SESSION 1

INTRODUCTION

Jerry L. Hamelink, Peter F. Landrum, Harold L. Bergman, and William H. Benson

Many current practices in environmental toxicology and chemistry, and in the resulting applications for risk assessment, are founded on empirical relationships; these relationships depend mainly on experience or observation. That does not mean that they are incorrect or inappropriate—just that they are limited because our understanding of the physical, chemical, and biological mechanisms underlying these empirical observations is often limited. The empirical approach has allowed us to address pressing issues and has facilitated regulation of toxic materials in the environment. However, as we work to produce the empirical data necessary to set allowable limits for chemicals in the environment, our understanding of the principles and processes controlling environmental exposure to, and effects of, toxic materials must advance beyond empirical relationships to a sound mechanistic framework.

The intent of this workshop, and the Proceedings volume published from it, was not to advocate abandoning, or in any way undermining, use of the important empirical relationships that currently underpin many of our environmental regulations for protection of aquatic life. These empirical relationships have often been used in setting water quality criteria and standards, and they have been used as the basis for extrapolating from constant exposure conditions in the laboratory to variable conditions in the field or for predicting long-term responses of organisms or communities from short-term laboratory test results. Examples of these important empirical relationships include the inverse relationship between water hardness and the toxicity of many metals to aquatic organisms,[1,2] the direct relationship between octanol:water partition coefficients and bioaccumulation for many organic chemicals,[3,4] and the relationship between early life-stage toxicity and full life-cycle toxicity for fish.[5] As stated above, these empirical relationships, and others, have been important tools in regulating water quality. Through their use we have established an approach for regulating on the basis of water quality criteria and standards, and by using this approach we have achieved considerable improvement in surface water quality. However, as laboratory and field research has progressed over the past several decades, it has become more and more apparent that each of these empirical relationships has exceptions or limitations.

The empirical relationship between water hardness and metal toxicity provides an excellent example of a variable water-quality standard with limitations. Without question, many heavy metals are less toxic to aquatic biota in hard water, and the relationship is sufficiently robust to allow adjustment of a water-quality standard to account for the effect of receiving water hardness on metal toxicity. However, it is now clear that the reported effects of hardness on metal toxicity were sometimes caused not by hardness, per se, but rather by pH or alkalinity.[2] The laboratory experiments that were used to establish the empirical relationship between metal toxicity and water hardness for some metals did not always control or even measure pH and alkalinity, and we now know that pH and alkalinity were confounding covariants in some of these experiments. It is also now clear that other water-quality factors that modify toxicity, such as dissolved organic matter, can have a very large effect on metal bioavailability and toxicity in many surface waters. As a consequence of these kinds of findings, the U.S. EPA has recently proposed revisions in methods for determining site-specific water-quality criteria to more fully account for the modifying effect of receiving water chemistry on bioavailability and toxicity of discharged metals.[6]

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Thus, though empirical relationships that can be used to predict environmental fate or effects of chemicals are useful and necessary, it is very clear that we also need to pursue other research strategies to better understand the physical, chemical, and biological mechanisms that control contaminant fate and effects in the aquatic environment. This kind of mechanistic knowledge can help us in several ways, including identifying and explaining the exceptions and limitations of existing or new empirical relationships and the application of these relationships to water-quality regulation; identifying and measuring the chemical species that are actually the bioavailable, toxic species and, therefore, the appropriate chemical species for measurement of exposure; predicting through extrapolation from the fate or effects of one chemical to another chemical in the same or a similar structural class; predicting through extrapolation from effects in one organism or community to effects in another organism or community; and predicting fate or effects of chemical(s) in the field under different and often more variable geochemical or physiological conditions than were used to measure fate or effects in the laboratory.

It should be evident, then, that we now need to go beyond and improve upon the empirical approach to water-quality research and regulation by achieving a mechanistic understanding of the many physical, chemical, and biological interactions that control contaminant bioavailability. Achieving a better understanding of mechanisms is not merely an esoteric, academic pursuit. Rather, better mechanistic understanding is required to predict accurately the fate and effects of environmental contaminants, and this knowledge may have substantial social and economic consequences. Underestimating the effect of chemicals may result in serious environmental contamination and adverse health effects, while overestimating potential hazards can result in social disruptions and undue economic burdens. Thus, a mechanistic understanding of exposure conditions, bioaccumulation processes, and chemical effects becomes imperative if we are to institute appropriate safeguards to maintain proper environmental health while maximizing economic activity.

This workshop was conceived to be the first of several possible workshops on the mechanisms controlling bioavailability of toxic contaminants in aquatic environments. The first workshop was to review key issues related to contaminant bioavailability as well as to focus on events external to the organism, while later workshops will emphasize events at the membrane-water interface and events within the organism. The workshop steering committee, consisting of Jerry L. Hamelink, William H. Benson, Harold Bergman, and Peter F. Landrum, first met in September, 1989, at the R. A. MacMullen Conference Center in Roscommon, Michigan, under support provided by the Dow Corning Corporation. After further planning and fund raising, coordinated through the SETAC Foundation for Environmental Education, the workshop was conducted August 17–22, 1992, at the University of Michigan Biological Station near Pellston, Michigan.

WORKSHOP OBJECTIVES AND AGENDA

The 1992 Pellston workshop, the 13th in the series, was titled: *Bioavailability: A Mechanistic Understanding*. The workshop was convened to address the following objectives:

- Provide a review of the state-of-the-art for developing a mechanistic understanding of processes affecting the bioavailability and bioaccumulation of toxic contaminants.
- Discuss limitations of the methods currently being used to assess the bioavailability of environmental contaminants.
- Identify research priorities for improving our understanding of bioavailability.
- Discuss the feasibility of incorporating environmental factors limiting bioavailability in appropriate regulations.

In addition to these overall objectives, the following questions were presented to the workshop participants for consideration during their deliberations:

- What important empirical observations/relationships are used to describe the behavior or predict the fate and effects of chemicals in the environment?
- Which of these observations or relationships are actually used directly in regulating chemicals?
- What are the known or suspected exceptions to these relationships?
- Do we know the fundamental physical, chemical, and biological mechanisms that underlie these relationships, and if so, what are they?
- What are the key hypotheses about suspected mechanisms that need to be tested?
- What problems may arise when any of the key empirical relationships are applied, and how will understanding underlying mechanisms help to resolve these problems?

Seven individual workshop sessions were conducted to address these objectives and questions. Each session was initiated by one or more well-defined discussion initiation papers which were prepared and presented by an invited author selected by the steering committee. These papers were presented during half-day plenary sessions of the workshop, followed by a discussion period open to all participants. Each discussion was lead by a session chairperson, who was also responsible for coordinating the activities of the respective consensus committees during the week. During the last session, each chairperson summarized the consensus conclusions of the participants regarding each individual session, and the chairperson of the overall workshop summary committee presented the consensus conclusions and recommendations for the entire workshop.

The workshop sessions and the roles of the participants are described below:

Session 1. Introduction

Jerry Hamelink first presented an overview of the goals and objectives for the workshop. He then introduced all of the session chairs and made team assignments. Harold Bergman followed with an informal, unpublished discussion initiation paper entitled *Improving on Empiricism.*

Session 2. Water Chemistry

Foster L. (Sonny) Mayer presented a discussion initiation paper that focused on freshwater, followed by John Knezowich with a paper that focused on saltwater. The discussion synopsis team for this session included Russ Erickson (chair), Jim Clark, Anne McElroy, Terry Bills, and Dave Hansen.

Session 3. Inorganic Toxicants

Mike Newman addressed some of the interactions known to occur with metals. By describing a ligand as an anion that forms a complex with metals, he was able to discuss some of the limitations to our current adsorption and speciation models. Both sediments and events at the gill membrane were drawn into the discussion session. The synopsis team consisted of Bill Benson (chair), Carlton Hunt, Herb Allen, and Jim Alberts.

Session 4. Organic Toxicants

Anne Spacie gave the first paper in this session. Because of illness, Frank Gobas was unable to present his discussion initiation paper, so Peter Landrum presented it with a set of overheads sent by Gobas. The discussion synopsis team consisted of I. H. (Mel) Suffet (chair), Lisa Williams, Chad Jafvert, Jussi Kukkonen, Mark Servos, Anne Spacie, and Jerry Hamelink.

Session 5. Dynamic Environmental Factors

Don Crosby opened the session with a paper concerning photochemistry, the generally forgotten but surprisingly active force in aqueous environments, even under cloudy conditions. Ulrich

Fostner then focused on pH-redox conditions, primarily as they affected the bioavailability of metals. Bjorn Sundby finished the session by teaching all of us to think of sediments as large, living, breathing, well-structured, dynamic organisms. The discussion synopsis team for this session consisted of Joe Meyer (chair), Bill Davison, Jisua Hong, Bjorn Sundby, Darrel Lauren, and Jim Oris.

Session 6. Kinetic Limitations or Dissolution

Don MacKay opened this session by discussing the kinetic limitations surrounding the dissolution of chemicals in aquatic environments. Jim McKim then described some of the limitations imposed by biological kinetics. Henry Lee capped this session off by briefly describing how different inhabitants of the same bed of sediments are subjected to very different exposures because of the differences in their life styles. The discussion session synopsis team consisted of Peter Landrum (chair), Bill Hayton, Henry Lee, and Lynn McCarty.

Session 7. Summary and Conclusions

The chairperson of each discussion session synopsis team first presented the consensus position derived by their team for each session. An overall workshop summary and conclusion paper followed these presentations before the floor was opened for discussion. The summary and conclusions team was chaired by Ken Dickson. The other team members were John Giesy, Lee Wolfe, and Rod Parrish.

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Bioavailability: Physical, Chemical, and Biological Interactions presents the collected papers stemming from a SETAC-sponsored Pellston workshop on developing a mechanistic understanding of the bioavailability of toxic chemicals. The workshop was held in Pellston, Michigan, August 17–22, 1992. The workshop focused on the array of physical-chemical factors influencing the effective exposure concentrations of chemicals. Hence, the papers herein critically evaluate the major abiotic and biotic controlling factors that affect bioavailability in aquatic environments.

Preface

This book is the result of the 13th "Pellston Workshop," the last nine of which were held under the auspices of the Society of Environmental Toxicology and Chemistry (SETAC). Unlike the previous eight meetings, this workshop was actually held at the University of Michigan Biological Station on Douglas Lake in Pellston, Michigan, where the workshop series began in 1977. Like all the previous workshops, participation was limited to invited experts from government, academia, and industry who were selected because of their experience with the workshop topic. The workshop provided a structured environment for the exchange of ideas and debate such that consensus positions would be derived and documented for some of the issues surrounding the fate and effects of chemical contaminants in aquatic environments.

This workshop continued to build on the concept that hazard assessment requires us to understand the relationship between the measured environmental concentrations of chemical contaminants and the true, biologically available exposure concentrations that have adverse effects on aquatic life in that environment. This is exceptionally challenging because the absolute amount of toxic chemical measured in any particular environmental compartment is seldom equivalent to the effective exposure concentration. Rather, the exposure concentration depends on an array of physical-chemical interactions that constitute the environment occupied by any particular organism. Hence, this book is intended to provide a synopsis on the major factors which are believed to control the bioavailability of toxic chemicals over time and space to different kinds and sizes of organisms in aquatic environments.

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