknown mechanisms." In the Bay/Delta ecosystem the first challenge is to incorporate the enormous amount of mechanistic information that is available. It will be a considerable challenge to do justice to simply the information in the above four enumerated sources. The bibliography of ecological information that the EET is currently compiling is a vast resource which covers, together with information referenced therein, enough material to construct several very respectable and useable configurations of a Bay/Delta ecosystem spatial model with both species population and biomass density resolution. It is absolutely impossible to know whether there are "too many unknown mechanisms" without doing the exercise. In any event, this is a question without a single answer—there certainly will be uses for model configurations for which there are plenty of data, and it certainly will be possible to ask questions of the system for which critical information will be, in the final analysis, missing. However the exercise will likely help to direct the appropriate research. The more relevant question is "What alternative approach can make use of the vast amount of ecological information which is available and direct the collection of further information?"

Here are two of the specific potential values and uses of such a research approach, in addition to those generic advantages pointed out above:

1. A configuration of this model system could be used to project zooplankton responses to various flow configurations in a range of water years. While some aspects of such a projection could be done based on empirical regression relations, this approach would not be dynamic or responsive to interactions among system components. It would also be incapable of extrapolation to novel conditions, such as exotic invasions. In short, it would not be an ecosystem approach. To use the dynamic model approach would require a considerable investment of time and effort, but the result would be a truly dynamic and interactive picture of zooplankton dynamics. This would be subject to the usual model caveats about assumptions and hypotheses, however, the regression method is also subject to such caveats. The inductive approach cannot hope to give the kind of detailed insight into the mechanistic operation of the system, based on an order of magnitude more data, that is possible with a mechanistic dynamic model.

2. A similar dynamic picture of fish population responses could be made. Since the model system would not include events occurring in the ocean, those population variables are driving functions of the system. For a range of variation due to whatever causes off the coast, a configuration of a Bay/Delta model could project the range of influence of factors within the modeled system. For striped bass, for example, causes of population fluctuation both within the Bay/Delta and extraneous to it have been proposed. It seems to me that it would be extremely valuable to have an objective tool with which to investigate the consequences, interactions, variability with weather, and other factors of these causes in a holistic ecosystem context.

Finally, let me comment on the degree of detail required for, and the predictability of, this approach. The specification calls for bioenergetic, population, feeding, physical environment, etc., mechanisms all in the same