WORKSHOP REPORT

SERDP and ESTCP Expert Panel Workshop on Research and Development Needs for Understanding and Assessing the Bioavailability of Contaminants in Soils and Sediments

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Contributing Authors

Todd Bridges, Ph.D.
U.S. Army ERDC-EL

Stephen Geiger, Ph.D.
ENSR

Marc Greenberg, Ph.D.
U.S. Environmental Protection Agency

Susan Griffin, Ph.D.
U.S. Environmental Protection Agency

Roman Lanno, Ph.D.
The Ohio State University

Andrea Leeson, Ph.D.
SERDP/ESTCP

Yvette Lowney
Exponent, Inc.

Richard Luthy, Ph.D.
Stanford University

Charles Menzie, Ph.D.
Exponent, Inc.

Danny Reible, Ph.D.
University of Texas, Austin

Stephen Roberts, Ph.D.
University of Florida

Michael Ruby
Integral Consulting, Inc.

Jason Speicher
FirstEnergy, Corp.

Hans Stroo, Ph.D.
HydroGeoLogic, Inc.

Tim Thompson
Science and Engineering for the Environment, LLC

Marvin Unger, Ph.D.
HydroGeoLogic, Inc.

Katherine von Stackelberg, Ph.D.
Harvard School of Public Health

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Acronyms and Abbreviations

AFCEE	U.S. Air Force Center for Engineering and the Environment
AVS/SEM	acid volatile sulfides/simultaneously extracted metals
BAF	bioaccumulation factor
BaP	benzo(a)pyrene
BSAF	biota-sediment accumulation factor
CSM	conceptual site model
DDT	dichlorodiphenyltrichloroethane
DGT	diffusion gradient in thin film
DoD	Department of Defense
DRS	diffusive reflectance spectroscopy
EcoSSL	Ecological Soil Screening Levels
EMPA	electron microprobe
ERA	ecological risk assessment
ER-L	effects range-low
ESTCP	Environmental Security Technology Certification Program
FWS	U.S. Fish and Wildlife Service
IRIS	Integrated Risk Information System
ITRC	Interstate Technology and Regulatory Council
IVBA	*in vitro* bioaccessibility assay
MERIT	Materials of Emerging Regulatory Interest Team
MGP	manufactured gas plant
MNR	monitored natural recovery
NIEHS	National Institute of Environmental Health Sciences
NJDEP	New Jersey Department of Environmental Protection
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCBRes	PCB Residue-Effects database
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofurans
PED	polyethylene device

POP	persistent organic pollutant
RAGS	Risk Assessment Guidance for Superfund
RDT&E	research, development, test, and evaluation
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
RITS	Remediation Innovation Technology Seminar
ROD	Record of Decision
RPM	remedial project manager
SEP	sequential extraction procedures
SERDP	Strategic Environmental Research and Development Program
SETAC	Society of Environmental Toxicology and Chemistry
SPMD	semipermeable membrane device
SPME	solid phase microextraction
SQT	sediment quality triad
TEC	threshold effect concentration
TGA	thermogravimetric analysis
TIE	toxicity identification evaluation
TNT	2,4,5-trinitrotoluene
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Acknowledgements

This report summarizes the results of a workshop sponsored by the Department of Defense's (DoD's) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) that sought to determine the research, development, test, and evaluation (RDT&E) needs for understanding and assessing the bioavailability of contaminants in soils and sediments.

A steering committee composed of Ms. Beth Anderson, Dr. Todd Bridges, Dr. Rufus Chaney, Dr. Nicholas Fisher, Dr. Richard Luthy, Dr. Charles Menzie, Dr. Ellen Mihaich, Dr. Stephen Roberts, and Dr. Randall Wentsel assisted SERDP and ESTCP in determining the scope and structure of the workshop.

To communicate DoD risk pathways and drivers, the state of the science in bioavailability, and bioavailability use in the decision-making process, background papers, and/or presentations were authored by Dr. Nicholas Basta, Dr. Todd Bridges, Dr. Rufus Chaney, Dr. Dominic Di Toro, Dr. Marc Greenberg, Dr. Susan Griffin, Ms. Yvette Lowney, Dr. Jim Ryan, Dr. Mark Sprenger, Dr. Hans Stroo, Mr. Tim Thompson, and Dr. Katherine von Stackelberg.

Breakout group discussions to identify key issues, barriers, and RDT&E needs were led by Dr. Todd Bridges, Dr. Roman Lanno, Dr. Richard Luthy, Dr. Charles Menzie, Dr. Danny Reible, and Dr. Stephen Roberts. Discussions were documented by rapporteurs, including Dr. Stephen Geiger, Mr. Jeff Houff, Ms. Sarah Hunt, Ms. Yvette Lowney, Ms. Kelly Magathan, Ms. Cara Patton, Ms. Deanne Rider, Ms. Alison Saulsbery, Mr. Jason Speicher, Dr. Hans Stroo, Mr. Tim Thompson, and Dr. Marvin Unger.

Most importantly, we acknowledge the input of all workshop participants, which has resulted in a strategic plan to guide investments by SERDP and ESTCP in the area of bioavailability of contaminants in soils and sediments over the next 5 to 10 years.

Executive Summary

The DoD is responsible for the management of thousands of sites with organic compounds and metals contamination in soils and sediments. The current regulatory paradigm for characterizing risks associated with the level of contamination in soils and sediments generally does not include measures of the actual bioavailability of these contaminants to human or ecological receptors. However, there is clear and growing evidence that demonstrates that some of these contaminants are less available to potentially harm humans or ecological receptors than is suggested by simply extrapolating effects based on total concentrations of contaminants in bulk soil or sediment. As a result, bulk soil or sediment concentrations frequently overestimate actual risks and cleanup levels based on such concentrations may be overprotective. Physical and chemical sequestration processes can reduce the potential for exposure and/or uptake by living organisms, but these changes in bioaccessibility and bioavailability are generally not addressed when setting risk-based cleanup criteria. Explicitly assessing contaminant bioavailability can result in setting more technically defensible cleanup goals and establishing more realistic cleanup priorities, while still ensuring protection of human health and the environment. Although the science supports incorporating site-specific bioavailability measurements into risk assessments and site management decisions, the current regulatory paradigm does not make this mandatory. This should change. Additionally, methods for assessing and reducing contaminant bioavailability should continue to be refined and validated.

The workshop described in this document was convened by SERDP and ESTCP on August 20-21, 2008, in Annapolis, MD, to determine future research and demonstration needs in the area of bioavailability and its use in the risk-based remedial decision-making process at DoD sites. Specific objectives of the workshop were to (1) examine the current state of the science and technology for understanding and assessing bioavailability processes in soils and sediments that may impact risk-based remedial action decisions, (2) evaluate current and potential future applications of bioavailability concepts and assess barriers to their implementation, and (3) identify and prioritize research and demonstration opportunities that, if addressed, can facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites. Over 80 experts participated in the workshop, which was designed to define the key issues and the critical and high-priority needs for both research and demonstration projects.

The overarching issues that emerged from the discussions are listed below. In this list, as in all lists in this document, no priority is implied by the order of listing.

1. **Improving the Technology Transfer Process.** While there are a number of good working tools and models relating to bioavailability, an outreach program is needed to help educate remedial project managers (RPMs), federal and state regulators, and the general public on the tools that are available and case studies relating to the application and long-term performance in remedial decisions of those tools.

2. **Building Consensus.** In order to increase the currently limited use of bioavailability concepts and tools, it will be necessary to develop scientific consensus in areas of technical uncertainty. Concepts marked by uncertainty include the ability to predict contaminant fate at higher trophic levels, understanding metal bioavailability in near surface, dynamic environments, bioaccumulation within the food chain, and emerging contaminants and nanomaterials.

3. **Enhance Science/Management Communication.** One of the identified challenges to making use of the bioavailability measures and information for management decisions is that the associated language and measures used by chemists, risk assessors, and other scientists are different from those commonly used by remedial managers and engineers.. Therefore, in order to facilitate use of bioavailability measures and information, a communication bridge is needed to tie the two together. It may make sense for all parties to reach common ground by talking in terms of risk and risk reduction.

4. **Need for Weight-of-Evidence Assessments.** A consensus position adapted by all workshop participants was that there is no single presumptive remedy for any contaminated soil or sediment site. Decisions concerning the need for, and the type of remedy, should incorporate bioavailability measurements into site decision making that will most likely involve using a weight-of-evidence approach.

5. **Challenges with Biological Assessments and Modeling Uptake.** Approaches for dealing with persistent contaminants in soils and sediments are similar and include monitoring to assess whether natural processes are reducing exposures or concentrations, isolating soils/sediments by capping, removing by dredging or excavating, and stabilizing by adding amendments. Regardless of approach, an important measure of success is the extent to which the management remedy reduces risk to humans and ecosystems. There is growing recognition that total contaminant concentrations may not reflect actual risk nor correlate with risk reduction measures. For these reasons, new physicochemical and biological indicators of contaminant risk and reduced contaminant availability are of interest.

The research and demonstration needs were prioritized into critical and high-priority needs for sediments and soils (Table 1). The research and demonstration needs identified by the expert panel for understanding and assessing the bioavailability of contaminants in soils and sediments will guide the strategic plan for research and development in this area by SERDP and ESTCP over the next five to ten years.

Table 1. Critical and High Priority Research and Demonstration Needs Identified

Sediments Working Group	
Research Needs	
Critical Priority	**High Priority**
Impacts of Contaminant Bioavailability in Sediments on Higher Organisms	Better Understanding of the Effects of Black Carbon on the Bioavailability of Contaminants in Sediments
Improved Understanding of Metal Bioavailability in Sediments	Better Understanding of Bioavailability across Small-Scale Gradients and Interfaces
In Situ Remedies to Reduce Bioavailability of Contaminant in Sediments	Better Understanding of the Relationships among the Various Concepts Used in the Bioavailability Decision-Making Process
Fundamental Understanding of polycyclic aromatic hydrocarbons (PAHs) Bioavailability in Sediments	Bioavailability of Emerging Contaminants and Compounds of Interest at DoD Sediment Sites
Fundamental Understanding of Chlorinated Organics Bioavailability in Sediments	
Improved Approaches for Biological Assessments of Bioavailability	
Demonstration Needs	
Critical Priority	**High Priority**
Long-Term Performance of Measures of Bioavailability Processes or Amendments to Bioavailability Added to Sediments as Part of Remedies	Standardize the Uses of Passive Diffusion Sampling Devices
Synoptic Evaluation of Passive Sampling Devices, toxicity identification evaluation (TIE) Approaches, and Other Measures of Bioavailability in the Field	Interpretation of Benthic Community Analysis Within the Context of Contaminated Sites
Fate and Transport Modeling	Better Understanding of the Seasonal and Long-Term Fluctuations in Bioavailability
Demonstrate and Validate Tools and Techniques to Monitor the Effects of Remedial Action on Bioavailability	
Develop Guidance and Demonstrate Methodologies to Make Weight-of-Evidence Decisions	
Soils Working Group	
Research Needs	
Critical Priority	**High Priority**
Extend In Vitro Lead Approach to Arsenic	Cost-Effective Methods for Determining Dermal Absorption of Organic
Mechanisms of Interaction of Contaminants with Soil Component	Mixture Effects
Develop In Vivo Database for DoD-Relevant Organics	
Develop In Vitro Methods for DoD-Relevant Organics	
Develop Soil [and Sediments] Repository for Bioavailability research and development (R&D)	
Develop/Adapt In Vitro Methods for Evaluating Treated Soils	
Develop Technically Valid Soil Limits for Equilibrated Contaminants	
Critical Priority Demonstration Needs	
Review and Prioritize Contaminants for Bioavailability Research	Demonstrate Long-Term Reductions in Bioavailability
Road Map to Expedite Process for New Contaminants	

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) are designed to develop and transition innovative research and technology to help the Department of Defense (DoD) perform its mission in several environmental areas, including cleanup of contaminated sites. The DoD is responsible for the management of thousands of sites with organic compounds and metals contamination in soils and sediments. The current regulatory paradigm for characterizing the level of contamination in soils and sediments generally does not include measures of the actual bioavailability of these contaminants to human or ecological receptors. However, there is a growing body of evidence that suggests that some of these contaminants are less available to cause harm to humans or ecological receptors than is suggested by extrapolating effects based on total soil or sediment concentration measurements. As a result, cleanup levels expressed as bulk soils or sediment concentrations may not correlate with actual risks. Physical and chemical sequestration processes can reduce the potential for exposure and/or uptake by living organisms, but these changes in bioaccessibility and bioavailability are generally not addressed when setting risk-based cleanup criteria. Explicitly assessing contaminant bioavailability can result in setting more technically defensible cleanup goals and establishing more realistic cleanup priorities, while still ensuring protection of human health and the environment. Although there is increasing interest in incorporating site-specific bioavailability measurements into site management decisions, many of the methods being considered have not been critically reviewed or validated (NRC, 2003).

The workshop described in this document was convened on August 20-21, 2008, in Annapolis, MD, to determine future research and demonstration needs in the area of bioavailability and its use in the risk-based remedial decision-making process at DoD sites. Specific objectives of the workshop were to (1) examine the current state of the science and technology for understanding and assessing bioavailability processes in soils and sediments that may impact risk-based remedial action decisions, (2) evaluate current and potential future applications of bioavailability concepts and assess barriers to their implementation, and (3) identify and prioritize research and demonstration opportunities that, if addressed, can facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites.

2. METHOD

Over 70 experts participated in the workshop (see Appendix A for the Attendee List). The participants were invited with the goal of including knowledgeable experts representing a broad range of perspectives, including academic researchers, regulators, remedial project managers (RPMs), industry representatives, consultants, and government agency representatives.

Participants were provided background material on the workshop objectives, DoD risk pathways and drivers, the state-of-the-science in bioavailability in soils and sediments, and the current state of bioavailability use in the decision-making process from a regulatory perspective (Appendix B).

The agenda (Appendix C) was designed to identify the most pressing needs in a focused manner, while ensuring that all participants could express their views. The workshop opened with several presentations intended to provide background information on bioavailability issues, as well as to highlight key challenges.

Participants were then divided into six concurrent breakout sessions to address specific questions regarding the state-of-the-science, and to develop and prioritize the key research and demonstration needs. Four of the breakout sessions focused on sediment issues, while two breakout sessions focused on soil issues. On Day 1, participants addressed either Charge A or Charge B (Appendix D), dealing with either fate and transport of contaminants or risk assessment issues:

Fate and Transport

- For what contaminants and conditions can bioavailability research make a significant impact on DoD's environmental liabilities?
- Identify the key scientific issues and current state of understanding of the processes that control fate and transport of organic and inorganic contaminants of concern in soils (or sediments) at DoD sites.
- What tools (biological, chemical, and physical) are available to measure and characterize the fate and transport of the potentially bioavailable pool of contaminants, and what new tools are needed?

Risk Assessment

- For what contaminants and conditions can bioavailability research make a significant impact on DoD's environmental liabilities?
- What scientific understanding is missing that would provide confidence in the use of bioavailability factors in risk assessment?
- What mechanistic models are available to predict organism uptake or exposure (including defining representative)?

On Day 2, all breakout sessions addressed Charge C (Appendix D), dealing with state of the practice and associated RDT&E needs:

- How are bioavailability concepts currently used as part of risk assessments and associated remedial action decisions in the field?
- What barriers need to be overcome in implementing bioavailability concepts?
- Identify and prioritize the research and development needs that will have the greatest impact on our understanding and use of bioavailability.
- Identify and prioritize the demonstration and technology transfer efforts needed to increase the use of and confidence in bioavailability.

The entire group participated in the final discussions and selection of the key issues and the critical and high-priority research and demonstration needs. Several of the participants contributed sections to this report describing specific issues and needs, and/or edited the draft versions.

3. CONTAMINANT RISK PATHWAYS AND DRIVERS AT DoD SITES

To better understand the DoD's greatest needs for research on bioavailability, a database was developed that extracted summary information from a set of Records of Decision (RODs) published by the U.S. Environmental Protection Agency (USEPA) in the last 5 years. Over 650 RODs were identified for soil and sediment cleanups at DoD sites. Each of those was reviewed, and a database was compiled that identified the media (soils, sediments), contaminants, pathways, and receptors that most often lead to the development of cleanup goals. A summary of the findings for contaminated sediments and soils is provided in the following sections.

3.1 Risk Pathways and Drivers Within Contaminated Sediments

For sediment sites, the key findings included:

1. Of the RODs reviewed, 86 had decisions related to sediment management.

2. The primary risk drivers at DoD sites for both human health and ecological risk include metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and chlorinated hydrocarbons.

3. Both human health and ecological protection are drivers of remediation.

4. For human health, the pathway of greatest concern is fish consumption. For ecological risk, the primary pathway is protection of benthic infauna.

5. For human health-related cleanup decisions, the principal chemicals of concern are PCBs, metals (arsenic), pesticides, and PAHs.

6. For ecological-related cleanup levels, the principal contaminants of concern are metals (arsenic, cadmium, copper, lead, and zinc) and total PAHs.

Human health-related cleanup levels for sediments at DoD sites have been derived principally by using bioaccumulation modeling to back-calculate sediment concentrations of chemicals that would result in acceptable levels of excess lifetime cancer risks associated with consumption of contaminated fish or shellfish. These models have ranged from relatively simple static biota-sediment accumulation factors (BSAFs), to more sophisticated toxicokinetic models that can incorporate varying contaminant levels, food pathways, life stages, or other elements that include some consideration of bioavailability.

For those DoD sites reviewed, ecological-related cleanup levels in the RODs have been principally based on benthic infaunal risks to conservative, empirically-based sediment screening levels (e.g., National Oceanic and Atmospheric Administration [NOAA] effects-range low (ER-L) values, USEPA Region 4 screening values). It should be noted that these screening levels were not developed to be default cleanup levels, although they are often used as such.

Bioavailability has not been considered in setting those screening values. More recently, cleanup values have been set for fish-eating wildlife (e.g., eagle, least tern) that apply the same food-web models that are used for human health.

3.2 Risk Pathways and Drivers within Contaminated Soils

Several efforts have been made to identify the principal pathways and contaminants that represent current soil-based liabilities for the DoD. The results do not always agree. For example, an analysis in the mid-1990s indicated that over 70% of the DoD sites where soil remediation was required were contaminated with metals (USEPA, 1997b), but a recent search of RODs issued in the last 5 years at DoD sites indicates that organic chemicals in soil are now the more common contaminants requiring remediation. However, there are general conclusions that can be drawn:

1. Metals in soil are common chemicals of concern at DoD sites.

2. The most common metals exceeding risk criteria at DoD sites are lead and arsenic, generally followed by chromium, cadmium, manganese, mercury, and antimony.

3. Human health protection is the principal reason for soil remediation.

4. Soil ingestion is the primary pathway of concern.

5. Organic contaminants also appear to be a common, and growing, driver of remediation at DoD sites.

6. The organic contaminants of most concern in soils at DoD sites are PAHs, PCBs and chlorinated pesticides, as well as a lesser number of sites where nitroaromatics such as 2,4,5-trinitrotoluene (TNT) or 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) were of concern.

The key studies of soil contamination at DoD sites include a broad-scale evaluation of the metals that form the basis of remedial decisions at DoD sites (Salatas et al., 2004), and a review of case studies of remedial decisions for 17 DoD facilities (von Stackelberg et al., 2007). Both studies identified the same metals as posing the greatest concerns (lead, arsenic, manganese, mercury, antimony), and both indicated that human health was the primary reason for regulatory decisions. However, the latter study also included several organic contaminants of concern, and both of these studies included contaminants exceeding risk criteria for ecological receptors. Although most corrective action objectives to date have been based on human health risks, there may well be situations now and in the future when protecting ecological receptors will be a more important consideration. These will likely involve sediment, rather than soil, contamination, or the need to protect endangered species.

There are also other factors affecting the importance of bioavailability in risk assessments for soil contaminants. These factors include the areal extent of the contamination with a specific

chemical, the magnitude of the concentration of the chemical in soil relative to risk-based concentrations (i.e., how likely is it that reduced bioavailability will result in actual exposures that are below risk thresholds), and the presence of "emerging contaminants" (compounds for which there are not yet regulations or precedents on remedial actions, but which may become significant drivers of remedial decisions in the future).

4. USE OF BIOAVAILABILITY CONCEPTS IN RISK-BASED DECISION PROCESSES

4.1 Current Use of Bioavailability Concepts

Evaluation and cleanup of contaminated sites is based on establishing risks to human health and ecological receptors that link sources to receptors via specific exposure pathways. Bioavailability directly impacts that link because it controls the potential for transfer of contaminants from an environmental matrix to the receptor during exposure. Because the uses of bioavailability differ somewhat between sediments and soils, these are discussed separately below.

Bioavailability concepts are implicit in the risk-based paradigms used for assessing both human health and ecological risks. Assessing exposures and uptakes requires formulating a conceptual site model (CSM) that considers the individual exposure pathways linking sources to potential receptors. Site-specific investigations of contaminated sites, as defined in USEPA's Risk Assessment Guidance for Superfund (RAGS) (USEPA, 1989a, USEPA, 1989b) are in concept structured to incorporate site-specific bioavailability through each step of the CSM. However, as noted by the National Research Council (NRC, 2003), while bioavailability processes should be an integral part of risk assessment and risk-based management of contaminated site management, the consideration of those issues is not always obvious or explicit. This is, in part, due to a greater burden of proof imposed upon incorporating bioavailability into decision making. The general public perception is that any contamination left behind when bioavailability information is incorporated into cleanup decisions is bad

The use of bioavailability concepts in estimating human health or ecological receptors in soils or sediments are fundamentally different but have in common defining how contaminants move from the solids and are either ingested or absorbed. Bioavailability precepts play an important role in estimating risks associated with contaminant fate, transport, uptake, and whether the ingested contaminant(s) are available. These are discussed in more detail in the following sections.

4.1.1 Use of Bioavailability Concepts in Sediments

4.1.1.1 Human Health Risk Assessment. Remedial action objectives for human health exposure at contaminated sediment sites are most often based on the management of unacceptable lifetime cancer or non-cancer risks from the consumption of fish or shellfish (see Section 3.1). Sediment cleanup levels are back-calculated from unacceptable tissue concentrations using models that range in complexity from simple BSAFs to sophisticated toxicokinetic models that are linked to system-wide fate and transport models (see Section 8.1.1.4). Contaminants involved in these risks typically include arsenic, mercury, PCBs, dioxins, and carcinogenic PAHs (e.g., benzo(a)pyrene [BAP]). Although fish consumption is the most common risk driver, at some sites direct contact with sediments also may be important. In those cases, the bioavailability

considerations are similar to those that apply to risk assessments for contaminated soils (see below).

As noted above, human health sediment cleanup levels are developed by integrating the standard RAGS equations for human health risk from tissue consumption with terms or models that link tissue concentrations to sediment concentrations. The areas in which bioavailability research could have the greatest impact on cleanup levels include:

- Cancer potency factors and reference doses
- Fish consumption rates (i.e., ingestion rates)
- Bioavailable fraction in fish
- Factors or models connecting sediment concentrations with tissue concentrations.

Cancer potency factors and reference doses are set by the USEPA and are relatively conservative for fish consumption risk estimates (USEPA, 2003a). Fish consumption rates are generally region-specific (Anderson et al., 1993; McCallum, 1985; Nakano and Lorenzana, 1996; OEHHA, 2001), and rarely incorporate "fractional intake" (i.e., it is assumed that all fish consumed come from the contaminated site). Bioavailability considerations have had little impact to date on these first two areas, but in a sense, bioavailability has been considered in models for consumption of fish tissue. For example, in some cases, the USEPA recognizes that the total concentration of a chemical present in fish tissue may not be as biologically available as the form for which the cancer potency factor or reference dose was developed. Thus, USEPA (1997) has incorporated a maximum value for inorganic arsenic levels in finfish of 4%, based on studies of arsenic forms in fish tissues (e.g., Chew, 1996; Donohue and Abernathy, 1999). Similarly, reductions are allowed in the exposure to lipophilic chemicals such as PCBs to account for fat loss from fish tissue during trimming (USEPA, 1993; Wilson et al., 1998).

In the future, the most significant use of bioavailability is likely to be in the models used to connect sediment concentrations to fish or shellfish tissue concentrations. These models have been as simple as static BSAFs or more sophisticated toxicokinetic models that incorporate varying contaminant levels, food pathways, life stages, or other elements that specifically consider bioavailability (Arnot and Gobas, 2006; Burkhard, 2003; NRC, 2003; USEPA, 2000, 2008). While these models have progressed to the state where they are needed and used to aid regulatory decisions, uncertainties remain and to date there is a lack of long-term validation testing (USEPA; OEHHA; ATSDR, 2004; NRC, 2003).

4.1.1.2 Ecological Risk Assessment. Like human health, ecological risk assessment and risk management decisions should incorporate site-specific bioavailability (NRC, 2003; USEPA 1992, 1998a). The recent *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (USEPA, 2005) is explicit in stating that bioavailability should be an integral part of site characterization and remedial decision-making.

While the specific organisms and uptake pathways are site-dependent, three general pathways are evaluated:

- Sediment-dwelling organisms (benthos)
- Fish or shellfish
- Aquatic-dependent wildlife

As discussed in Section 4.1, most ecological-based remedial decisions to date at DoD sites have been based upon risks to sediment-dwelling organisms. The risks to benthic fauna are generally assessed first, based on comparisons of the total concentrations in the sediment to conservative empirically-derived sediment quality guidelines (e.g., Long and Morgan, 1990; Ecology, 1988; USEPA, 2006). These values are intended to be used as screening levels or toxicity reference values but have been used as sediment cleanup levels (e.g., Washington State Sediment Quality Standards). Site-specific bioavailability is not considered in this screening-level approach.

However, bioassays are often conducted to directly measure the toxicity of the sediments. Such bioassays can directly assess the site-specific bioavailability to aquatic organisms, although if toxicity is observed, cleanup levels are generally set without consideration of conditions that may render at least some of the chemicals biologically unavailable. In addition, site-specific population counts also could be used to evaluate the overall health of the resident benthic infauna, and indirectly assess the bioavailability of site contaminants (Chapman et al., 1987; Long et al., 2001; Long and Morgan, 1990). However, benthic population investigations have not been widely used because population surveys are labor-intensive and it is difficult to distinguish effects from contaminants from the natural variations in population levels over time

More recently, the USEPA has recommended that bioavailability should be explicitly considered in risk assessments (Greenberg and Sprenger, 2008-see Appendix B). Multiple studies have demonstrated that the toxicity of chemicals in sediments is highly variable. The same chemical tested using the same organism will exhibit quite different toxicity in different sediments depending on the chemical state of the toxicant in that sediment. Many promising new technologies that potentially evaluate bioaccessibility/bioavailability of contaminants within the abiotic media or act as surrogate biological uptake measurements remain under development. These include the equilibrium partitioning sediment benchmark approach for metals, some pesticides, and PAHs that combines chemistry and toxicology for screening. Sediment toxicity has been demonstrated to be reduced by the presence of acid volatile sulfides, organic carbon, and other factors that bind free ions and decrease bioavailability (see Di Toro, 2008-see Appendix B).

Evaluating risks to fish or shellfish, or wildlife that feed on fish is dependent upon the same models discussed under human health that link sediment concentrations of contaminants to those measured in fish or shellfish. The USEPA has been actively involved in developing tools for the consideration of bioavailability, including predicting exposure and effects from contaminated sediments exposure modeling (BSAF dataset www.epa.gov/ecotox), and predicting effects associated with tissue residues (PCB Residue-Effects database [PCBRes] http://www.epa.gov/med/Prods_Pubs/pcbres.htm).

Despite progress in developing bioavailability tools over the last decade, significant data gaps and uncertainties related to bioavailability remain not only in ecological risk assessment, but also in assessing risks of specific remedial actions. These include:

- Release, bioavailability, and risks from contaminants in suspended sediments and/or porewater during episodic events or from dredging.
- Partitioning and kinetics of particle desorption in the water column.
- Fraction of contaminants released into the water column that are truly dissolved (absent constituents associated with dissolved organic carbon or colloids).
- Timeline of changes in key geotechnical and geochemical characteristics (e.g., concentration and density profiles within days to weeks following dredging, mixing rates, and stability) that influence the bioavailability of residuals.
- The relative bioavailability of contaminants in dredged residuals and/or how thin caps placed on top of residual layers affect either bioavailability or bioaccessibility of contaminants.

4.1.2 Use of Bioavailability Concepts in Soils

4.1.2.1 Human Health Risk Assessments. The common approach for risk assessments for contaminated soils relies on default bioavailability factors that are based on the original critical toxicity studies. Although most agree that this approach is overly conservative, national guidance on developing appropriate media- or chemical-specific numbers is lacking. Although individual regions and states may adjust bioavailability factors based on information from the scientific literature, such adjustments are rare and inconsistent. Further, risk assessors are often unaware that *in vitro* animal studies can be conducted to develop a site-specific factor, or the costs and time required for *in vivo* studies for a specific site are not justified.

USEPA Region 8 has developed protocols for testing the bioavailability of lead and arsenic using juvenile swine models, extraction testing, and geochemical speciation methods. These protocols are used to adjust bioavailability factors for lead- and arsenic-contaminated soils. Based on the research done in USEPA Region 8, national guidance has been developed for using bioavailability for lead. For lead, an *in vitro* bioaccessibility assay (IVBA) has recently been accepted, allowing relatively rapid and inexpensive testing of soils on a site-specific basis (http://epa.gov/superfund/bioavailability/guidance.htm). Arsenic, however, remains more problematic, and the IVBA test conditions have not yet been optimized for arsenic. Currently, USEPA Region 8 recommends a weight-of-evidence approach that combines the *in vitro* studies and geochemical speciation results at the site in question with the *in vivo* and geochemical results from the library of *in vivo* studies on arsenic bioavailability.

On the regional or state level, individual risk assessors may adjust the bioavailability factor for other contaminants based on IVBA results, geochemical speciation, and/or the scientific literature. However, to date, there are few examples of the use of bioavailability adjustments for contaminants other than lead and arsenic.

4.1.2.2 Ecological Risk Assessments. Bioavailability may be considered in ecological risk assessment models, although to date it has had relatively little impact on cleanup decisions. Bioavailability may be particularly important for compounds that are subject to biomagnifications, because the key first step controlling the potential for transfer to higher trophic levels is the uptake of contaminants from soil by earthworms and other soil organisms. Bioavailability testing protocols for use in ecological risk assessments have been developed. While there is certainly potential for greater use of bioavailability factors in ecological risk assessments, there are numerous uncertainties involved. Consequently, regulators and the public tend to be uncomfortable with using bioavailability adjustments, and the concern over human health protection usually is more important in determining cleanup criteria, unless there is little potential for human exposure.

4.2 Barriers to Implementing Bioavailability Concepts

4.2.1 Uncertainty

The limitations in our understanding of bioavailability processes raise doubt within the public, regulatory, and DoD communities regarding the use of bioavailability testing to adjust cleanup levels, or the use of technologies designed to “decrease bioavailability". Trying to resolve the associated uncertainty has become a very time-consuming process. The paucity of validated tools and methods contribute to the uncertainty associated with implementing effective remediation. New methods and tools are needed, both for screening-level assessments and for determining cleanup goals. Additional bioavailability implementation challenges include lack of information on:

- Translation of measurements to uptake in higher organisms
- Methods and technologies associated with temporal and long-term monitoring
- Understanding how and when to integrate tools
- Extrapolations from one site to another
- Tools to assess hydrocarbon bioavailability, including a better understanding of the more labile fractions
- Better understanding of components making up the organic carbon pool in background and at contaminated sites
- Differences between human and ecological endpoints
- Variability in interpretation of total PCBs analyses in risk assessments
- Limitations to current contaminant equilibrium derivations
- More effective ways to determine growth and reproduction endpoints
- Appropriate indicator organisms
- Impact of co-contaminants on relative and absolute bioavailability
- Pathways of concern—what and when?

4.2.2 Site Specificity

As bioavailability tools continue to be developed, there is mounting confusion regarding which are the best and how many to choose. Regulatory acceptance of the bioavailability concept for use in hazardous waste risk assessment is uneven across different regions and sites marked by

different media and contaminants. An additional complicating factor is that variability and conflicting results have been experienced among various tests performed at the same site.

The high variability observed in the results from different individual sites can be attributed to a number of factors, including soil and sediment types and loading rates. Key issues include:

- The mechanism(s) by which contaminants are bound to soil and sediment, and the rates of contaminant release are not well understood.
- The bioavailability of organics is difficult to predict and is compounded by the extent and nature of the organic carbon phase in soil/sediment.
- Uncertainty in the reversibility of contaminant-media reactions.
- Adsorption/desorption may not be necessarily linear with loading rates (e.g., partition coefficients will often exhibit differences over different concentration ranges). Also, the partition coefficients can exhibit variability due to the use of different soil-to-solution ratios used during the experimental procedure.

These conditions illustrate the need for good field demonstrations and predictive models that account for site-specific conditions along with guidance on how to use this information to make decisions. Realistic experimentation is needed, in particular on the bench- or pilot-scale level, that addresses the uncertainty in working with variable soil and sediment systems.

Site specificity remains a challenge to the risk assessment manager. Along with identification of the correct contaminant pathways associated with bioavailability concepts, site-specific contaminant mobility factors need to be addressed including the correct use of migration models, their associated contaminant dissociation factors, and normalized tests that account for preferential binding (e.g., bioaccumulation factor [BAF]/BSAF). Further, as decision makers address public concerns where contaminants are left in place and cleanup is based on risk, there is a need to address the issues of longevity and permanence. The concept of "aged" sediments/soils needs further definition, and the actual cause(s) of impact or bioaccumulation need to be identified.

Currently, bioavailability approaches vary from site to site and there is little consensus. Comparisons to "clean sites" pre- and post-remediation will likely be helpful if we are to put all the pieces together towards a "big picture bioavailability tool box" that can effectively be used site-to-site.

4.2.3 Communication

Bioavailability concepts are often not accepted by the regulatory community and public interests because they are sometimes seen as a "do nothing" or "do less" approach, with the perception that the responsible party is trying to avoid their cleanup responsibilities. This lack of understanding on the part of the regulators, the public, and the site managers may stem from poor communication, individual personalities, and politics. The perceived lack of scientific consensus on the various metrics associated with the bioavailability concept (which may form the basis of regulatory decision making) contributes to bioavailability not being used more effectively.

Science and technology must be better communicated to the user community in order for bioavailability to be integrated into risk management decisions.

4.2.3.1 Public Sector. Public acceptance of bioavailability concepts remains a challenge marked by social barriers and a lack of trust in the risk assessment decision-making process. Stakeholders often have a conservative lean toward site remediation, and cleanups based on bioavailability determinations are often unpopular. Given the importance of real and continuous stakeholder involvement, effective bioavailability information transfer is vital.

4.2.3.2 Regulatory Community. Bioavailability acceptance by regulatory agency personnel varies among states and USEPA Regions. In addition, regulatory regions and states are at different positions on the bioavailability learning and implementation curve and, in some states, there is particular difficulty in using bioavailability concepts due to lack of site precedents.

Currently, regulators lack consistent guidance as well as a clear technical consensus on methods and uses associated with bioavailability concepts. General bioavailability concepts warranting further definition include:

- Understanding the assumptions regarding bioavailability within risk assessments.
- The development of complete conceptual site models (CSMs) that include bioavailability information.
- The determination of acceptable cleanup endpoints.
- The development of effective in situ and ex situ methodologies to measure bioavailable contaminant fractions.
- An understanding of the concept of critical populations.
- The correct use of predictive models.

There is a need to recognize a regulator's perspective, which is inherently risk averse. Accordingly, regulators need to be included in bioavailability research projects from the beginning with particular focus on individual contaminant classes. Agency funding toward bioavailability research should be encouraged; a possible model or roadmap for the adoption of bioavailability concepts may be the current use and acceptance of natural attenuation.

4.2.3.3 Site Managers. Currently there is no national policy on the appropriate use of bioavailability to characterize contaminated sites, so site managers are faced with questions regarding the scientific validity of bioavailability as well as the validity of associated tools and models. DoD site managers are also faced with a timing challenge because DoD's internal Remedy- In-Place (RIP) or Response Complete (RC) requirements typically do not coincide with the time frame for bioavailability technology development. DoD has set goals to have all IPR sites at RIP/RC by 2014 with some services electing to meet the goal by 2012. Further, regulatory agencies often emphasize mass removal as the cleanup goal, incorrectly correlating mass removal and contaminant detection with actual risk.

In a real-world remediation scenario, it is presumed that contaminant removal results in lower costs for follow up monitoring as opposed to a full blown site-specific risk assessment where

collecting the “correct” data may appear overly costly and outside the timeline for project completion. Unfortunately, without incorporating bioavailability data, generally-derived screening levels (e.g., ER-Ls) may be relegated to unsubstantiated and costly default cleanup levels. The result is an unnecessary cleanup, because the bioavailability data may show that the contaminant is not bioavailable and therefore there would be not actual risk to remediate

5. HOW CAN BIOAVAILABILITY RESEARCH ADVANCE ENVIRONMENTAL RESTORATION

As described in Section 2 (Methods), attendees were divided into six breakout sessions on each of the two meeting dates. On Day 1, each breakout session addressed questions relevant to the issue of how bioavailability research can advance environmental restoration as follows:

- For what contaminants and conditions can bioavailability research make a significant impact on DoD's environmental liabilities?
- What scientific understanding is missing that would provide confidence in the use of bioavailability factors in risk assessment?

These questions were intended as a starting point for the discussions; therefore, the discussion was not necessarily limited to these questions, and in some instances, these initial questions were modified to address issues the group believed were more relevant. The following sections provide a summary of the key issues identified during these breakout sessions on how bioavailability research can advance environmental restoration. The discussions are summarized by sediments and soils issues.

5.1 Sediments

Bioavailability processes can be an integral part of risk assessment and risk-based management of contaminated sediments. Throughout the workshop, participants noted that, while the science demonstrating bioavailability concepts is well advanced, the barriers to implementation in environmental restoration programs include (1) the availability of cost-effective tools based in good science that link measures of sediment chemistry with effects to human health and the environment; (2) decreasing the uncertainties associated with those tools through field demonstration and validation; and (3) increasing the level of confidence in those tools through education and outreach. The research, demonstration/validation, and outreach needs defined in the subsequent sections of this document are designed to address those needs for DoD RPMs, federal and state regulators who make the decisions, and the general public who ultimately bears the cost of those decisions.

DoD RPMs bear the dual responsibilities of achieving environmental restoration and closure at a site while maintaining a fiduciary responsibility to manage taxpayer dollars in the cleanup. In balancing those responsibilities, the RPMs at the workshop were consistent in pointing to the need for investigation or remedy tools that are inexpensive to implement, have a direct and demonstrated tie to observable effects in the environment, and are readily understandable by regulators and the public.

For regulators, the greater the degree of uncertainty, the less likely it is that bioavailability will be part of the remedy decision. When faced with a high level of uncertainty, regulators by default will make conservative remedial decisions. Thus, a greater burden of proof is imposed

on incorporating bioavailability into the decision-making process. Furthermore, there is a general public perception that any contamination left behind when bioavailability information is incorporated into cleanup decisions is bad. That many of the cleanup decisions at DoD sites have been based on default conservative sediment screening criteria (Section 3.1) is demonstrative of the need for a better understanding of how more realistic cleanup levels can be achieved by incorporating bioavailability into the decision-making process (for example, considering how chemical bioavailability effects on benthic populations can positively effect cleanup-level decisions rather than using default ER-L or threshold effect concentration (TEC) values).

Porewater chemistry, determined directly or indirectly (i.e. using in situ tools such as solid phase microextraction [SPME], polyethylene devices [PEDs], or diffusion gradient in thin film [DGTs]) can be used to predict the bioavailable fraction of contaminants in sediments. When coupled with traditional toxicity testing or benthic infaunal population analyses, the porewater analyses are examples of cost-effective tools that could aid in setting risk-based cleanup levels. Bioavailability of metals in anoxic sediments has been demonstrated to be controlled by acid volatile sulfides (AVS) in sediments in several studies (see Di Toro, 2008-see Appendix B), and this approach could be incorporated into remedial decisions. Reducing the uncertainties associated with contaminant fate, transport, and uptake models would aid in setting risk-based cleanup levels, and would support in situ remedies such as capping or monitored natural recovery (MNR). While the resulting cleanup levels might differ by less than an order-of-magnitude from the most conservative sediment guideline values (e.g., NOAA ER-L), the reduction in management volumes, and hence costs, could be significant (NRC, 2001; NRC, 2003; USEPA, 1998b).

5.2 Soils

Bioavailability is at least implicitly recognized in establishing risk-based criteria because the original critical studies used for determining cancer slope factors or reference dose incorporate an absolute bioavailability value (the bioavailability of the contaminant in the form used to administer the dose in the critical studies). So site-specific (or matrix-specific) testing is designed to establish the relative bioavailability (i.e., the bioavailability from the environmental media of concern relative to the assumed availability based on the original testing).

In the case of lead, for example, the assumed absolute bioavailability is 60%, but the actual bioavailability from environmental media may be higher or lower, depending on the form of the lead in soil particle size and any matrix effects due to the presence of soil constituents. The relative bioavailability of many inorganic and organic contaminants in soil is often (but not always) assumed to be 100% because of lack of information to the contrary, or failure to understand that the bioavailability of chemicals in soil may be less than it was in the critical toxicity studies.

The relative bioavailability to humans of contaminants in soil has been measured in several studies (e.g., NRC, 2003), and values of 10 to 50% appear common—that is, the availability for uptake may be reduced by a factor of 2 to 10 relative to the forms used in toxicity studies,

although there are cases of even lower relative bioavailability. Such decreases in bioavailability can significantly reduce the actual exposure to soil contaminants and hence affect risks and volumes of soil exceeding risk-based criteria (and therefore the resulting costs) (e.g., Battelle, 2003; Stroo et al., 2000; Kreitinger et al., 2007.).

To date, most research and regulatory efforts on bioavailability in soils have focused on a few metals, notably lead and arsenic, and the availability of these metals to humans via ingestion. So far, the only protocol with broad regulatory acceptance is for adjusting the oral ingestion bioavailability factor for lead in soil by measuring the bioavailable fraction through a physiologically-based extraction test. Nevertheless, this protocol has had significant impacts on the scope of a few large sites (primarily former mines) where remediation costs were reduced by tens of millions of dollars. Expanding on this protocol to include other contaminants and pathways will require additional research and demonstration.

In practical terms, bioavailability assessments can be completed at some sites for a few thousand dollars ($200 to $300 per sample), given an accepted *in vitro* method. Currently, the only accepted *in vitro* method for soil bioavailability testing accepted by the USEPA is for lead. For all other contaminants, a site-specific bioavailability assessment is likely to involve *in vivo* testing and require several hundred thousand dollars and several months to generate relevant, site-specific data. In addition, because of the uncertainty, skepticism, and lack of guidance, the results may not affect the final remediation strategy or costs. As a result, bioavailability testing is used only on moderate-to-large lead-contaminated sites and on a few large sites where other metals represent the primary risks. It is rarely used for soils contaminated with organic compounds, despite the prevalence of sites with organic contaminants that may have low bioavailability in soils, based on the few studies that have been done (notably PAHs, chlorinated pesticides, and PCBs).

Expanding the number of metals for which there is an accepted protocol for evaluating bioavailability could reduce remediation costs at numerous DoD (and other) sites, and increase the regulatory and public confidence in this approach. Accepted methods to adjust risk assessments to reflect the actual bioavailability of organic contaminants to humans, via oral and dermal exposure, could similarly lead to large reductions in soil remediation costs.

Although human receptors have been the major concern for DoD to date in soil remediation efforts (see Appendix B), bioavailability to ecological receptors can also be important. For example, as bases continue to close, several large tracts of military land have been transferred to other agencies, such as the U.S. Fish and Wildlife Service (FWS). These lands are often remote, and may have few or no human inhabitants. However, there is often residual contamination in some areas, and agencies such as FWS understandably wish to understand the potential risks to ecological receptors. Bioavailability may largely determine these risks and therefore the need for any remediation or mitigation on large and remote sites, although such ecological risk assessments must also consider whether leaving contamination behind may be the better alternative if remediation means significant habitat destruction.

6. OVERARCHING ISSUES

This section provides a broad overview of overarching themes that were repeatedly mentioned during the workshop discussions. These issues reflect critical needs in the area of understanding and assessing the bioavailability of contaminants in soils and sediments. Overarching issues range from fundamental to applied questions.

6.1 Improving the Technology Transfer Process

A general consensus emerged among workshop participants that, while there are a number of good working tools and models relating to bioavailability, an outreach program is needed to inform RPMs, federal and state regulators, and the general public on what tools are available, and to provide case studies relating to the application and long-term performance of those tools. Conversely, it was also recognized that the researchers and developers of such tools and models must be aware of the real-world issues and experiences of those responsible for managing contaminated sediment sites.

Direct, face-to-face contact is often the best way to exchange ideas and information and many vehicles exist for such interactions. Section 9.0 provides detail on developing a technology transfer strategy to improve communication between the research and end-user community.

6.2 Building Consensus

Bioavailability is now being recognized as an inherent part of the risk assessment process. However, there is a lack of scientific consensus on certain key bioavailability concepts, which results in a lack of confidence in utilizing bioavailability concepts for decision making on the part of end users. In order to increase the currently limited use of bioavailability concepts and tools, it will be necessary to develop scientific consensus in areas of technical uncertainty. Ultimately, scientific consensus can only be reached by conducting additional research and demonstrations to address areas of uncertainty. This document presents data gaps identified during the workshop, which, if addressed, will increase scientific consensus and consequently increase confidence in the use of bioavailability concepts for decision making.

6.3 Enhance Science/Management Communication

One of the identified challenges to making use of bioavailability measures and information for management decisions and in RODs is that the associated language and measures used by chemists and other scientists are different from those commonly used by remedial managers and engineers. For example, sediment chemists may refer to “activity”, porewater concentrations, and biologically available fractions while remedial managers and engineers may talk in terms of bulk concentration cleanup levels and chemical mass. Therefore, in order to facilitate use of bioavailability measures and information, a communication bridge is needed to tie the two together. While a common language may be desirable, it may not be achievable and perhaps is not the right goal. Instead, it may make sense for all parties to reach common ground by talking

in terms of risk and risk reduction. It is possible, for example, to incorporate bioavailability information into risk assessment. However, in order to establish a common communication thread from assessment to remediation, risks and risk reduction should be considered in physical dimensions. Environmental chemists and risk assessors should be able to translate assessment results into spatial and vertical zones that pose or contribute to the risks. This spatial and vertical zone construct then provides a basis for considering the appropriateness and efficacy of various remedial alternatives. These alternatives can be evaluated with respect to risk reduction.

Bridging the communication gap will require thinking about the same areas and depths not in terms of bulk concentrations but in terms of risks. It may be the case that on a site-specific basis there is a relationship between bulk concentrations and risk. An assessment of risk using bioavailability measures would serve to indicate if this is the case. In such cases, the information on bulk concentrations could provide a useful guide. However, in order to insure that the communication bridge is maintained, the focus should remain on risks and risk reduction, and there will need to be recognition that these may not track with bulk concentrations across sites or even within some sites.

The responsibilities for establishing the communication bridge and common ground will fall to the chemists, other scientists, and the risk managers and engineers. All parties will need to be thinking in terms of risks as these relate to impacted sediments in both the horizontal and vertical dimensions.

6.4 Need for Weight-of-Evidence Assessments

Decisions concerning whether bioavailability should be incorporated into site decision making will most likely involve using a weight-of-evidence approach. This is necessary because there is no definitive bioavailability measurement tool; any one bioavailability measurement has limitations. Decisions based on bioavailability measurements are influenced by the fact that bioavailability is often highly site-specific, depending on soil/sediment type, effects of aging/weathering, fate and transport issues related to the contaminant or the media in which it is found, and the target organism(s). Therefore, a single measurement, such as the use of SPME for organics in sediments or a physiologically–based extraction test for metals in soils, often does not provide sufficient information to determine whether bioavailability concepts are important and should be incorporated into site management.

Since bioavailability will be used in higher tiers of the decision-making process (i.e., after generic screening and background level analysis) the decision as to what measurements need to be collected to assess the role of bioavailability should be made with all involved stakeholders. The specific metrics to be used to assess bioavailability should be determined, as should the manner in which they support a final decision.

An example for contaminated sediments is the three-tiered evaluation called the sediment quality triad (Triad), which is often used to determine the need for remedial action. The Triad approach consists of three distinct measurements: chemistry, toxicity, and community analysis. Chemistry can consist of an analysis of one or more of the media involved (i.e., bulk sediment, porewater,

or water column) and comparison to screening values. Toxicity corresponds to a controlled (i.e., laboratory) aquatic toxicity evaluation, and community analysis refers to a comparison of benthic or aquatic community structure at the site and at a representative area not impacted by the site. However, while the Triad can indicate where remediation may be needed, it does not provide any information on which chemicals are bioavailable, which chemicals may be causing the apparent toxicity, and what would be "safe" levels of those chemicals on which to adapt sediment cleanup levels. Examples for lead in soils is the adjustment of the relative bioavailability within the adult or child lead models, or through the use of physiologically–based extraction tests in combination with knowledge of previous site history, and in vivo validation with surrogate animals.

The National Research Council's report *The Bioavailability of Contaminants in Soils and Sediments* (NRC, 2003) indicated that weight-of evidence refers to the method whereby the combined results of multiple tests are used. This

> "multiple lines of evidence approach provides an opportunity to make near-term progress at sites and to overcome some of the pessimism felt by the regulatory community regarding bioavailability because of the lack of mechanistic tools currently available. Its use is an implicit recognition that although our empirical techniques are not able to unambiguously predict bioavailability, they represent progress over the assumption that receptors are exposed to the total contaminant mass bound to soils or sediments. Nonetheless, because of the limitations of empirical tools in their ability to make predictions or be applicable to other sites, the multiple lines of evidence approach should be accompanied by substantial efforts to promote the development of more precise tools."

The integration of disparate measures of the extent and bioavailability of contamination will determine the influence of bioavailability within the decision-making process. To that end, a weight-of-evidence framework that will support a definitive conclusion should be established on a site-specific basis to support the conceptual site model.

6.5 Challenges with Biological Assessments and Modeling Uptake

Approaches for dealing with persistent contaminants in soils and sediments are similar and include monitoring to assess whether natural processes are reducing exposures or concentrations, isolating soils/sediments by capping, removing by dredging or excavating, and stabilizing by adding amendments (NRC, 2007). Regardless of approach, an important measure of success is the extent to which the management remedy reduces risk to humans and ecosystems.

Measures of risk reduction may include reduction in total concentrations, in the accurate quantification of the bioavailable fraction (i.e., porewater concentrations in sediments and the labile fraction in soils), and/or in the effect of contaminants on organisms as measured in bioassays. As discussed elsewhere in this report and in other studies (e.g., NRC, 2003) there is growing recognition that total contaminant concentrations may not reflect actual risk nor correlate with risk reduction measures. For these reasons, new physicochemical and biological indicators of contaminant risk and reduced contaminant availability are of interest.

Biological assessments of reduced contaminant availability play an important role in risk assessment of persistent or bioaccumulative contaminants. This is a consequence of the readily apparent linkages between the contaminants and ecosystem health via environmental exposures. However, establishing direct cause-and-effect relationships between remedial approaches and biological indicators of success is challenging.

Bioassays suffer from various factors when employed to assess risk and the success of remedial measures. Some of these challenges include the following:

Organism variability, feeding behavior, and biodynamic characteristics

- **Feeding strategies affect the sensitivity to bioavailability changes.** For example, an aquatic organism that predominately filter-feeds may not respond to changes in sediment bioavailability if the porewater flux of contaminants is small compared to advective transport and exposure to overlying water in a river or estuary.
- **Feeding strategies and uptake responses differ between organisms.** For example, macroinvertebrates such as worms, benthic bivalves, mussels, and amphipods exhibit different degrees of filter feeding, deposit feeding, growth, and elimination, all of which contribute to uptake and exposure. These physiological and life history characteristics must be considered in evaluating organism response to changes in contaminant availability (McLeod et al., 2008).
- **Physiological parameters vary significantly within a species.** Essential parameters for biodynamic modeling, (e.g., growth rates, ingestion rates, or lipid content) can vary significantly among individuals of a species, even in relatively homogeneous environments (Arnot and Gobas, 2006). For example, the feeding rate of deposit-feeding organisms depends highly on the food quality, and ingestion rates may vary significantly with the organic carbon content of the food source (Cammen, 1980; Cowles et al., 1988). These variations are important to consider for data interpretations and for making body burden predictions (McLeod et al., 2008). Since biological parameters are not necessarily constant like chemical/physical properties, e.g., K_{ow} values, the use of average physiological parameters may hinder interpretation of data and judgments about contaminant bioavailability.

Site variability and difficulty of biological monitoring

- **Treatment areas may be small compared to system-wide contamination.** For example, fish that roam over a large area may reflect average system-wide contaminant exposures, whereas sedentary, deposit-feeding organisms may be more responsive to improvements in sediment quality from remedial actions within localized areas. Many forms of terrestrial wildlife have territories that extend well beyond the area of contamination.
- **Sediment transport complicates performance assessments.** The temporal changes resulting from sediment deposition, re-suspension, or erosion subsequent to remedial actions can make it difficult to assess the success of a remedial measure. For example, newly deposited material from sources beyond the area of treatment will confound bioassays conducted long periods of time after a remedial action.

Deposited material may have a stronger influence on organism uptake and thereby mask the beneficial effects of the remedial measures.

- **Testing can stress the organisms used for bioassays.** The stresses induced by deploying organisms can affect ingestion, uptake, growth, and reproduction. For example, thermal stress, salinity changes, or sediment reconsolidation may affect the viability and burrowing activity of deployed organisms. This stress may result in a response not directly related to the remedial action.

Modeling and communicating uncertainty and variability

- **The assumptions and limitations of bioassays and modeling should be communicated.** For example, greater attention to the limitations and uncertainties will help decision makers successfully translate biological results to remediation goals.
- **The stability of sediments and in situ remedial approaches is uncertain.** Models that predict the long-term effectiveness of in situ remedial solutions to reduce the bioavailability of persistent contaminants in sediments must address the hydrodynamic conditions and physical stability of the area of treatment (e.g., Zimmerman et al., 2008).
- **The kinetics and mass transfer of contaminants are often slow**. The slow mass transfer of contaminants in sediment porewater under field conditions will affect significantly the time for in situ treatments to achieve an equilibrium state and realize the full benefit of the treatment (Werner et al., 2006). Models are needed to bridge laboratory and field results and make predictions on the time scale of treatment benefits.
- **The permanence and robustness of reductions in bioavailability are uncertain.** For example, previously immobilized contaminants might become available again when the chemistry of the sediment/soil changes (e.g., metals and redox conditions, influence of continuing releases on sorbent amendment).

7. RESEARCH AND DEVELOPMENT NEEDS TO IMPROVE BIOAVAILABILITY UNDERSTANDING AND USE

During the second day of the workshop, participants were divided into breakout sessions, each with the same charge (Charge C in Appendix D). Participants were asked to integrate the key issues identified from the Day 1 breakout sessions into discussions of RDT&E needs to improved our understanding and assessment of the bioavailability of contaminants in soils and sediments. Specifically, participants were asked address the following issues:

- How are bioavailability concepts currently used as part of risk assessments and associated remedial action decisions in the field?
- What barriers need to be overcome in implementing bioavailability concepts?
- Identify and prioritize the research and development needs that will have the greatest impact on our understanding and use of bioavailability.
- Identify and prioritize the demonstration and technology transfer efforts needed to increase the use of and confidence in bioavailability.

Research and demonstration needs were classified as either critical or high priority, according to the definitions in Appendix D. The following sections describe the research and development needs identified by the workshop participants, grouped by either sediment or soil issues. Demonstration needs are addressed in Section 8.

7.1 Sediments

7.1.1 Critical Priority Needs

7.1.1.1 Impacts of Contaminant Bioavailability in Sediments on Higher Organisms. Bioaccumulation of contaminants from sediments by aquatic organisms is the most important process governing the ecological and human health risk associated with contaminated sediments. While considerable work has been done linking bioavailability and bioaccumulation to effects on benthic infaunal populations, the linkages to higher organisms through the pelagic food chain is less well defined. Measurements of tissue residue levels of contaminants are useful in that they represent an integrated assessment of the biologically-available contaminants from all sources, and can be directly relevant to assessing ecological and human health risks. However, developing scientifically-defensible linkages from sediment contaminants to the receptor tissues remains a continuing research need. How the links and bioavailability measures are integrated using a weight-of-evidence approach for risk-communication and decision making are critical to gaining acceptance of the use of the measures. Specific critical research needs are as follows:

Develop better models to predict the impacts of sediment contaminants on higher trophic level organisms. Simple models, such as biota-sediment accumulation factors, represent a ratio of chemical residue in tissue to the chemical concentration in sediments. Both the USEPA and the U.S. Army Corps of Engineers (USACE) have placed relatively comprehensive BSAF databases online as tools for considering bioavailability in risk assessments (USEPA at

http://cfpub.epa.gov/ecotox/, USACE at http://el.erdc.usace.army.mil/bsaf/BSAF.html). An implicit assumption associated with BSAFs is that the source of the contaminant is entirely from site sediments, and that a fish spends 100% of its exposure time within the site boundaries. This assumption is appropriate for organisms that live in the mud (e.g., shellfish) or have small ranges, but it is less useful for fish with wide foraging ranges that may be exposed to other sites, or contaminants from industrial or urban discharges.

More complex models have been developed and used in remedial decision making (Brenner et al., 2004; Chadwick et al., 2008; HydroQual, 2007; Ruiz et al., 2000). Such models may consider mass balance, fate, and transport of contaminants as a result of passive or advective flux, physical disturbances, desorption rates of contaminants from sediment particles, interactions with water column organic carbon, external loading, bioaccumulation into phytoplankton, and transfer or biomagnifications from prey to higher level organisms.

Considerable progress has been made in developing these models over the last 10 years, but uncertainties remain that limit application of food web models. Understanding the partitioning between sediment particles, water, and fish remains a critical research need. Trophic transfer models require detailed understanding of the food webs they represent, including inputs to factors such as feeding and assimilation rates, growth dilution, excretion, and/or loss during sexual reproduction (e.g., through egg lipid mass).

In order to improve the predictive capabilities of these models, the following research is needed:

- Develop understanding of benthic/pelagic coupling (i.e., relationships between the water column and the sediments).
- Develop and demonstrate linkages between sediment exposure to contaminants to uptake and transfer to fish and wildlife.
- Better understand the relative contributions of environmental compartments contributing to fish tissue uptake.

Develop tools to evaluate contaminant source apportionment into fish and higher trophic levels for use in risk assessments. An implicit assumption often applied in human health or ecological risk assessment measures of contaminant concentrations in tissues is that the site sediments represent the entire pool of contaminant exposure. With the exception of small enclosed pond systems, fish are exposed to contaminants in the water that come from other sources such as industrial or municipal discharges, urban storm water runoff, other upstream or up current contaminated sites, and/or atmospheric deposition. Apportionment is especially important when considering risks from PCBs, dioxins, PAHs, and mercury. Research is needed to develop better characterization tools and models that could incorporate sediment and tissue contaminant apportionment into risk assessments.

7.1.1.2 Improved Understanding of Metal Bioavailability in Sediments. The bioavailability of metals from contaminated sediments remains an important area of continuing research (SERDP and ESTCP, 2004). Data on total sediment concentrations of specific metals, typically taken during remedial investigations, have some value in comparison to empirical sediment quality

guidelines. In the absence of information on metal bioavailability, there is limited ability to infer toxic effect to benthic organisms, to understand potential food chain transfers, or derive cleanup levels that are protective of human health and the environment. Metal bioaccumulation in general is rarely related to the total concentrations in sediments (Bryan and Langston, 1992; Luoma and Bryan, 1982). Furthermore, there has not been a single chemical fraction that is universally the bioavailable fraction for all metals (Griscom and Fisher 2004; Luoma, 1996; Griscom et al., 2000). Research needs to improve the ability to predict bioavailability of metals in sediments are described below.

Build confidence in the AVS/SEM model through field demonstrations and integrated fate-and-transport models. The AVS/SEM model has been a useful tool for predicting metals bioavailability to benthic organisms in sediments (Di Toro et al., 1990; Hansen et al., 1996; Di Toro, 2008-see Appendix B). The model predicts that under the reducing conditions typically found in sediments, metals bioavailability will be reduced as a result of precipitation as insoluble sulfides, because the stability constants for most metal-sulfide associations are very high, and exchange from metal sulfides to water is low (NRC, 2003). The model has been used in making remedial management decisions at some sites, but broader application of AVS/SEM is limited due to concerns related to overall in-field validity of the model, the permanence of the existing redox conditions at sites, and whether changes in redox conditions due to episodic disturbances would result in increased metal bioavailability.

Building confidence in the application of AVS/SEM is identified as a critical need. The use of synoptically collected *in situ* measures of metals in porewater, tissue concentrations, and toxicity testing with measurements of AVS/SEM measures would assist in validating the overall model. Permanence of the existing site redox conditions can be addressed by evaluating the site relative to hydrologic conditions using a fate and transport model with a focus on changes to site geochemistry during episodic sediment disturbance events. Concerns over changes to metals bioavailability during episodic events could be evaluated in the laboratory, with the data used to integrate and validate a predictive fate-and-transport model.

Develop and validate tools and techniques to assess site-specific bioavailability of metals in sediments. As a corollary to developing mechanistic approaches to predicting metals bioavailability, surrogates such as DGT samplers (Harper et al., 1999), gel probe equilibrium samplers (Campbell et al., 2008), and acid volatile sulfide gel probes (Edenborn, 2005), or adaptation of direct sampling devices such as the Benthic Flux Sampling Device (Hampton and Chadwick, 2000) should be investigated as evaluation tools. Such bioavailability tools need to be validated with biological tests in field conditions. There is a need to conduct synoptic chemical, laboratory, and field-scale studies to determine the predictive ability of various chemistry-based tools. Research should help guide modifications of the tools to enhance predictability.

Develop an understanding of the uptake, assimilation, and efflux of metals in benthic organisms and fish that prey on benthos. Biokinetic modeling of contaminant uptake that includes assimilation efficiencies, growth, dilution, and excretion is needed in order to improve predictive capabilities in the relatively few models that exist for metals. For persistent organic

pollutants (POPs), model parameters such as uptake and assimilation rates, growth dilution and efflux rates for benthic infauna fish are fairly well understood (Arnot and Gobas, 2006). Because the processes responsible for bioaccumulation of metals in benthic animals are not well understood, it is difficult to predict residual levels in biota, although some progress has been made in this area (Lee et al. 2000; Griscom et al. 2002). Research is needed on the mobility and bioavailability of arsenic, cadmium, chromium, mercury, and lead into benthic organisms in both oxic and anoxic sediments as individual metals, and potentially as mixtures of metals.

Improve modeling methods for predicting metal availability and benthic toxicity in oxic sediments. While the AVS/SEM has been demonstrated to be useful in predicting metal bioavailability in anoxic sediments, the factors controlling metal bioavailability in oxygenated sediments are less defined. In particular, the sorption to iron and manganese oxides and clay minerals become important in organic, carbon-poor oxic sediments. This research need focuses on the development and verification of a model that would estimate critical metal concentrations in oxic sediments and predict toxicity of metals to benthic organisms. Di Toro et al (2005) demonstrated how the Biotic Ligand Model (see Di Toro, 2008-see Appendix B) could be applied to sediments, estimating the critical metal concentration on the organic carbon normalized excess SEM. In addition, the model needs to address the potential oxidation of the metal sulfide binding during resuspension events and the reformation of metal sulfide binding. An adequate modeling framework is needed that addresses the permanence issue, i.e., whether metals that are bound as metal sulfides can be considered to pose no reasonable risk, to the same extent as organic chemicals bound to organic carbon.

Complete basic research on the bioavailability of oxy-anions (As and Cr) and Hg. Improved techniques are needed to measure biologically available forms of these metals that can be used to enhance the predictive capability for transformation and uptake into biological receptors. While some models that predict the bioavailability and uptake to fish for arsenic, chromium, and mercury have been developed (Gandhi et al., 2007; USEPA, 2003b), there remains an overall research need to improve the basic understanding of the mobility and bioavailability of these metals.

7.1.1.3 In Situ Remedies to Reduce Bioavailability of Contaminants in Sediments. Recognizing the difficulties and costs associated with removal and treatment of contaminated sediments, there is a pressing need for the development and demonstration of in situ treatment technologies. These technologies should be directed toward containment or treatment measures that reduce the bioavailability of contaminants by direct incorporation of amendments and additives to the sediments or through improved means of containment or treatment in capping layers.

Demonstrate effectiveness and permanence of in situ remedies through demonstration/ validation field studies. Although several technologies for both capping and in situ treatment have been developed, there remains a need for demonstration and validation of the effectiveness and permanence of these remedies. Fundamental and applied studies examining the influence of sediment and overlying water processes on amendment and amended layer effectiveness and permanence are required.

Develop methods for predicting and monitoring the effectiveness and permanence of in-situ remedies. Specific areas of interest include developing an understanding of the dynamics of sorption and desorption processes and the implications of these processes on bioaccumulation and risk to benthic and higher organisms. It is expected that a better understanding of the effect of black carbon and system dynamics on bioavailability will aid in the development and assessment of organic contaminant remedies. A better understanding of the dynamic oxidation-reduction behavior in sediments and caps and the transport and complexation of metals on iron/manganese oxides and organic matter will aid in the development and assessment of inorganic contaminant remedies.

7.1.1.4 Fundamental Understanding of PAH Bioavailability in Sediments. PAHs are generated during pyrogenic and petrogenic processes, and are fairly ubiquitous within industrial and urban environments. PAHs were identified during the workshop as key compounds that need to be addressed in sediments at DoD sites. Often PAHs at DoD sediment sites are found in conjunction with other contaminants, including metals, other semivolatile organic compounds, and PCBs. Characterization of PAH bioavailability at DoD sediment sites is often confounded by the presence of these other contaminants. Methods to assess the contribution of PAHs to any detrimental effects on benthic or pelagic organisms at DoD sites are necessary in order to establish the causal agent(s) for toxicity (if it/they exists). Therefore, while a standard aquatic toxicity test at DoD sediment sites might indicate an adverse effect to a target organism, further analysis may be needed to determine the cause of that toxicity.

Two critical priorities were identified relating to PAHs: (1) assessing chronic toxicity and (2) understanding the range of hydrophobicity of PAHs that are bioavailable. In addition, two high priorities were identified relating to PAHs: (1) alkylated versus non-alkylated PAHs and (2) fate and effects of PAH metabolites. The two high priorities are discussed further within Section 7.1.2 (High Priority Needs). The two critical priorities are discussed in the following sections.

Develop methods for the assessment of chronic toxicity of PAHs for freshwater and marine sediments. Current USEPA guidance on the assessment of toxicity of PAHs to benthic organisms suggests both acute and chronic toxicity testing using a sensitive species as an acceptable endpoint (USEPA, 2003; USEPA, 2007a). Acute measures PAH toxicity (i.e., 28-day tests using *Hyalella azteca*) have been demonstrated for some organisms, but a barrier to broader acceptance of bioavailability measures for PAHs is a similar demonstration for chronic aquatic toxicity tests that includes sensitive life stage measures (e.g., growth, reproduction). These assessments must include both freshwater and marine endpoints in order to gain broader regulatory acceptance. In addition, there is considerable variability in growth and reproduction measurements, as opposed to survival endpoints when conducting chronic toxicity tests. The correct interpretation of these three endpoints for determining toxic effects and ultimately site cleanup levels should be addressed.

Identify methods to ascertain causality of toxicity to test organisms exposed to sediments with multiple contaminants at DoD sites. Sediment remedial decisions are currently based on some variant of the Triad approach, without a careful consideration of what chemicals may be responsible for the apparent observed toxicity, or what would be “safe levels” of those chemicals

upon which to establish cleanup levels. This is especially true for PAHs where conservative default cleanup levels such as ER-Ls are often used when toxicity is observed.

Bioavailability measures to assess multiple contaminants are needed to help inform the remedial decision process. These can take the form of a TIE, the use of multiple aquatic toxicity test species, or the use of multiple in situ or ex situ tests (or combinations of these). Further research is needed to assess:

- The duration of chronic toxicity testing for PAHs
- The selection of potential target species that would be most suitable for testing PAH-impacted sediments at DoD sites
- Methods to determine causal agents of toxicity and their bioavailability at DoD sediment sites containing multiple contaminants.

Advance the understanding of the range of hydrophobic bioavailable PAHs. There are hundreds of PAH compounds present in the environment. The USEPA recommends testing for 16 parent PAH compounds during sediment site characterization (USEPA, 2003). Recently, interest has been expressed in including 18 alkylated PAHs in the analysis (USEPA, 2007a), as the alkyl groups may actually contribute more to toxicity to benthic organisms than their parent homologues (Hawthorne, et al., 2007). PAHs by nature are highly hydrophobic (range in K_{ow} from 3.4 to 6.5), which means that they are tightly sorbed to organic carbon phases within sediments. The presence of anthropogenic carbon (i.e., black carbon) increases the sorption of PAHs in sediments, further reducing their bioavailability. Several methods exist to determine porewater PAH concentrations (i.e., SPME, PE, POM). These methods by-pass the complexity of knowing all of the individual anthropogenic carbon-phase sorption characteristics within a particular sediment. However, an understanding of the relationship between the organic carbon phase(s) in sediments and type(s) of PAHs present is necessary to predict their bioavailability and fate within sediments at DoD sites.

7.1.1.5 Fundamental Understanding of Chlorinated Organics Bioavailability in Sediments. PCBs, dioxins, and pesticides are the most often regulated classes of POPs for both human and ecological risks at contaminated DoD sediment sites. POPs are chemical substances that persist in the environment, biomagnify through the food web, and pose a risk of causing adverse effects to human health and the environment. The importance of PCBs as the overall dominant environmental contaminant is underscored in the NRC's *A Risk Management Strategy for PCB-Contaminated Sediments* (NRC, 2001). Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) share similar toxicological and persistence properties with the so-called "dioxin-like PCB congeners". Pesticides, such as dichlorodiphenyltrichloroethane (DDT), aldrin, endrin, or dieldrin, do occur in sediments at DoD sites but are more typically a result of agricultural use and runoff to the site. Specific research needs are discussed in the following paragraphs.

Continue to develop understanding of dehalogenation processes in persistent organic pollutants. The continued research and development into understanding dehalogenation processes, along with the potential for in situ degradation remedial alternatives, remains a high

priority research need. The partitioning process should be defined not only for bedded sediments but also to critically understand what happens to POP desorption and interaction with aqueous organic carbon during resuspension events. Development of in situ amendments for enhancing dehalogenation of mixtures, refinement and in situ testing of tools and methods for monitoring the effectiveness of amendment placement and mixing, and development of model frameworks to track contaminant fate and transport during in situ biostimulation are crucial for the successful management of contaminated sediments and remain a priority.

Develop, evaluate, and validate cost-effective tools to measure PCB congeners and other POPs in porewater and surface water. Risk assessments for PCBs are most often conducted using bulk measures of Aroclors in sediments and tissues. In fact, most of the studies entered into the Integrated Risk Information System (IRIS) to establish cancer slope factors are based on commercial Aroclor formulations (EPA, 2003a). More recently the emphasis has been on measuring and estimating risks based on a complete set of congener analyses, with an emphasis on the dioxin-like congeners (Bernhard and Petron, 2001; USEPA, 2000; USEPA, 2005). While yielding a more accurate assessment of the levels of risk, the cost of conducting a congener analysis is far more expensive than Aroclor analyses ($1,200/sample versus $200/sample). Given the sampling densities frequently required from remedial investigations and remedial closure reports, congener analyses are not cost-effective. In addition, there are no demonstrated in situ methods for measuring PCB congeners or other POPs. In order to effectively understand bioavailability in sediments and biological uptake of POPs from the truly dissolved phase, there is a need to develop definitive field analysis methods for PCB congeners, and some of the other key POPs.

Quantify POP uptake, accumulation, and biomagnification through the food chain, with consideration of interspecies variability. Tissue residue measures of fish tissue concentrations of POPs frequently show high degrees of interspecies, spatial, and seasonal variability. Modeling the uptake of POPs into fish from contaminated sediment sites would be enhanced by research that could yield measures to account for different feeding strategies and times at the contaminated site. When modeling bioaccumulation, risk assessments have assumed 100% site fidelity, apportioned a percentage of time foraging on the site based on published values for home ranges for the fish species, or used a surface-weighted average concentration over a broader area to account for fish mobility. Some models will account for seasonal variations that consider increased/decreased prey bioavailability, growth dilution, or stage of sexual maturation. In most cases, these are usually loosely parameterized, based on what can be gleaned from the scientific literature. There is a need to document what is known about uptake through food webs and a continued need to develop a better understanding of transfer mechanisms.

As a corollary, PCB-congener distributions will differ significantly in sediment, water, fish, and piscivorous wildlife. Presumably, this occurs due to preferential release of less-chlorinated PCBs to the water, the preferential accumulation of more-chlorinated PCBs through the food web, and the potential metabolism of some PCB congeners (NRC, 2001). Data to support these transfers, and hence with which to develop predictive models, remains to be developed.

7.1.1.6 Improved Approaches for Biological Assessments of Bioavailability. Significant uncertainty concerning bioavailability processes limits the use of bioavailability information in risk assessment and risk management decisions. While recent advances in our understanding of the chemical and physical interactions contributing to contaminant bioavailability are notable, our limited understanding of the role and contribution of biological interactions governing bioavailability is a source of considerable uncertainty. Ultimately, quantifying bioavailability processes requires approaches for collecting data on the relevant physical, chemical, and biological interactions controlling exposure to plants and animals (NRC, 2003). The outstanding gaps concerning relevant biological interactions relate to the information needed to translate knowledge about physical and chemical interactions into the quantitative descriptions of exposure rates that are required to make predictions about biological effects.

Priority targets for R&D concerning biological interactions include approaches for relating bioavailability indicators to estimates of exposure and effect and of integrating such into cleanup targets. Ecological and physiological differences among the numerous species inhabiting or associated with sediments will influence how organisms come into contact with contaminants, the rate and duration of that contact, and the kinetics of contaminant uptake into the tissues of organisms. The organisms of relevance to risks posed by contaminated sediments include microbes, meiofauna inhabiting pore spaces within sediment, and bioturbating macrofauna that build structures within the sediment fabric. Organisms living in the water column are exposed through direct contact with sediment particles, feeding on sediment-dwelling organisms whose tissues are contaminated, and through flux of contaminants out of the sediment bed. Current in situ and ex situ testing protocols for evaluating sediment toxicity do not supply sufficient information to estimate rates of exposure and effect across the diversity of relevant organisms and pathways. Thus, we lack approaches for predicting changes in benthic community structure or function using information about contaminant bioavailability. New approaches for conducting biological assessments of sediment are needed that provide information for relating data on contaminant physical and chemical properties/interactions with quantifications of biological exposure and effect using relevant and appropriate biological endpoints. This information should increase our mechanistic understanding of the factors that influence movement of contaminants into organisms and consequent effects.

Most contaminated sediments contain a diverse mixture of contaminants. The lack of resolution provided by current approaches for describing bioavailability for the mixture hinders our efforts to identify the subset of contaminants responsible for the risk, quantifying the contribution of each contaminant to overall risk, and setting risk- and science-based cleanup levels. Research and development is needed that will advance approaches for identifying risk drivers and providing the basis for quantifying exposure mechanistically, which will support the development of clean targets.

7.1.2 High Priority Needs

7.1.2.1 Better Understanding of the Effects of Black Carbon on the Bioavailability of Contaminants in Sediments. Hydrophobic organic compounds sorb strongly to black carbon (i.e., anthropogenic carbon), which is found in most sediment sites within urban/industrialized areas

of the United States. This sorption has a direct effect on the bioavailability of those contaminants. A more fundamental understanding of the types of black carbon, as well as different competitive sorption effects and kinetics of sorption/release, is needed to be able to adequately provide a mechanistic model of hydrophobic organic chemical dynamics in sediments.

7.1.2.2 Better Understanding of Bioavailability Across Small-Scale Gradients and Interfaces. The distribution of contaminants in sediments is often extremely heterogeneous, resulting in large concentration gradients at short distances. A better understanding of these effects on 1) the influence of redox on metal bioavailability, 2) the complexation of metals with iron/manganese oxides and organic carbon, and 3) the vertical structure and behavior of parameters related to bioavailability, are needed. This effort is expected to lead to the development of in situ field tools and predictive models.

7.1.2.3 Better Understanding of the Relationships Among the Various Concepts Used in the Bioavailability Decision-Making Process. The bioavailability of contaminants in sediments can have different meanings, depending on the point of reference (i.e., sediment solid and aqueous phases, type of organism). For example, processes such as bioaccumulation and biotoxicity are considered components of the bioavailability concept; however, how these processes might translate to cleanup goals or endpoints at DoD sediment remediation sites needs clarification. A clear definition of components comprising bioavailability along with the means by which each component is measured is also needed. Of additional importance is identifying which bioavailability components are currently being used as approved metrics at sediment remediation sites.

7.1.2.4 Bioavailability of Emerging Contaminants and Compounds of Interest at DoD Sediment Sites. The extent and availability of emerging contaminants and nanomaterials at DoD sites has not been adequately addressed. SERDP and ESTCP work closely with the Materials of Emerging Regulatory Interest Team (MERIT), a DoD group supported by the Emerging Contaminants Directorate and consisting of individuals throughout DoD with a common interest in emerging contaminants. It is possible that such compounds are creating concern nationwide, and the DoD will need to be aware of any potential environmental liabilities arising from the presence of these compounds.

7.2 Soils

7.2.1 Critical Priority Needs

7.2.1.1 Extend In Vitro Lead Approach to Arsenic. Given the cost and time requirements for *in vivo* measurement of bioavailability from soil, there is high demand for more rapid, less expensive *in vitro* methods. *In vitro* methods for measuring bioavailability must gain regulatory as well as scientific acceptance in order to be of value. Currently, the only *in vitro* method for relative oral bioavailability estimation accepted by the USEPA for human health risk assessment is the one for lead in soils and soil-like materials (USEPA, 2005). The *in vitro* method for assessing lead bioavailability from soil is an extraction-based, bioaccessibility procedure. Its

suitability for regulatory use is based on demonstration that its results predict, with satisfactory accuracy, the relative oral bioavailability of lead from a variety of soils as measured *in vivo* using an animal model (juvenile swine). The case built for the *in vitro* bioaccessibility method for lead can serve as a road map for other contaminants. Essential elements include 1) the availability of a battery of soil samples, representing a broad range of soil types and contamination scenarios, for which the relative bioavailability has been measured using a suitable *in vivo* model; 2) an *in vitro* method whose results correlate highly with the *in vivo* measurements; and 3) application of statistical methods that adequately address variability in both the *in vitro* and *in vivo* data.

In addition to lead, the contaminant that is arguably closest to having elements in place to develop an *in vitro* bioavailability estimation tool capable of regulatory acceptance is arsenic. Arsenic bioavailability has been measured *in vivo* for several soil samples using widely accepted animal models (swine and monkeys). Collectively, these soil samples represent, or are close to representing, a robust library of soils of different types and sources of arsenic contamination. Extensive efforts have been completed or are underway to characterize the soil geochemistry and mineralogy of these samples, and in some cases, to develop predictive *in vitro* extraction models. There are numerous sites with arsenic contamination for which relative bioavailability information would be useful and could lead to more accurate prediction of exposures from environmental media. For a relatively modest research investment to "finish the job" with arsenic, significant benefits could be realized.

There are some challenges that remain in the development of an *in vitro* model for arsenic bioavailability. One is that evidence to date suggests that arsenic has more complex dissolution behavior from soil than lead, so the simple extraction test that works for lead may not be adequate to predict arsenic bioavailability from a range of soil types. Additional research is needed to better understand the factors controlling arsenic dissolution behavior in soil in order to provide a mechanistic basis for model development. A second complicating factor is that the *in vivo* bioavailability data for arsenic come from more than one animal model, whereas the lead model was validated essentially against a single model. The use of bioavailability data from more than one animal model for comparison with *in vitro* model predictions adds an element of robustness to the effort and makes available collectively a sufficient number and variety of types of soil samples to provide a meaningful test of capabilities. However, data from more than one animal model may make it more difficult to achieve model validation, especially if bioavailability is different in the different species and if variability in *in vivo* bioavailability measurements is not properly characterized and addressed in the comparisons. Given that *in vivo* arsenic bioavailability data are the "gold standard" against which all potential *in vitro* models will be compared, additional research to understand the relationship among the models and solidify the benchmark *in vivo* dataset are needed if this effort is to be successful.

7.2.1.2 Mechanisms of Interaction of Contaminants with Soil Components. Better understanding the nature of the chemical and physical interactions of contaminants with soil constituents can increase the scientific, regulatory, and public confidence in the use of bioavailability adjustments. Predictions of long-term stability and development of reliable remediation methods both depend on a mechanistic understanding of the sequestration and release of contaminants in soil.

The speciation, or chemical form, of metals governs their fate, toxicity, mobility, and bioavailability in contaminated soils, sediments, and water. Different chemical forms of metals, for example, can differ greatly in the amounts taken up by organisms. For example, lead phosphate (chloropyromorphite) is virtually unavailable for uptake, while lead acetate is almost completely available for human uptake following ingestion (Dieter et al., 1993). The varying bioavailability values of different lead species is a large reason for the wide range of bioaccessibility values (4 to 87%) measured using standardized *in vitro* analyses of different soils (USEPA, 2007b). Other interactions between metals and soil components may also affect bioavailability. For example, nickel and zinc can be effectively sequestered over time as Ni and Zn-aluminum layered double hydroxides (Roberts et al., 2002; Scheckel et al., 2000). Other such weathering phenomena may also be important in determining bioavailability in soil.

However, determining speciation is not a trivial task, particularly at low concentrations in a complex matrix such as soil. To assess these chemical properties and to accurately gauge their impact on human health and the environment we need to characterize metals at the atomic level. One can employ an array of techniques to address speciation, including X-ray diffraction (XRD), diffusive reflectance spectroscopy (DRS), electron microprobe (EMPA), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). In addition to these tools, researchers have used advanced synchrotron radiation methods to elucidate the true, in situ speciation of metal contaminants. Synchrotron techniques include X-ray absorption near-edge spectroscopy (XANES), which identifies the oxidation state and first coordination shell, and X-ray absorption fine structure (XAFS) spectroscopy, which provides information on the coordination environment of a selected element as well as interatomic bond distances and identity of nearest neighboring atoms to identify speciation. These methods can also be used in conjunction with statistical methods (principal component analysis and linear combination fitting) to determine chemical phases via a fingerprinting process with a library of known reference standards. These innovative research tools are expanding our ability to directly identify the role of metal speciation on many dynamic processes that influence risk.

It is also important to highlight the limitations of speciation research. Many researchers have attempted to determine the speciation of metals in soils with sequential extraction procedures (SEP) (Lima et al., 2001; Maskall and Thornton, 1998; Song et al., 1999); however, these methods are operationally defined and yield only the amount of metal released for a particular extraction solution. Synchrotron research can only be conducted at Department of Energy synchrotron facilities and therefore requires travel to the facilities, although some facilities are now offering experimental access remotely.

For organics, the interactions are also complex. Organic contaminants may be tightly bound or physically sequestered within the soil. For example, binding of PAHs and other hydrophobic organics to black carbon may greatly reduce their bioavailability, far more than would be suggested by typical measured partition coefficients for oils or natural organic matter. Another example is the reduction in the bioavailability and toxicity of TNT and its metabolites that occurs during bioremediation, apparently as a result of irreversible binding during humification processes. However, for organics we lack the analytical procedures to establish speciation at the

micro-scale and must rely on bulk chemical data to infer binding states or degree of sequestration.

As is the case with metals, the nature and permanence of the binding processes are not well understood, and the bioavailability over time can be difficult to study because there can be several interacting biological and chemical processes occurring. There are questions about the stability of these bound organics under different environmental conditions, or in the case of changed exposure pathways. Better understanding the mechanisms could answer such questions.

7.2.1.3 Develop In Vivo Database for DoD-Relevant Organics. Developing cost-effective methods for determining the oral bioavailability of organic chemicals in soil is a critical priority need for conducting more realistic risk assessments, which may result in increased cleanup goals at DoD sites. These methods will be most valuable for PAHs, PCBs, and PCDDs and furans (PCDFs), both because these chemicals are found on DoD sites and because these hydrophobic chemicals partition strongly to soils resulting in reduced bioavailability. Because PAHs appear to be the organic contaminants responsible for the greatest human health risks, and associated remedial costs at DoD sites, the following discussion is focused on PAHs.

In order to understand the relative bioavailability of PAHs from soil, a robust and accepted animal model will be needed. USEPA guidance requires the use of a "validated" methodology for site-specific assessment of absolute or relative bioavailability of metals from soil (USEPA, 2007b). It is therefore likely that a similar requirement will eventually be made for organic compounds. To ensure that any animal model developed by SERDP is ultimately acceptable to EPA, it is recommended that the EPA Technical Review Workgroup (TRW) for bioavailability participate in the development and application of these animal models.

These models will be contaminants-specific because they must account for differences in the design of the critical toxicity study to which they will be compared, and for differences in the metabolism of different chemicals and the target organs affected. For example, one model that has been used for PAH bioavailability (Weyand et al., 1996) used mice and measures the levels of pyrene metabolites in urine and the formation of DNA adducts in lung and forestomach tissue. Other PAH bioavailability models have relied on rats and measured parent compounds and metabolites in blood, feces, and urine, or have relied on mass balance approaches. In contrast, the currently accepted model for the bioavailability of PCDDs and PCDFs uses female Sprague-Dawley rats and measures accumulation of PCDDs/PCDFs in liver (Budinsky et al., 2008). It is also important to measure induction of certain metabolic enzymes because they are responsible for the metabolism and clearance of certain PCDDs/PCDFs, and significant induction of these enzymes may confound PCDDs/PCDF bioavailability estimates.

The current default assumption is that the relative oral bioavailability of PAHs soil is 100% (relative to the absorption in the critical toxicity study). Several animal studies have demonstrated that this value is overly conservative, most likely by a factor of two- to four-fold (Magee et al., 1996; Ramesh et al., 2004). Animal studies, such as those described above, have been used to develop site-specific bioavailability adjustments for PAHs, but only at the largest sites because they are complex, costly ($25K to $50K per soil) and time-intensive to conduct.

Part of the cost and much of the time and complexity is involved in designing a new animal study for each site because different companies, researchers, and regulators are involved. Thus, the availability of a standardized model would be of great benefit.

Once such a model is available, a broad array of contaminated soils of different soil types and chemical compositions could be evaluated to provide a database of *in vivo* bioavailability estimates. These soils would then be available for further research to determine the soil factors that control oral bioavailability or for the development of *in vitro* tests that are predictive of oral bioavailability.

7.2.1.4 Develop In Vitro Methods for DoD-Relevant Organics. As mentioned before, the organic chemicals of greatest concern to DoD include PAHs, PCBs, pesticides, and possibly dioxins and furans. Existing studies have shown that soil aging and soil properties (such as organic carbon content) can significantly influence the bioavailability of such hydrophobic chemicals following exposure. Conversely, the studies that form the basis for regulatory toxicity values for these chemicals included dosing methods and vehicles (e.g., via gavage, administered in corn oil) that result in high levels of absorption following exposure. Therefore, it is likely that actual exposures to some organics present in soil may be significantly reduced relative to the total amount associated with a dose of soil, and many of the factors controlling the bioavailability may be site-specific. As discussed in Section 7.2.1.3, animal studies of the relative bioavailability of organic chemicals from soil are likely to be expensive, technically challenging, and time-consuming, thereby precluding such animal research broadly on a site-specific basis. The high resource demands for *in vivo* research and prominence as risk drivers at DoD facilities were the considerations in identifying as a critical priority the need for development of *in vitro* methods for estimating or predicting the bioavailability of organic chemicals from soil.

Some *in vitro* methods for assessing the relative bioavailability of organic chemicals from soil do already exist (e.g., Oomen et al., 2000; Oomen et al., 2001; Peterson, 1998; Ruby et al., 2002; Sardar et al., 2008; Stroo et al., 2005; Hawthorne et al., 2002, 2003), using biotic or abiotic extraction systems. Some of this research indicates that the fraction of soil-bound organic chemicals is significantly reduced. However, validation of the predictiveness of these methods against animal data has not been conducted or is inadequate to support broader-scale application or regulatory acceptance.

Development of inexpensive and reproducible methods to predict the relative bioavailability of organic chemicals of relevance to DoD has therefore been identified as a critical priority need and area for additional targeted research. Meaningful methods will have to account for chemical- and site-specific controls on bioavailability, as well as address the complexities introduced by the fact that many of the organic chemicals of interest to DoD are present in the environment as mixtures, as well as the challenges introduced by chemical specific issues such as metabolism, in addition to issues of dissolution. An ideal method would correlate (or be adequately predictive of) results from a relevant standard, such as animal testing. Alternatively, assays or methods that quickly and accurately assess a maximum possible bioavailability that would allow for a worst-case adjustment may also be of value.

Although review of available resources indicates that consideration of human health risk drives remedial decisions for DoD sites, calculated exposures by ecological receptors in contact with organic chemicals in soil can be significant risk drivers and may take on increased relevance to remedial decisions in the future. Therefore, more accurate, site-specific tools for assessing exposures by ecological receptors could be useful. In the ecological risk assessment (ERA) of terrestrial ecosystems, exposure characterization is complicated by the interactions of organic compounds with soil solid phase components such as organic carbon. In sediment systems, equilibrium partitioning has been proposed as a means of estimating organic chemical exposure, but this approach has limitations in terrestrial systems. Thus, predictions of organic chemical exposure in terrestrial systems are usually based on total chemical concentration, possibly with normalization based on soil organic carbon levels. Regardless, the prediction of organic chemical exposure dose is compromised by soil modifying factors. *In vitro* methods for measuring and predicting the bioavailability of organic chemicals in soils are required to reduce the dependency of ERA of contaminated soils on organism bioassays. Techniques such as solid-phase extractions (e.g., SPME) may be used to screen soils for the potential bioavailability of organic chemicals. Infinite sink methods (e.g., PAHs in manufactured gas plant [MGP] soils using Tenax resins) and various liquid extraction techniques (e.g., supercritical fluid) have been used to assess the rapidly desorbable fraction (maximum bioaccessible fraction) of organic chemicals in soils.

While these methods are valuable in developing proof of concept, methods need to be developed for assessing organic chemical bioavailability in situ at contaminated sites. Such methods for monitoring the bioavailability of organic chemicals in sediments have been developed (e.g., SPME, SPMD), but are lacking for terrestrial ecosystems. Whether *in vitro* or in situ techniques are developed, it is imperative that they are correlated with *in vivo* doses (organism residues) or and organism responses (i.e., lethal or sublethal) at either the individual, population, community, or soil function level.

7.2.1.5 Develop Soil [and Sediments] Repository for Bioavailability R&D. One of the biggest problems in the development of regulatory criteria for various chemicals is the great heterogeneity of soil physical/chemical characteristics across the United States. Inevitably, almost all tests conducted with natural soils are conducted on soils of differing physical and chemical characteristics, with few laboratories actually sharing the same soils. One approach to standardizing test soils is to develop a repository for soils and provide access to these soils for any interested researchers. This repository could take the form of a physical storage area, such as a warehouse, but this may be overly costly and logistically difficult. Another option is to establish “virtual” repositories or sites containing a soil that has be extensively characterized with respect to basic physical and chemical properties such as organic carbon, texture, and pH, as well as baseline performance in bioassays with soil invertebrates and plants. An example of such a soil is the Sassafras sandy loam that has been used for a decade by researchers at the Aberdeen Proving Ground for plant and soil invertebrate bioassays. Batches of soil from this site are collected, sieved, homogenized, and analyzed for physical/chemical characteristics. Mean parameter values are then compared to previous batches of soil collected from the same site, and, if they do not deviate any more than x%, then the soil is considered essentially the same and can be used in testing. In this manner, the site acts as a virtual repository for a characterized soil that

can then be collected and distributed to researchers. A critical research need to advance the management of chemical contaminated soils is consistent access to a series of well-characterized soils differing in physical and chemical characteristics. The development of a database of soils containing basic physical and chemical characteristics and bioassay response data would provide an opportunity for researchers to share soils, directly compare test results, and select soils with specific characteristics for hypothesis testing.

7.2.1.6 Develop/Adapt *In Vitro* Methods for Evaluating Treated Soils. Recently, intentional alteration of the bioavailability of contaminants in soils (and sediments), by stabilizing the contaminants in a manner that reduces bioavailability to target receptors, has been proposed and, in some instances, developed as a method of in situ remediation. Although it is understood that natural weathering, geochemical interactions, and other soil-contaminant interactions can have a significant influence on the bioavailability of chemicals in soil, inexpensive methods for demonstrating the long-term stability of amended soils and reduced bioavailability of soil contaminants continues to be a high priority research need. *In vitro* methods to demonstrate the effectiveness of in situ soil amendments, or other forms of sensors for long-term monitoring of soil-contaminant interactions and stability would be useful additions to the arsenal of scientific methods, as they could significantly affect the number and types of remedial approaches available for addressing contaminated soils.

7.2.1.7 Develop Technically Valid Soil Limits for Equilibrated Contaminants. Soil management parameters or limits (e.g., Ecological Soil Screening Levels (EcoSSLs), ECx values) derived from site-specific field data would provide the most accurate assessment of toxicity. Since these data are not readily available, lower levels of integration and less sensitive endpoints are used to derive various soil limits. The endpoints selected to support the derivation of these limits should be critical parameters that could ultimately be reflected in population level effects: survival, reproduction, and possibly growth. By necessity, data for deriving soil limits will be based on laboratory soil bioassays, with chronic toxicity data (primarily reproduction) providing the most direct theoretical and practical link with populations. Laboratory toxicity measures have traditionally been derived using soils or substrates amended with relatively pure chemicals that provide conservative exposure dose estimates for a number of reasons. Due to the lack of time for equilibration of the test chemical and test soil prior to conducting toxicity tests, much of the amended chemical remains in a highly bioavailable form. When metals are amended to soils, the counter ion present in the salt may also present problems by increasing the ionic strength of soil solution, while the metals themselves can decrease soil solution pH at higher concentrations. Many organic compounds are rapidly degraded by soil microbes and other fate processes during equilibration and test periods, resulting in a declining exposure dose that violates major assumptions related to chemical exposure in bioassays. As a result, while data derived using soils spiked with chemicals has proven useful in proof-of-principle investigations of various toxicological phenomena, useful application of these data to real-world conditions is limited. One approach to reduce artifacts created by spiking soils with chemicals is to subject amended soil to laboratory aging and weathering procedures. Though this approach has been relatively successful with some metals, its application to more polar organic compounds is limited. For these reasons, methods need to be developed for developing technically valid soil limits for

contaminants that are equilibrated in soils. These approaches need to consider chemical speciation and the effect of soil properties on speciation, bioavailability, and toxicity.

7.2.2 High Priority Needs

7.2.2.1 Cost-Effective Methods for Determining Dermal Absorption of Organics. As described in Section 7.2.1.3, PAHs appear to be the organic contaminants responsible for the greatest human health risks, and associated remedial costs, at DoD sites. The current default assumption is that 13% of PAHs in soil are absorbed from soil that adheres to skin. However, in the study from which this default value was derived (Wester et al., 1990), the BaP was mixed with soil and then applied immediately to the skin. The absence of time for the BaP to react with the soil suggests that absorption was higher than it would have been with environmental soil samples.

In a standard residential scenario that considers oral and dermal exposure to PAHs in soil and house dust, the dermal pathway generally accounts for about 25% of the total exposure. Thus, development of an inexpensive dermal absorption assay for organic chemicals in soil may be less important than such an assay for the oral pathway, but is still needed to address a significant aspect of overall exposure. In addition, it should be noted that as use of oral bioavailability estimates becomes more widespread, the relative importance of the dermal exposure pathway will increase (i.e., dermal exposures will be perceived to contribute a greater proportion of total exposures).

The existing methods for measuring dermal absorption from soil include small animal models (mostly mice) and *in vitro* methods using human cadaver or other animal skin. Results from studies using these models suggest that the 13% default value may be overly conservative. Thus, a simple and inexpensive *in vitro* method for determining the dermal absorption of organics would be of significant value for exposure assessment.

7.2.2.2 Mixture Effects. Contaminated sites seldom have only one contaminant, and there is increasing evidence to support the concept that the bioavailability of a chemical from soil can, under some circumstances, be influenced by the presence of co-contaminants. This evidence includes empirical findings indicating that combinations of metals in soil produce different uptake into plants than is observed when the plants are exposed to the metals individually (e.g., Peralta-Videa et al., 2002; An et al., 2004). Different results are seen with different plants, and different parts of plants, e.g., cadmium and zinc interactions on uptake in lettuce versus spinach, (McKenna et al., 1993), making it difficult to formulate generalizations regarding these interactions. It is likely that similar interactions also occur in animal species, including humans, but there is almost no literature on the subject other than in the context of potential effects of soil amendments on bioavailability.

Conceivably, mixture effects on bioavailability of chemicals can occur through interactions of the chemicals with soil affecting their soil-binding properties. For example, competition for soil adsorption sites between two fungicides, carbendazim and iprodione, led to increased porewater concentrations (and by inference, increased bioavailability) compared to soil with either fungicide alone (Leistra and Matser, 2004). In addition, some studies suggest that contaminants

with solvent properties can increase the solubility and bioavailability of other contaminants, e.g., the increase in PAH bioavailability to earthworms by the presence of volatile hydrocarbon fractions in soil (Bogan et al., 2005).

Interactions can also occur affecting the uptake of bioaccessible chemicals into the organism. The gastrointestinal absorption of many inorganics are tightly controlled, but can be influenced by the presence of other inorganics. For example, the effects of zinc on the gastrointestinal absorption of iron has been well studied in humans (e.g., Olivares et al., 2007). Contaminants present at sufficient levels to produce hepatic enzyme induction or inhibition could, at least theoretically, affect the systemic bioavailability of chemicals subject to hepatic first pass metabolism.

Although consideration of contaminant interactions on bioavailability potentially adds a substantial layer of complexity to bioavailability assessment, it will be necessary in order to produce reliable risk assessments and can help direct development of new in situ stabilization methods. New research is needed in order to be able to predict scenarios in which mixture effects are likely to be significant, i.e., where the predicted bioavailability of one or more chemicals of concern is impacted substantially by the presence of other contaminants. This research will need to consider the possibility of interactions at the levels of soil chemistry as well as biological uptake and distribution within the target organism(s).

8. DEMONSTRATION NEEDS TO INCREASE USE OF AND CONFIDENCE IN BIOAVAILABILITY MEASUREMENTS

As discussed in Section 7, during the second day of the workshop, participants were divided into breakout sessions, each with the same charge (Charge C in Appendix D). Research and demonstration needs were classified as either critical or high priority, according to the definitions in Appendix D. The following sections describe the demonstration needs identified by the workshop participants, grouped by either sediment or soil issues. Research and development needs are addressed in Section 7.

8.1 Sediments

8.1.1 Critical Priority Needs

8.1.1.1 Overarching Issue: Synoptic Demonstrations. There are now various methods for characterizing sediments, measuring bioavailability, examining sediment toxicity, and evaluating benthic communities. Therefore, there is not a lack of potential tools. However, there are questions about the reliability of available tools and about their strengths and limitations. The workshop also revealed a desire on the part of a number of attendees to consider bioavailability measures and information as part of an overall weight of evidence approach rather than relying on individual measures. Therefore, field demonstrations should emphasize the use of synoptic approaches in which various potentially valuable tools are used and various lines of evidence are gathered. This would provide an opportunity for learning about the relative performance of the measures and for ground truthing measures with field data. The synoptic approaches should include biological measures along with chemical measures.

8.1.1.2 Long-Term Performance of Measures of Bioavailability Processes or Amendments to Bioavailability Added to Sediments as Part of Remedies. The addition of sequestering agents to reduce contaminant bioavailability is increasingly becoming an important component of sediment remedial actions. These have included direct additions to sediments (Luthy, 2004; Ghosh et al., 2003; Zimmerman et al., 2004, 2005), as well as incorporation of organic carbon or other sequestering amendments directly into caps (SERDP Project ER-1493[1]; Knox et al., 2006; Knox et al., 2008; Melton et al., 2005; Murphy et al., 2006; Olsta and Darlington, 2005; Reible et al., 2006). A barrier to broader acceptance of sediment amendment remedies is field demonstration and validation of the success of amendment additions; tools to confirm that bioavailability of the target contaminant has been reduced or eliminated; and a standard of practice for assessing, implementing, and monitoring long-term effectiveness of sediment amendment remedies.

Conduct field validation and demonstrations at contaminated DoD sites of in situ treatment technologies. To date, most of the sediment amendment-based remedy research has been in the lab, bench-scale microcosms, or relatively small field plots (e.g., <100 m^2). While these studies

[1] http://www.serdp.org/Research/upload/ER_FS_1493.pdf

have provided invaluable information on selection of sequestering agents and demonstration of short-term reductions in bioavailability, comparisons of the bench-scale research and field-scale demonstrations of in situ treatment technologies are needed before they can be routinely applied in the field. What is less apparent but equally important is the need for multiple field tests because of the heterogeneous nature of sediment sites. The need is similar to that identified in the 2004 Sediment Workshop (Research Needs A21 and A22 in that document), emphasizing again the requirement that the technology be demonstrated at an "appropriate scale", allowing for properly constrained cost and feasibility evaluation.

Develop, evaluate, and/or validate characterization tools to evaluate the long-term trends and fluctuations in bioavailability in pre- and post-amendment sediments and/or caps. This need calls for continued research and demonstration/validation of tools that can be used to confirm sequestering of contaminants in amended sediment remedies. Tools such as semi-permeable membrane devices, solid-phase microextraction fibers, or polyethylene devices have been demonstrated to be effective at the lab or bench-scale testing for rapid and effective characterization of organic compound bioavailability, but lack field confirmation. Similar tools for identifying metal bioavailability are lagging in both the experimental and field applications.

Refine and demonstrate in situ risk characterization methods to evaluate pre- and post-remedial impacts of sediment amendment remedies. Many of the methods developed to assess *in situ* effectiveness of amendments focus on chemical measures of bioavailability. This need calls for research into methods that can demonstrate the reductions in risk to biological resources living in, or are in contact with the treated contaminated sediments. Examples of risk reduction as a result of amendment addition would include toxicity response of representative benthic and epibenthic organisms, reductions in mass of contaminants in fish prey, and reductions in uptake to shellfish or trophic transfer to fish. Accompanying this research would be a protocol to assess and compare baseline and post-remedial short- and long-term risks, seasonal changes in bioavailability, and, where practicable, means to assess changes in risks to higher trophic level organisms (e.g., piscivorous birds) and human health.

Development of guidance and demonstrate methodology for most effective deployment of in-place treatments to reduce bioavailability. While the field of sediment amendment remedies to reduce bioavailability continues to develop, it is timely to summarize the existing experience into a single source that could be accessed by DoD site managers, EPA, and state regulators. While amendment remedies are recognized and have been implemented at many federal and state contaminated sediment sites, guidance on how to evaluate, design, and implement these amendment remedies is lacking. The increasing maturity of amendment remedies, along with increasing acceptance by EPA and states, lead to an opportunity to create a DoD guidance document that provides direction to DoD RPMs, their support contractors, and agencies in the design, implementation, and evaluation of amendment remedies.

To meet that need, a guidance document, web-based decision tools, and an educational outreach program that would provide the needed information to design, implement, monitor, and demonstrate the long-term effectiveness of amendment addition remedies for contaminants commonly found at DoD sites is warranted. This integrated approach would include (1) tools

and techniques to determine relevance and appropriateness of amendment remedies, (2) engineering principles and considerations needed to assess and apply sequestering agents to sediments or caps, (3) methods for construction and monitoring of amendment-based remedies, and (4) case studies highlighting design, application, effectiveness, and permanence of amendment remedies.

8.1.1.3 Synoptic Evaluation of Passive Sampling Devices, TIE Approaches, and Other Measures of Bioavailability in the Field. The assessment of the exposure and risks posed by contaminated sediments has traditionally been accomplished through bulk chemical measures, supplemented with bioassays in the laboratory. Potentially the best measures of bioavailability and risks, however, are in situ measurements that truly reflect site conditions. There is a need to develop and demonstrate in situ biological and chemical assays that realize this potential. In situ bioassays that allow identification of toxicity (TIE) and directly indicate biological response should be developed and demonstrated. Protocols in both marine and fresh water and for both organics and metals are needed. In addition, chemical measures that support and help interpret the biological assessment tools are needed. Passive sampling of porewater concentration has shown great promise for both organics (polyethylene samplers, solid phase microextraction, semipermeable membrane devices) and metals (AVS versus SEM, DGT devices). Full realization of this promise requires demonstration of these approaches under a wider variety of conditions. Such demonstrations should include direct comparisons to biological measures and examine the effect of site characteristics and dynamic processes such as oxidation, reduction, and porewater exchange with overlying water. No single in situ assessment tool is likely to be universally applicable so the conditions, contaminants, and organisms to which individual approaches are applicable needs to be identified and demonstrated. Some approaches, such as AVS/SEM, are relatively mature technologies but require evaluation under a wider range of conditions, particularly dynamic conditions, to demonstrate applicability. Other approaches, such as DGT, remain largely research tools and evaluation under field-simulated and field conditions is needed to demonstrate their applicability and relevance.

8.1.1.4 Fate and Transport Modeling. Fate and transport of contaminants within the sediment column continues to be an important focus research need. In recent decades, the important physical, chemical, microbiological, and biological processes that affect the fate, bioavailability, and effects of contaminants within the sediment column have been identified (SERDP and ESTCP, 2004). However, the linkages between in-place sediment contamination and transfer of contaminants within and up the food chain through fish that impact human health or higher trophic level ecological receptors remain vexing. The understanding of bioavailability on risk to higher level trophic organisms and humans consuming fish or shellfish is contingent upon understanding and quantifying sediment exchange processes with overlying water.

Contaminants may be released from contaminated sediments into the overlying water column by a number of physical process, including molecular-scale diffusion from porewater, biologically enhanced mixing of sediments and porewaters (bioturbation/ bioirrigation), tidal pumping and resuspension of contaminated sediments by natural (storms, tides) and anthropogenic (dredging, prop wash, construction) processes (Electric Power Research Institute, 2007).

Contaminant movement from sediments through a food web is dependent on many complex interacting processes. These include the nature and extent of physical disturbances, desorption rates of contaminants from sediment particles, interaction with water column organic carbon, external loading, bioaccumulation into phytoplankton and transfer or biomagnifications from prey to higher level organisms. Both simple and complex mathematical models that incorporate many of these elements have been developed and used in remedial decision making (Brenner et al., 2004; Chadwick et al., 2008; HydroQual, 2007; Ruiz et al., 2000) (Figure 1).

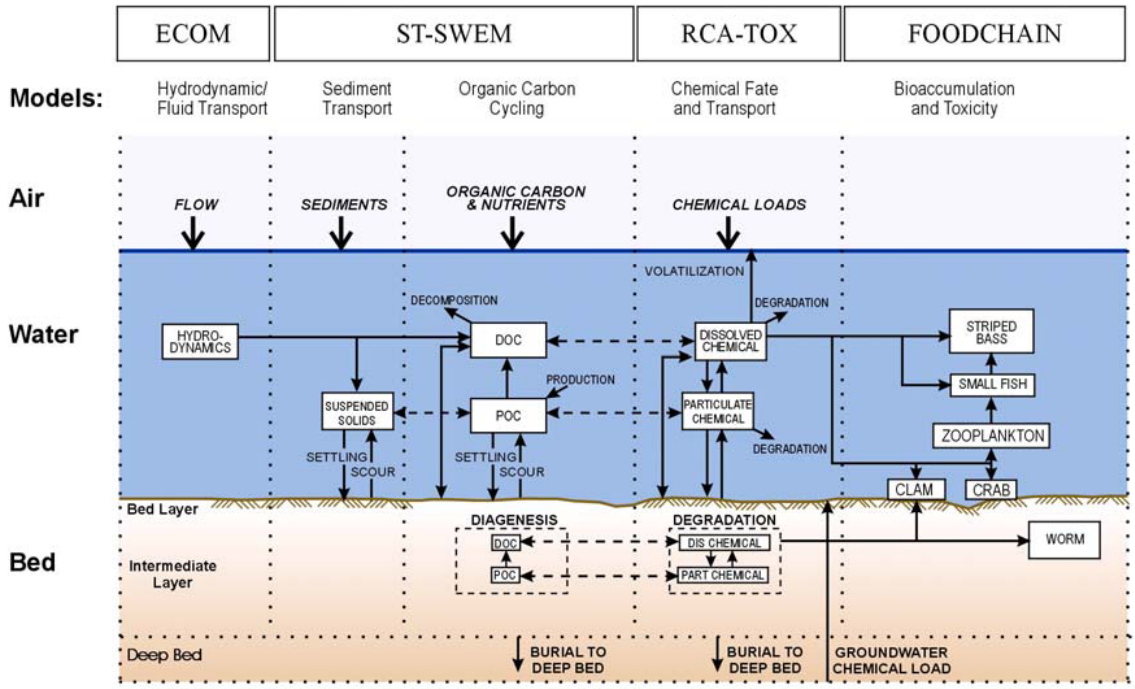

Figure 1. Contaminant Assessment and Reduction Project (CARP) Modeling Framework for Contaminated Sediments in New York-New Jersey Harbor (HydroQual, 2007)

The primary research need in this area is to increase certainty and confidence in fate and transport models. The research, development, and demonstration efforts should therefore focus on the areas where reductions in uncertainty would make a significant difference in the decision-making process. Three major, overarching areas with respect to the fate and transport of contaminants that need further research are (1) fate and transport process understanding, including in situ and ex situ sediment processes that effect bioavailability to ecological and human health processes and (2) demonstration, validation, and education on the application of fate and transport modeling in remedial management investigations and decision making.

Develop understanding of key parameters that influence both in situ and ex situ sediment contaminant partitioning and bioavailability. This need calls for research to identify the key parameters that control bioavailability, uptake, and trophic transfer through the food web. A better understanding is needed regarding flux from sediments into the water column and into the food chain. Synoptic chemical and biological data, both in the laboratory, and field-scale

studies, are needed to reduce uncertainty in these parameters. The major emphasis of this work would be to conduct work that reduces the uncertainties associated with forecasting uptake to fish, and the ability to back-calculate safe sediment concentrations for the protection of human health and ecological receptors. Identification of key parameters, and field should follow the USEPA's Data Quality Objective (DQO) Process to help collect data and to help demonstrate how the DQO process may be used in future sampling and analysis plan development for site-specific parameterization.

Demonstration, validation, and education on incorporation of bioavailability and fate and transport models into the decision-making process. The state of the science of fate, transport, and uptake models has progressed to the point where a number of different simple and complex models have been used to aid remedial decision making at both federal and state contaminated sediment sites. Incorporation of bioavailability terms into these decisions requires at a minimum an estimate of the long-term stability and effectiveness of bioavailability-based remedies such as monitored natural recovery, direct sediment amendment addition, and conventional or amended sediment caps.

This need is to provide DoD RPMs, as well as federal and state regulators, with technical training and modeling tools for conducting contaminated sediment site assessments and for evaluating in situ sediment remediation strategies (including capping, sediment amendments, and monitored natural recovery). The information on how models were developed and applied in decision processes to date is scattered among a myriad of reports associated with the individual sites. There is no single reference or training tool available to DoD RPMs or federal and state guidance on how to evaluate, design, and implement these amendment remedies. To meet that need, a guidance document, web-based decision tools, and an educational outreach program that would provide the needed information to design, implement, monitor, and demonstrate the long-term effectiveness of amendment addition remedies for contaminants commonly found at DoD sites should be developed.

8.1.1.5 Demonstrate and Validate Tools and Techniques to Monitor the Effects of Remedial Actions on Bioavailability (Multiple Remedies). With the increasing development and implementation of in situ remedial approaches (e.g., standard caps, reactive caps, addition of amendments, and the use of MNR) to address contaminated sediments, the monitoring tools and techniques utilized in relation to assessing contaminant bioavailability need to be further developed and refined. When in situ remedial approaches are implemented and are dependent solely or partially upon the decrease of the bioavailability/bioaccessibility (e.g., through sequestration, isolation, and/or sorption) of contaminants typically found in sediments, concerns regarding the long-term permanence and performance of these approaches exist. For example, there is little understanding of how these promising new technologies may perform over their engineered design life with regard to specific dynamic environmental factors, including but not limited to, fluctuation in flow conditions, bottom scour, changes in redox chemistry, and, advection of porewater. For regulatory agencies and the public, validation of the predicted decreases in bioavailability/bioaccessibility associated with these in situ remediation approaches under environmentally realistic conditions must be provided through carefully developed demonstration studies and post remedy monitoring plans. For the DoD and industry PRPs, tools

and techniques utilized to monitor these decreases in bioavailability/bioaccessibility must be balanced with the type and quality of data needed, along with the resources available after a remedial action is taken. Therefore, to gain the acceptance of these in situ remedial approaches by multiple stakeholders, it is a high priority need to further develop, and subsequently validate, tools and methods that can assess changes in bioavailability/bioaccessibility at contaminated sediments as part of monitoring, and can serve to validate the performance and permanence of in situ remedies over time.

8.1.1.6 Develop Guidance and Demonstrate Methodologies to Make Weight-of-Evidence Decisions. The workshop emphasized the value of weight-of-evidence approaches and of incorporating bioavailability measures and information as lines of evidence within the overall weight of evidence. With respect to sediments, weight-of-evidence approaches might include some combination of sediment characterization, exposure measures that account for bioavailability, toxicity studies, and community analyses. While much has been written on the topic of weight of evidence, there is a need to consider how such information, including bioavailability measures, can be used to inform management decisions.

Develop a consistent approach to interpreting lines of evidence, or weight of evidence in complex risk assessments and environmental decision making. Weight-of-evidence approaches enable risk assessors and site managers to evaluate multiple types of evidence and multiple lines of evidence within a type. While many risk assessment practitioners prefer to consider all available relevant evidence, some consider bioavailability measures in the process of weighing evidence to be too subjective. This research need would develop a standard of practice for interpreting lines of evidence or weight-of-evidence, with an emphasis on application of bioavailability in decision making and risk communication.

8.1.2 High Priority Needs

8.1.2.1 Standardize the Uses of Passive Diffusion Sampling Devices. A critical review of passive sampler technologies is warranted. This effort should include their availability, their uses, what contaminants (PAHs, PCBs, dioxins/furans) they are targeted to, and under what conditions they should be used. An effort to standardize the types and uses of passive diffusion devices would help remedial program managers and site environmental regulators to use these devices cost-effectively.

8.1.2.2 Interpretation of Benthic Community Analysis Within the Context of Contaminated Sites. The standard sediment quality triad (sediment chemistry, aquatic toxicity, and benthic community analysis) is often used to evaluate contaminant bioavailability at sediment sites. However, the interpretation of benthic community data is difficult within the context of determining site impacts, as there is no standard set of metrics that can be used to evaluate these data. A consensus on the proper methods of interpreting benthic community data and how to apply this within the decision-making process at contaminated sediment sites over a wide range of ecosystems is needed.

8.1.2.3 Better Understanding of the Seasonal And Long-Term Fluctuations in Bioavailability . A common concern of remedial program managers and environmental regulators is whether a bioavailability measurement taken at one point in time will still be applicable at a site in the near or distant future. For example, will the bioavailability of a compound at a particular site change over time due to processes such as aging, sedimentation, scouring, etc. Long-term field demonstrations are needed to demonstrate the permanence or change in parameters effecting bioavailability over short (i.e., seasonal) and long (i.e., 5- to 10-year) time scales. These measurements can be conducted at existing demonstration sites.

8.2 Soils

8.2.1 Critical Priority Needs

8.2.1.1 Review and Prioritize Contaminants for Bioavailability Research. There have been attempts to determine which contaminants are most common at DoD sites (see Appendix B). These efforts provide a useful starting point but do not include other important information on the potential for bioavailability adjustments to impact risk-based criteria, or on the potential economic impacts of bioavailability research.

The potential to impact risk-based criteria may differ for different contaminants. The original critical studies that provide the basis for risk assessment (such as the cancer slope factor studies) sometimes incorporate an absolute bioavailability, and in some cases, the default absolute bioavailability may be so low that there may be little value in developing site-specific adjustments. For example, the critical study used to develop criteria for oral ingestion of cadmium included an absolute bioavailability of only 5% (USEPA, 2003a). Further adjustments to risk-based criteria based on such low absolute bioavailabilities may be difficult to measure (or defend), even if the relative bioavailability is reduced due to site-specific conditions. A review of the critical studies, detection levels, and potential for adjusting bioavailability factors should be integrated with the information on the prevalence of different contaminants at DoD sites.

Additionally, the economic importance of different contaminants is not clear. Key differences between different contaminants may affect their economic priority to DoD. These potential differences include the magnitude by which a contaminant exceeds remedial goals, average volumes associated with different contaminants, the average remediation costs per unit volume, and their co-occurrence with other contaminants that would also require remediation. Given these uncertainties, it is difficult to prioritize bioavailability research targets.

8.2.1.2 Road Map to Expedite Process for New Contaminants. *In vitro* methods have been developed for estimating the relative bioavailability of metals from ingested soils to humans. Good estimates exist for lead and are in the latter stages of development for arsenic, where ingestion is a significant exposure pathway in risk assessment. Since validated *in vitro* methods exist for lead, it may no longer be necessary to duplicate the entire process of method development for each additional element of concern. Commonalities in the pathway of method validation need to be identified and adaptations suggested for different elements.

8.2.1.3 Demonstrate Long-Term Reductions in Bioavailability. There is some concern that reductions in bioavailability due to natural processes or remedial actions may not be permanent. Environmental conditions such as the oxidation-reduction status or pH may change over time, and changes in these conditions may cause bioavailability to increase. There is also a natural skepticism that contaminants left in place may become more available over time, and there are few long-term studies providing direct evidence for long-term reductions in bioavailability.

Studies designed to evaluate the long-term protectiveness of natural or engineered reductions in bioavailability could increase our understanding of bioavailability in general, and increase the regulatory and public confidence in proposed uses of bioavailability. Ongoing testing of previously-remediated sites or continued testing of sites with an existing database could help in understanding the long-term effectiveness of treatments designed to reduce bioavailability. Similarly, field studies designed to test the impacts of changing conditions on bioavailability could provide valuable empirical data.

9. TECHNOLOGY TRANSFER STRATEGIES

The attendees discussed technology transfer throughout the workshop's sessions. Key technology transfer issues were identified along with associated follow up responses. This section provides a "roadmap" for bioavailability technology transfer; that is, a strategy outlining specific tasks and interactions needed to facilitate acceptance of bioavailability concepts and tools into the user community.

9.1 Understanding Available Resources

The National Research Council recently considered the use of bioavailability in soil and sediment management and determined that regulatory acceptance of the use of bioavailability concepts in hazardous waste risk assessment varies across regions and different environmental media types. Although there is no consistent national policy nor formal guidance on bioavailability, the USEPA has issued several guidance documents that promote understanding bioavailability to assess risk and to adjust remedial decisions. These documents include, but are not limited to, the following:

- Framework for Metals Risk Assessment. USEPA March 2007 (Document No. 120/R-07/001)
- Estimation of Relative Bioavailability of Lead in Soil and Soil-Like Materials using In Vivo and In Vitro Methods, USEPA, May 2007 (OSWER Document No. 9285.7-77.
- Guidance for Evaluating the Oral Bioavailability of Metals in Soils for Use Human Health Risk Assessment, May 2007 (OSWER Document No. 9285.7-80).
- Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil, EPA May 2008 (OSWER Document No. 9200.1-86).
- Guidance for Developing Ecological Soil Screening Levels, USEPA, Feb. 2005 (OSWER Directive 9285.7-55).
- Guide for Incorporating Bioavailability Adjustments into Human Health and Ecological Risk Assessments at U.S. Navy and Marine Corps Facilities, U.S. Navy, July 2000 (NFESC User's Guide No. UG-2041-ENV).

While the documents listed above are excellent resources, there is a continuing need to transfer this information within the user community and among the state regulatory agencies so that bioavailability concepts can be appropriately and effectively incorporated into risk assessments and risk management decisions.

9.2 Stimulating User Community Interaction

SERDP and ESTCP bioavailability research and demonstration results would be most useful if accompanied by ongoing communication with the user community. Such communication should be built into projects early on so that not only can research and demonstration results be provided

to end users, but that end users can provide information to researchers on management challenges they face.

Many options exist for interaction with the communities of interest. Key to a successful technology transfer effort is to aggressively seek out technology transfer opportunities and to frequently assess which mechanisms have the most impact. Listed below are relevant communities with potential options for successful technology transfer. This listing should serve as a starting point and be expanded as new opportunities become available and as technology transfer efforts can be assessed for their efficacy.

RPMs/site regulators:

- Short courses (road shows, webinars)
- Technical data sheets on bioavailability tools/methods
- Protocols tailored towards RPMs and the regulatory community
- Presentations/short courses at the annual National Association of Remedial Project Managers (NARPM)

General regulatory community:

- Interactions with existing USEPA Headquarters/Regional groups (e.g., Federal Remediation Technologies Roundtable [FRTR], Triad, Contaminated Sediments Technical Advisory Group [CSTAG])
- Interactions with existing state groups (ITRC, Association of State and Territorial Solid Waste Management Officials [ASTSWMO])

General scientific and DoD community:

- Interact with existing DoD work groups and conferences (Tri-Service Risk Assessment Workgroup; U.S. Air Force RPM Workshop; U.S. Navy RPM Workshop, Alternative Restoration Technology Team [ARTT] and Remediation Innovative Technology Seminar [RITS])
- Identify and highlight current research at key professional symposia (SETAC)
- Identify and highlight current research at key industry conferences (e.g., Sediment Management Work Group [SMWG])
- Develop materials/courses for the SERDP/ESTCP Partners in Environmental Technology Technical Symposium & Workshop.

10. CONCLUDING THOUGHTS

The DoD is responsible for the management of thousands of sites with organic compounds and metals contamination in soils and sediments. The current regulatory paradigm for characterizing risks associated with the level of contamination in soils and sediments generally does not include measures of the actual bioavailability of these contaminants to human or ecological receptors. However, there is clear and growing evidence that demonstrates that some of these contaminants are less available to potentially harm humans or ecological receptors than is suggested by simply extrapolating effects based on total concentrations of contaminants in bulk soil or sediment. As a result, bulk soil or sediment concentrations frequently overestimate actual risks and cleanup levels based on such concentrations may be overprotective. Physical and chemical sequestration processes can reduce the potential for exposure and/or uptake by living organisms, but these changes in bioaccessibility and bioavailability are generally not addressed when setting risk-based cleanup criteria. Explicitly assessing contaminant bioavailability can result in setting more technically defensible cleanup goals and establishing more realistic cleanup priorities, while still ensuring protection of human health and the environment. Although the science supports incorporating site-specific bioavailability measurements into risk assessments and site management decisions, the current regulatory paradigm does not make this mandatory. This should change. Additionally, methods for assessing and reducing contaminant bioavailability should continue to be refined and validated.

To address these issues, research, demonstration, and technology transfer needs were identified and prioritized. Overarching issues throughout all breakout sessions included the need for improving the technology transfer process to bridge the perceived communication gap between scientists and managers. A key component of improving the communication process is to build scientific consensus in areas of technical uncertainty.

The result of this workshop is a strategic plan to guide SERDP and ESTCP investments in research and demonstrations associated with understanding and assessing the bioavailability of contaminants in soils and sediments over the next five to ten years, ultimately beneficially impacting environmental restoration efforts at DoD sites.

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APPENDIX A: ATTENDEES

Beth Anderson
National Institute of Environmental Health Sciences

Anne Andrews, Ph.D.
SERDP/ESTCP

Joel Baker, Ph.D.
University of Washington

Desmond Bannon, Ph.D.
U.S. Army, CHPPM

Nicholas Basta, Ph.D.
The Ohio State University

Barbara Beckingham
University of Maryland, Baltimore County

Michael Beringer
U.S. Environmental Protection Agency

Rebecca Biggers
NAVFAC ESC

Karen Bradham, Ph.D.
U.S. Environmental Protection Agency

Karole Braunstein
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Todd Bridges, Ph.D.
U.S. Army, ERDC-EL

Samuel Brock, Ph.D.
HQ AFCEE-TDV

Kim Brown
NAVFAC

Steven Brown, Ph.D.
Rohm and Haas Company

Robert Burgess, Ph.D.
U.S. Environmental Protection Agency

G. Allen Burton, Ph.D.
University of Michigan

Stan Casteel, Ph.D.
University of Missouri

Bart Chadwick, Ph.D.
SPAWAR Systems Center San Diego

Rufus Chaney, Ph.D.
USDA-ARS

Mark Chappell, Ph.D.
U.S. Army, ERDC-EL

Ronald Checkai, Ph.D.
U.S. Army, Edgewood Chemical Biological Center

Celia Chen, Ph.D.
Dartmouth College

John Christopher, Ph.D.
California Department of Toxic Substances Control

Charles Coyle
U.S. Army Corps of Engineers

John Cullinane, Ph.D.
U.S. Army, ERDC

Gregory Cutter, Ph.D.
Old Dominion University

Dominic Di Toro, Ph.D.
University of Delaware

Stephen Ells
U.S. Environmental Protection Agency

Kevin Farley, Ph.D.
Manhattan College

Nicholas Fisher, Ph.D.
Stony Brook University

Thomas Fredette, Ph.D.
U.S. Army Corps of Engineers

Lia Gaizick
U.S. Army Environmental Command

Kevin Gardner, Ph.D.
University of New Hampshire

Stephen Geiger, Ph.D.
ENSR

Rajat Ghosh, Ph.D.
ALCOA

Upal Ghosh, Ph.D.
University of Maryland, Baltimore County

Marc Greenberg, Ph.D.
U.S. Environmental Protection Agency,
Environmental Response Team

Susan Griffin, Ph.D.
U.S. Environmental Protection Agency

Philip Gschwend, Ph.D.
Massachusetts Institute of Technology

Karl Gustavson, Ph.D.
U.S. Army, ERDC-EL

Paul Hatzinger, Ph.D.
Shaw Environmental, Inc.

Steven Hawthorne, Ph.D.
University of North Dakota

Heather Henry, Ph.D.
National Institute of Environmental Health Sciences

Wanda Holmes
Chief of Naval Operations, N45

Jeffrey Houff
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Sarah Hunt
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Elisabeth (Lilli) Janssen
Stanford University

Philip Jardine, Ph.D.
Oak Ridge National Laboratory

Anna Knox, Ph.D.
Savannah River National Laboratory

Roman Lanno, Ph.D.
The Ohio State University

Andrea Leeson, Ph.D.
SERDP/ESTCP

Laura Lockard
University of Maryland, Baltimore County

Rainer Lohmann, Ph.D.
University of Rhode Island

Yvette Lowney
Exponent, Inc.

Richard Luthy, Ph.D.
Stanford University

Mark Maddaloni, Ph.D.
U.S. Environmental Protection Agency

Kelly Magathan
SERDP/ESTCP Support Office
HyrdoGeoLogic, Inc.

Jeffrey Marqusee, Ph.D.
SERPD/ESTCP

Keith Maruya, Ph.D.
Southern California Coastal Water Research Project

Kathleen McDonough, Ph.D.
ENSR

Larry McShea
ALCOA

Charles Menzie, Ph.D.
Exponent, Inc.

Ellen Mihaich, Ph.D.
Environmental and Regulatory Resources, LLC

Ravi Naidu, Ph.D.
University of South Australia

David Nakles, Ph.D.
ENSR

Edward Neuhauser, Ph.D.
National Grid

Michael Paller, Ph.D.
Savannah River National Laboratory

Paul Paquin
HydroQual, Inc.

Cara Patton
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Frederic Pfaender, Ph.D.
The University of North Carolina

Joseph Pignatello, Ph.D.
Connecticut Agriculture Experimental Station

Michael Pound
Naval Facilities Engineering Command, Southwest Division

Danny Rieble, Ph.D.
University of Texas, Austin

Deanne Rider
SERDP/ESTCP Support Office
HyrdoGeoLogic, Inc.

Stephen Roberts, Ph.D.
University of Florida

Michael Ruby
Integral Consulting, Inc.

Jim Ryan, Ph.D.

Alison Saulsbery
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Kirk Scheckel, Ph.D.
U.S. Environmental Protection Agency

Timothy Sinnott
New York Department of Environmental Conservation

Jason Speicher
FirstEnergy Corporation

Hans Stroo, Ph.D.
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Geoffrey Sunahara, Ph.D.
Biotechnology Research Institute

Jennifer Sutter
Oregon Department of Environmental Quality

Timothy Thompson
Science and Engineering for the Environment, LLC

Marvin Unger, Ph.D.
SERDP/ESTCP Support Office
HydroGeoLogic, Inc.

Katherine von Stackelberg, Ph.D.
Harvard Center for Risk Analysis

John Wakeman
US Army Corps of Engineers

Kimberly Ward
New Jersey Department of Environmental Protection

Randall Wentsel, Ph.D.
U.S. Environmental Protection Agency

APPENDIX B: BACKGROUND PAPERS

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BIOAVAILABILITY OF CONTAMINANTS IN SOILS

Yvette Lowney, Susan Griffin, Hans Stroo

Background Paper, SERDP Workshop on Bioavailability Research Needs
20-21 August 2008, Westin Hotel, Annapolis, MD

1.0 INTRODUCTION

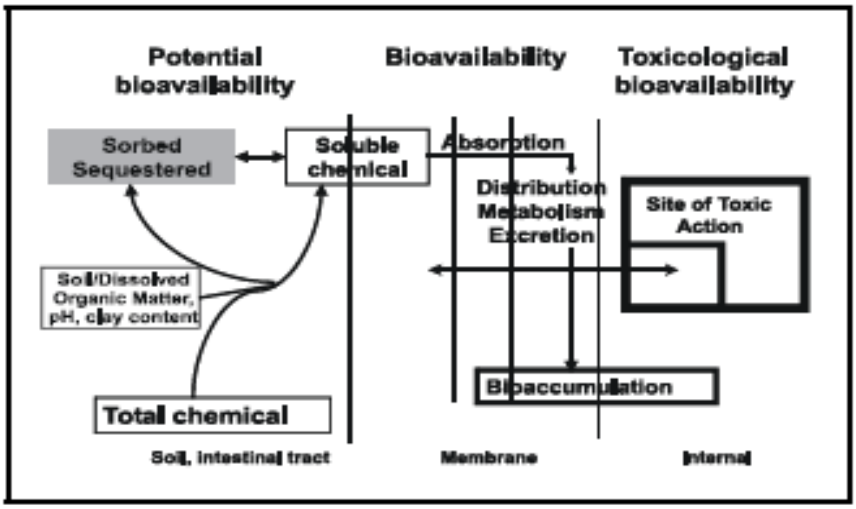
The U.S. Department of Defense (DoD) has significant liabilities associated with soil contamination, with many sites awaiting cleanup (USEPA, 2004). Because cleanup decision are dictated, in part, by the potential health risks associated with chemical contaminants at these sites, DoD has a keen interest in understanding the actual risks posed by contaminants in soil. A better understanding of these risks and reduction in the uncertainties in the risk assessment process would allow DoD to prioritize sites based on real risks and should also enable more effective and cost-efficient remediation.

As noted in the recent National Research Council (NRC) report, *Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications* (NRC, 2003), "chemicals in soils and sediments behave differently than when those chemicals are present in other media, notably water and air". The fact that the environmental matrix can strongly affect the potential for exposure has been known for well over a decade (e.g., Alexander, 1995), and regulatory frameworks explicitly recognize the influence of bioavailability on risks (e.g., Metals Framework, RAGs, Navy Guidance). However, bioavailability adjustments are still not broadly incorporated into risk assessments and regulatory decisions (particularly for soils), largely because of the uncertainties in our fundamental understanding in this area. Uncertainties include the nature and magnitude of the "bioavailability processes," the strengths and limitations of various methods used to measure bioavailability, and the appropriate uses of such data in risk assessment.

For these reasons, SERDP/ESTCP has funded several projects in recent years to better understand and measure bioavailability of chemicals from environmental media and seeks more coordination and strategic vision in leveraging existing data and developing new information. Given the high importance of this technical area, and the desire to develop an integrated and appropriately targeted research program, SERDP has convened a workshop to identify the key issues and research needs. This background paper for that workshop is intended to briefly summarize the current understanding of which chemicals are of the greatest importance in the risk assessment process and what is known about the bioavailability of these chemicals from soils, and to identify the contaminants and situations for which incorporating bioavailability adjustments is likely to be of most value to DoD.

1.1 Background

The importance of bioavailability in understanding chemical exposures, toxicity, and risks has been recognized for a long time, but the term itself has varying definitions because several different disciplines have addressed the subject over the years. For purposes of the workshop, we will generally use the definitions and concepts described in the previously-cited NRC report (NRC, 2003, Table 1-1). For the term "bioavailability," the NRC panel did not provide one definition, but instead explicitly chose to recognize the value of several different definitions, and to focus instead on the processes that influence exposure. Figure 1 illustrates the bioavailability processes of interest, and also shows some of the ways in which the term has been used.



Schematic of Chemical Bioavailability in Soils

Figure 1. Bioavailability Processes (Lanno, 2002: SERDP Project ER-1210[1]).

Although this workshop will consider all these processes, the focus is primarily on the environmental processes that control the extent to which environmental media (e.g., soil) bind chemicals, interfering with the chemical solubility and thereby affecting the amount accessible to an organism for systemic absorption. These environmental processes include desorption, dissolution, sequestration, and dissociation of contaminants from the environmental medium in which they occur. This focus on environmental processes, with concomitantly less emphasis on the internal biological processes that are also important in toxicity and bioaccumulation, reflects the assumption that the inherent toxicity of a chemical is related to the amount of chemical available for absorption across the surface of biological membranes (e.g., gastrointestinal tract, skin), irrespective of the media from which exposure occurs[2]. Therefore, an important distinction (outlined by NRC, 2003) to keep in mind in assessing exposures from environmental media is issues of "absolute bioavailability" and "relative bioavailability." The former is

[1] http://www.serdp.org/Research/upload/ER_FS_1210.pdf

[2] It should be noted that, SERDP/ESTCP is not authorized to fund human-health toxicity research and therefore has focused efforts on understanding the nature and magnitude of exposures to chemicals from environmental media.

assumed to be accounted for in toxicity research that serves as the basis of regulatory toxicity values (e.g., carcinogenic potency factors and reference doses), while the latter may be specific to the chemical characteristics, environmental medium, or other site-specific factors.

Bioavailability must also be viewed in the context of specific receptor-pathway combinations:

- There are differences in the ability of different receptors to absorb contaminants from a given matrix; for example, following oral exposures absorption from the gastrointestinal (GI) tract may be much different in species or individuals having different GI pH values or other differing anatomical or physiological characteristics.
- The availability of soil-bound contaminants for absorption across the skin may be much different than the availability for absorption in the GI tract.
- Measurement is also complicated by the fact that bioavailability of a chemical from soil can change over time (e.g., weathering), or with changes in environmental conditions (e.g., redox status).

There are additional hurdles to generating meaningful data for understanding the influence of environmental matrices on contaminant bioavailability. For human exposures, it is difficult to directly test bioavailability, so alternate measures must be developed and calibrated to human exposures and responses. These measures may be *in vivo* (e.g., using surrogate species) or *in vitro*, using controlled laboratory conditions designed to mimic the target pathway and receptor or methods that have been calibrated against data from animal studies. For other species, direct testing is often possible, but the test conditions and the endpoints considered in those tests are critical, and the inevitable variability within test populations and the difficulties in performing animal testing can make bioavailability assessments cumbersome and expensive. So there is great interest in efficient and inexpensive standardized and calibrated *in vitro* assays. In addition, several physical and chemical analyses have been proposed to characterize specific processes that may control bioavailability by limiting "bioaccessibility," and extensive testing and calibration is needed for any such analysis.

There has been (and continues to be) controversy regarding the appropriate methods to use when evaluating the controls imposed by environmental media on contaminant bioavailability, and the appropriate interpretations of the results (e.g., Richardson et al., 2006). The NRC (NRC, 2003, Tables 4-1 and 4-2) defined criteria for assessing the strengths and limitation of research tools available, including consideration of:

- Applicability
- Specificity of the process being evaluated
- Direct relevance to understanding bioavailability
- Ability to generalize to allow predictions
- Relevance to regulations
- Usefulness as a research tool.

The NRC panel reached several conclusions regarding bioavailability tools that are relevant to this workshop, including:

1) A suite of tools will likely be needed at any given site;
2) Users need to understand the environmental setting for which specific tools were designed and intended; and
3) An intensive effort is needed to develop mechanistic tools and models.

In addition to the conceptual guidance provided by NRC and detailed research findings available from various sources (e.g., published literature, government reports), the DoD has published a guidance document (http://web.ead.anl.gov/ecorisk/related/documents/Bioavail_Part_1-final.pdf), which offers practical guidance on when and how to incorporate bioavailability adjustments in risk assessments for environmental media.

1.2 Implications

The implications of site-specific adjustments to regulatory standards to account for the bioavailability of chemicals in soil (relative to the bioavailability of the soluble forms that generally provide the basis of toxicity criteria) can be significant. For example, bioavailability testing at one metal-contaminated site (National Zinc Company Superfund Site, OK) demonstrated that the site-specific bioavailability was significantly less than the default assumptions. The results of site-specific testing provided the basis for increasing the residential soil cleanup levels for lead (from 500 to 925 mg/kg), cadmium (from 30 to 100 mg/kg), and arsenic (from 20 to 60 mg/kg). Because of the nature of this specific site, even these relatively modest two- to three-fold adjustments reduced the remediation costs for this site by more than $40 million over initial estimates of remediation costs (Battelle, 2003).

Lead provides an important example of both the difficulties and promise of research on bioavailability. It has long been recognized that the bioavailability of lead in soil can vary widely, depending on the chemical form of the lead, the provenance, and the environmental conditions. These factors can be very site-specific, and therefore it has been difficult to develop a generic adjustment value to address lead bioavailability from soils on a wide-spread, or default, basis. Given the widespread occurrence of lead contamination of soil, there has been a concerted effort to better understand its bioavailability and the effects of chemical speciation, as well as to measure lead bioavailability in different samples using available protocols (including SERDP- and ESTCP-funded work described below).

This research on lead has resulted in the recent regulatory acceptance of a protocol for measuring lead bioavailability (discussed in more detail in the following section). However, bioavailability testing is still costly and time-consuming, and the accepted protocol has not yet been extended to other contaminants. The research has also led to promulgation of a default bioavailability factor of 60% for lead in soils. Unfortunately, it has become clear that using the default value may lead to significantly overestimating, or underestimating, the actual risks because lead bioavailability can vary so widely depending on the site-specific conditions.

In summary, the concept of using bioavailability to adjust risk-based criteria has a solid scientific foundation and has achieved limited regulatory acceptance and use in decision making. However, a great deal of work remains, and there is debate regarding the likely quantitative impact of bioavailability adjustments, or even the wisdom of using bioavailability at all in risk assessments until we have a much firmer mechanistic understanding of the processes involved.

The remaining sections of this background paper discuss the key issues of concern for inorganic and organic compounds present in soils, the past SERDP/ESTCP research in the area, and the regulatory perspectives on bioavailability research.

2.0 SOIL BIOAVAILABILITY AND RISK DRIVERS

Several focused efforts have been conducted to better understand the chemicals that are the primary contributors to calculated risks and remedial decisions at DoD sites. Understanding the chemical drivers of risks (to human or ecological receptors) from chemicals in soil (or sediment) should help focus the research and technology transfer efforts. In particular, Salatas et al. (2004) examined the metals that are the most common risk drivers at DoD sites, and von Stackelberg et al. (2007) evaluated the frequencies of risk drivers at U.S. Army sites. Also, in preparation for this workshop, we have reviewed a sample of recent Records of Decision (ROD) for DoD sites. Each of these efforts provides different insights into understanding which chemicals should be at the forefront of evaluation when developing priorities for a future research agenda. The results, for both inorganic and organic contaminants, are briefly summarized in the following sections.

2.1 Inorganic Contaminants

Based on an analysis from the mid-1990s U.S. EPA has indicated that for DoD sites with identified soil contamination that requires cleanup, over 70% are contaminated with metals (U.S. EPA, 1997b). More recently, an informal search of RODs for DoD sites that were issued in the last 5 years indicates that organic chemicals in soil now predominate the need for remedial decisions. Whether this represents a true change in the nature of regulatory actions (or the underlying toxicity database, or analytical chemistry), or whether the analyses are too informal to support major conclusions regarding trends in chemical risk drivers for contaminants in soil, is not yet clear.

Three sources of information were generally relied upon for information regarding the inorganic chemicals that emerge as principal contaminants that either predominate risks in assessments conducted at DoD sites, or that factor most significantly in remedial decisions for these sites. The most recent of these was a raw survey of recent RODs for DoD sites (i.e., for decisions issued in the last 5 years). In this analysis—for the sites where metals were listed as a basis for remedial decisions—arsenic, lead, chromium, manganese, copper, mercury, and antimony emerge as the metals of primary concern (Table 1).

Table 1. Inorganic Contaminants of Concern (COC) at DoD Sites with Soil Contamination (Review of 105 OUs)

Metal	No. of Sites
Arsenic	69
Lead	54
Chromium	44
Manganese	31
Copper	30
Mercury	29
Antimony	29
Thallium	26

Note: Total (312) higher than number of sites because some sites have multiple COCs

These findings are not inconsistent with an earlier, but more broad-scale evaluation of the metals that form the basis of remedial decisions at DoD sites (Salatas et al., 2004). In this more detailed evaluation, databases of risk assessments were acquired from all branches of the military and combined with other national databases to identify target metals. This analysis indicated that, for human health endpoints of toxicity, primary metals of concern at metals-contaminated sites were lead, arsenic, chromium, cadmium, antimony, and manganese. For ecological receptors, several of these metals, plus mercury and selenium, emerge as metals of concern. When attempting to identify whether the magnitude of exceedance of health-based criteria was consistently high for any specific metal, none except for lead show a consistent pattern in terms of the magnitude of the exceedance of human health-based criteria. Similarly, no particular pattern emerged for metals consistently being more highly elevated in comparison to ecological screening criteria, except for selenium and avian receptors, for which the ratio of the site metal concentration to the screening criterion was consistently high.

In reporting on "case studies" of remedial decisions for 17 DoD facilities (von Stackelberg et al., 2007), it appears that organic chemicals (such as PAHs and DDx) appear more frequently than metals in site evaluations, and with higher reported potential risks (as measured by toxicity quotients). However, after these two categories of organic chemicals, a suite of metals emerge as present in remedial evaluations, including lead, aluminum, copper, cadmium, chromium, barium, and zinc. When focusing solely on human receptors, then arsenic emerges as a target metal that drives calculated health risks, especially when based on potential carcinogenicity from site contaminants.

The issue of what target receptor serves as the basis for regulatory decisions merits consideration. Interviews with toxicologists in all regional offices of U.S. EPA indicated that human health considerations usually drive remedial actions for metals in soils, and that ecological receptors typically become an issue only if wetlands and sediments are part of the assessment (Salatas et al., 2004). Although this contrasts with the findings from screening of site concentrations against toxicity thresholds for human and ecological receptors, it is consistent with information reported by von Stackelberg (2007), who reports that most corrective action objectives for the sites they evaluated were based on human health risks, and that exceedance of toxicity thresholds for ecological receptors are frequently dismissed as overestimates, and not as indicative of the same potential for risk as human health exceedances. If it is true that site management decisions for contaminated soils target human health considerations (and that these are considered adequately protective for ecological receptors), then any future research agenda may be most appropriately focused on assessing the human health endpoints, despite the fact that health-based screenings of sites indicate higher risks for ecological receptors.

Salatas et al. (2004) also point out that different metals are associated with different site operations, so while a variety of metals may be found at a particular site, the areas of contamination may be divergent. For example, lead contamination occurs at former firing ranges, arsenic in areas of historical pesticide use, and chromium at locations of plating shops. Therefore, the areas impacted by some metals may be localized (e.g., chromium from plating shops) while others are dispersed (e.g., arsenic from former pesticide use). This may be

important in considering target metals for bioavailability research, as the costs of remediation may be low for chemicals with localized impacts, and the benefits from RBA adjustments in risk assessments more important for chemicals with broad distribution.

2.2 Organic Contaminants

Based on an initial survey of RODs at DoD sites, the principal organic contaminants of concern in soils are PAHs, pesticides (primarily chlorinated pesticides like DDT and related compounds), PCBs, volatile organic compounds (VOC) (including chlorinated aromatic hydrocarbons and non-chlorinated VOCs such as benzene, toluene, ethylbenzene, and xylene [BTEX] compounds), and nitroaromatics (explosive compounds such as RDX and TNT (Table 2). This review of 105 site RODs is not meant to be complete, but it provides a realistic evaluation of the relative frequencies of different organic soil contaminants present at DoD sites.

A separate and more thorough evaluation of risk drivers was conducted recently by identifying contaminant-pathway-receptor combination exceeding regulatory criteria at several U.S. Army sites (von Stackelberg et al., 2007). As mentioned above, that review concluded that most of the proposed remedial goals were based on human health risks. Ecological risks were generally addressed by default, in a qualitative fashion. By far the most common cancer risk driver was PAH ingestion via home-grown produce, followed by ingestion of VOCs in groundwater. For noncancer hazards, the greatest number of exceedances was for exposure to explosives in groundwater.

Table 2. Organic Contaminants of Concern at DoD Sites with Soil Contamination (Review of 105 OUs)

Contaminant Class	No. of Sites
PAHs	47
Pesticides	29
PCBs	27
CAHs	22
VOCs	15
TPH	11
Phthalates	7
Dioxins/Furans	6
Nitroaromatics	5

Note: Total (169) higher than number of sites because some sites have multiple COCs

Bioavailability is thought to be of the greatest potential value for adjusting risk-based criteria for the hydrophobic contaminants, particularly PAHs and PCBs, because these compounds are the most likely to be tightly sorbed to the soil matrix. Although a fraction of the more soluble compounds also may be unavailable for uptake, the fraction that is not bioaccessible is likely to be greater for the highly hydrophobic organic compounds (NEPI, 2000). Also, research to date on the bioavailability of organic compounds in soils has focused primarily on these hydrophobic contaminants (e.g., Linz and Nakles, 1997). In fact, the first studies of bioavailability to adjust

exposure assessments focused on hydrophobic organics, including PAHs, PCBs, and dioxins/furans (e.g., Fries et al., 1989; Goon et al., 1990). It has become clear that a significant fraction of the PAHs and PCBs can be virtually unavailable for uptake by humans, either through dermal contact or oral ingestion (e.g., Stroo et al., 2005; Oomen et al., 2000). Extraction testing has been conducted to "ballpark" the bioavailability of some of these chemicals from soils and detailed evaluations with animal studies conducted for some large sites. However, despite over two decades of research showing decreased bioavailability of these contaminants in soil, there has been little regulatory acceptance of bioavailability adjustments for any organics.

There has been less research on the bioavailability of explosives such as RDX and TNT, but the work that has been done suggests that bioavailability could also be reduced for these compounds when they are present in soil (e.g., Reifenrath et al., 2002; Zhang et al., 2006). Recent SERDP-funded work also suggests that the bioavailability of these compounds may be decreased in soils, although to date this work has focused on ecological receptors and the development of soil screening levels for ecological risk assessments (see Attachment A).

3.0 REGULATORY PERSPECTIVES

3.1 Status of Bioavailability Adjustments for Soils

The human health risk assessment process estimates risk by comparing a site-specific intake or exposure to a toxicity reference value, such as a Reference Dose or cancer slope factor. The current practice at U.S. EPA is to assume that the site-specific intake from contaminated soils or sediments is absorbed from the GI tract into the bloodstream at the same rate as the media the toxicity reference value is based on. Even though the oral toxicity values are typically based on chemicals administered via water, gavage or food, the practice at most Superfund, Federal Facility, and RCRA sites, is to assume that contaminants in soils and sediments are equally available for absorption from the GI tract into the blood stream.

Most risk assessors agree that this approach is overly conservative, but no national guidance exists on appropriate media-specific numbers. Although individual regions and states may adjust bioavailability factors based on information from the scientific literature, the reported bioavailability factors vary enormously. So application on a site-specific basis is inconsistent. Further, risk assessors are often unaware that *in vivo* animal studies can be conducted to develop a site-specific factor, or the cost of the *in vivo* studies is not justified when compared to the overall site cleanup costs.

In U.S. EPA Region 8, lead and arsenic are contaminants of concern at approximately 60-70% of the Superfund sites. Many of these sites extend over tens to hundreds of square miles, with remediation costs (predominantly soil removal and disposal) ranging from tens to hundreds of millions of dollars. Reductions in the default bioavailability assumptions for lead and arsenic in soil could result in significant cost savings without endangering public health. U.S. EPA Region 8, in conjunction with academic and consulting scientists, has therefore developed protocols for testing the bioavailability of lead and arsenic, using juvenile swine models and geochemical speciation methods. These protocols were used to adjust bioavailability factors for lead- and arsenic-contaminated soils from mining, smelting, milling, wood treating, and lead-based paint sites. These testing protocols have been reviewed and accepted within the scientific community, and the results have been accepted at the national level, by state regulatory agencies and regulated industries (http://epa.gov/superfund/bioavailability/guidance.htm). Bioavailability studies have also been conducted successfully in cynomolgus monkeys for arsenic in soils.

However, these studies are expensive (approximately $100,000 per study), and time-consuming (approximately 3-6 months). So U.S. EPA Region 8 joined together with scientists from industry, academic, consulting, and state/federal government (known collectively as the Solubility/Bioavailability Research Consortium, or SBRC) to develop a faster and less costly *in vitro* bioaccessibility assay (IVBA). The IVBA is based on the concept that the rate of solubilization in the GI fluid is an important determinant of bioavailability *in vivo*. The SBRC validated the IVBA method by testing soil samples in side by side comparisons with the results of *in vivo* studies and optimizing the parameters for the IVBA until an acceptable correlation was

measured. Based on these results, U.S. EPA has accepted use of IVBA tests to quantify lead bioavailability in soils and sediments (http://epa.gov/superfund/bioavailability/guidance.htm).

Arsenic, however, remains more problematic, because the correlation between the IVBA results and the *in vivo* animal results was poor. However, the IVBA test was optimized for lead, and optimizing the test conditions for arsenic has not yet been done. Currently, Region 8 recommends a weight-of-evidence approach which combines the *in vitro* studies and geochemical speciation results at the site in question with the *in vivo* and geochemical results from the studies in the arsenic library conducted to date. If the geochemical speciation results of the site in question are similar to the speciation results of a site in the arsenic library, the *in vivo* bioavailability results from the library site may be used as a reasonable surrogate.

In summary, the U.S. EPA accepts the results of an *in vivo* animal bioavailability study to quantitatively adjust the bioavailability of arsenic and lead from soil and sediment, and nationally, the U.S. EPA also accepts the results of the IVBA method to quantitatively adjust the bioavailability of lead from soil and sediment. On the regional or state level, individual risk assessors may adjust the bioavailability factor for other contaminants based on IVBA results, geochemical speciation, and/or the scientific literature.

3.2 Summary of Current Lead Protocols

The following section summarizes the approach taken to adjust the bioavailability factors for lead in soil. The detail is provided because this guidance and experience may set the stage for allowing faster adoption of bioavailability adjustments for other chemicals. To adjust the lead bioavailability factor at a given site, standard operating procedures (SOP) have been developed for (1) the geochemical speciation of lead in soil/sediment, (2) the bioavailability of lead in soil/sediment using an *in vivo* animal model, and (3) the bioavailability of lead in soil/sediment using an IVBA method.

3.2.1 Geochemical Speciation

The bioavailability of lead in any test soil is dependent upon the mineral and physical nature of the metal-bearing grains in the soil. Valuable information on mineral forms, particle size distribution, and matrix associations for metal-bearing grains can be found upon examination of the mineralogy of the soil. A wide variety of chemical and analytical techniques have been used to characterize a metals speciation in various media. Electron microprobe analysis is one such technique which has been routinely used for site characterization and offers the most complete data package on metal speciation than any of the other tools. Briefly, electron microprobe analysis (EMPA) uses a finely focused electron beam to produce a combination of characteristic x-rays for elemental quantification, and secondary electrons for visual inspection of a sample. SOPs for conducting geochemical speciation of lead in soil/sediments by EMPA were developed by Dr. John Drexler (available at http://www.colorado.edu/geolsci/legs/speciation1.html).

3.2.2 Determination of Bioavailability Using Animal Studies

The basic approach for measuring lead absorption *in vivo* is to administer an oral dose of lead to test animals and measure the increase in lead level in one or more body compartments (blood,

soft tissue, bone). To calculate the relative bioavailability of a test material, the increase in lead in a body compartment is measured both for that test material and a reference material (lead acetate). The relative bioavailability of the test material is calculated as the ratio of doses (test material and reference material) that produce equal increases in lead concentration in the body compartment. SOPs for conducting an *in vivo* bioavailability study in juvenile swine can be found at http://epa.gov/superfund/bioavailability/guidance.htm. These SOPs include development of study design, animal dosing, sample collection, and analysis and data reduction/ statistical analysis. SOPS for *in vivo* bioavailability studies using cynomolgus monkeys can be found at web.ead.anl.gov/ecorisk/related/documents/Bioavail_Part_2-final.pdf (Appendix E).

3.2.3 Determination of Bioavailability Using IVBA tests

IVBA tests do not measure absorption into actual tissues but rather measure the solubilization of Pb in simulated GI fluid. In brief, samples of test material are mixed with a defined extraction fluid for a specified time under specified conditions. The eventual filtered sample of extraction fluid is analyzed to quantify the fraction of the Pb or As in the sample which has dissolved. SOPs for the IVBA tests were developed by the SBRC, and are available at http://www.colorado.edu/geolsci/legs/invitro1.html.

3.3 Barriers to Use of Bioavailability Adjustments

The barriers to using bioavailability adjustments are similar to those for incorporating any new scientific information into the risk assessment process. Most risk assessors have a limited understanding of the processes affecting the bioavailability of contaminants from soil or sediments, the mechanisms by which geochemistry affects the dissolution of contaminants from soils and sediments into the GI tract, or how physiology and toxicokinetics impact absorption of contaminants within the GI tract. As a result, they often look for guidance from U.S. EPA (or other regulatory agencies). Lacking such guidance, they understandably fall back on conservative default assumptions because risk assessment and cleanup decisions must be explained and defended to an often skeptical and concerned public.

Removing or reducing those barriers requires working closely with the state and regional risk assessors to share information on the environmental and physiological processes that influence bioavailability and to develop an approach for deriving a site-specific bioavailability adjustment. All interested parties should communicate and work together to determine if such an adjustment will significantly impact the remediation decisions and be cost effective. If so, they must work together to agree on the best approach or methodology to use, develop SOPs, and define decision criteria. If this communal approach is used, the probability of developing a bioavailability adjustment that is used in the risk assessment and cleanup decision is greatly increased.

On the national level, it would be useful to work with U.S. EPA to produce national guidance. There is no one bioavailability adjustment factor for all sites. Based on the lead and arsenic *in vivo* and *in vitro* studies conducted to date, bioavailability estimates range from very low to high depending on the contaminant levels present, the source of the contamination, and the geochemistry of the soils/sediments present. Any determination of a bioavailability adjustment must be done on a site-specific basis. National guidance will be most useful if it provides

information on how the sources and levels of contaminants, and the geochemistry, are expected to influence bioavailability in soils and sediments. It would also be helpful to include recommendations on test methods, SOPs, and decision criteria needed to develop a site-specific bioavailability factor.

3.4 Potential Uses of Bioavailability for Decision Making

Prior to any decision to develop a site-specific bioavailability adjustment, it is important to determine if the adjustment will significantly impact the costs and scope of the remediation decision, and if the cost of the bioavailability study relative to the project costs is worthwhile. Initial estimates can be done by calculating cleanup levels based on a range of reasonable bioavailability factors (e.g., 100%, 60%, 30%, etc.) and estimating the corresponding costs for excavation, hauling, and disposal (or treatment) of the soil. In such cases, a good sampling plan with representative spatial coverage and a statistically significant number of sample points can be very helpful.

The other factor is the cost (and time) for the bioavailability study relative to the overall project costs. Using the current *in vivo* protocols, bioavailability testing is unlikely to be useful for projects costing less than $1,000,000 or that need to be completed in under a couple of years. However, an IVBA study that costs approximately $200 per sample ($600 with geochemical speciation) and takes about 1-2 weeks to run may be cost effective for many more sites.

Typically, the larger the site and project budget, and the more heterogeneous the contamination, the greater the potential for bioavailability to impact the site decision. One example in U.S. EPA Region 8 is the Anaconda Smelter Site in Montana, a former smelter encompassing 100 square miles and five communities. Arsenic in soils was the primary concern. An assumption of 100% bioavailability of arsenic from soil would have resulted in approximately 5,000 homes being remediated at a cost of $25 million. An *in vivo* animal bioavailability study was conducted showing a bioavailability of 18% from the soils. This site-specific bioavailability factor was used in the risk assessment and remedial decision, reducing the scope of cleanup to 350 residential homes at a cost of $2 million. When a site-specific bioavailability study can have a significant impact on the final cleanup levels and is conducted in a manner which is accepted by the regulatory community, the overall cost and scope of the remediation project can be greatly reduced.

The methodology developed for lead and arsenic should also be applicable to other contaminants. There would seem to be no technical barriers to the use of juvenile swine or cynomolgus monkey *in vivo* studies to develop bioavailability adjustment factors for other contaminants. These methods are most likely to be useful for situations where oral ingestion by humans is the primary risk driver and cleanup costs are high enough to justify the necessary efforts. Attractive targets, considering their widespread occurrence and prior evidence of low bioavailability in soils, include PCBs and dioxins.

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ATTACHMENT A
SERDP/ESTCP Soil Bioavailability Research

A.1 INTRODUCTION

SERDP/ESTCP in particular has funded several research and demonstration projects intended to advance our understanding of bioavailability processes and to develop improved tools for use in assessing bioavailability. It is important to note that SERDP/ESTCP is not authorized to fund human-health toxicity studies, so the work described below has focused on the soil factors controlling the potential for uptake and absorption.

Much of the recent SERDP/ESTCP-funded work has primarily addressed bioavailability in sediments, but bioavailability of contaminants in soil has also been important. The work on soil bioavailability has been primarily focused on a few metals of concern, notably lead. In addition, bioavailability has been addressed as one component of several other projects dealing with other contaminants. For example, some research has been focused on the potential for bioremediation and has addressed the impacts of limited bioavailability on biodegradability. Other work has used bioavailability measurements as one means to evaluate remediation success (for example, when demonstrating technologies designed to stabilize metals).

The following sections briefly summarize the SERDP/ESTCP work in the area of bioavailability of contaminants in soil, emphasizing those projects that have been primarily concerned with bioavailability and its potential use risk assessment. Relevant Statements of Need (SON) are first described, and then the results and methods used in a few key projects are highlighted to help panel members appreciate the past and ongoing efforts. Links to project fact sheets and reports are provided for those wanting further information.

A.2 STATEMENTS OF NEED

SERDP projects are selected in response to relatively specific SONs, so relevant SONs are described below to help understand the past research interests.

A.2.1 Metal Bioavailability

The first directly applicable SON is from Fiscal Year 2000 (FY00), and was titled Bioavailability and Long-Term Stability Issues Associated with Metals. The overall objective was to "a greater knowledge of the science regarding the behavior/chemical state of metals in soils and improved measurement techniques to assess bioavailability so as to address the technology gaps that adversely influence risk assessments and remediation of metals in contaminated soils. The research should focus on increasing the knowledge base regarding the bioavailability/speciation of metals and measurement approaches."

Key "research foci" under the FY00 SON included:

1. Determine the effect of the physical/chemical form of heavy metals (focus on Pb, Zn, Cu, Cd, As, and Ni) on bioavailability.
2. Critically examine free metal ion and pore water concentration as a measure of the bioavailability of heavy metals.
3. Determine metal ion speciation in soils.
4. Develop methods to identify metal species in mixed soil matrices.
5. Develop and validate a simple physicochemical extraction/assay system correlated with risk of heavy metals in soil or sediments.

Two projects were selected under this SON: ER-1165 and ER-1166 (Sections A.3 and A.4). A follow-on ESTCP project is currently ongoing (ER-0517 – Section A.5).

A.2.2 Ecological Soil Screening Levels

A SON was issued for FY01 for the Development of Ecological Soil Screening Levels. Bioavailability represents a key aspect of this SON, intended to develop risk-based soil screening levels for ecological receptors for chemicals of concern to DoD (primarily metals and munitions constituents). The two objectives listed were 1) to determine the relationships between contaminant concentrations in soil and soil biota toxicity and 2) to characterize bioavailability across all trophic levels.

Two projects were selected. These projects (ER-1210 and ER-1221) are described briefly in Section A.6.

A related SON was issued for FY05, titled Ecological Soil Screening Levels and Wildlife Toxicity Reference values for Improved Risk Assessment at DoD Sites. This SON was a follow-up to the earlier one and included development of data to support EcoSSLs for wildlife species. The SON indicated that the research should be limited to collecting data that can be used by the Eco-SSL Workgroup (comprised of EPA, other federal agencies, states, and industry groups) to further develop an Eco-SSL for explosives contaminants.

Two projects were selected under this SON, one to develop wildlife toxicity values (ER-1420[3]) and ER-1416, which built on the results from the earlier EcoSSL projects. ER-1416 is also described in Section A.6, as bioavailability in soil is a larger emphasis for this project.

A.2.3 Reducing Bioavailability of Metals in Soil

For FY03, one of the SONs sought methods to reduce the bioavailability of metals in soil. Titled In Situ Sequestration Enhancement and Engineered Bioavailability Reduction of Metals in Soils, the SON was intended "to develop a better understanding of the enhancement of *in situ* sequestration and/or engineered reduction of metal bioavailability in soils." Fundamental and mechanistic studies were sought "to increase the knowledge base regarding the mechanisms by

[3] http://www.serdp.org/Research/upload/ER_FS_1420.pdf

which different soil amendments or other approaches alter the form of metals in soil and the resulting impacts on bioavailability."

Three projects were selected—ER-1350, ER-1351, and ER-1352. All of these projects focused on the use of soil amendments to reduce metal bioavailability, and all are described in Section A.7.

A.3 DEVELOPMENT OF EXTRACTION TESTS FOR BIOAVAILABILITY OF METALS IN SOIL (ER-1165[4]).

This project ([principal investigators [PI] Mike Ruby and Yvette Lowney) was originally intended "to develop a suite of simple and easy-to-use extraction tests to predict human and ecological exposures to metals in soil." The project, briefly summarized in Section 2 of this document, was completed in 2005 and has provided a valuable foundation for future research and development. The Final Report[5]) can be accessed on the SERDP website (www.serdp.org).

The project was performed in three phases:

1. The metals representing the primary risk drivers at DoD sites were identified.
2. *In vivo* testing was conducted to understand the parameters that control absorption and to generate a database of information to guide development and validation of *in vitro* approaches to assessing bioavailability.
3. The applicability of *in vitro* methods for estimating bioavailability was evaluated.

The risk driver evaluations showed that, for DoD sites, lead was the most frequent soil contaminant exceeding screening criteria, for both human health and ecological scenarios. Other metals of concern for human health include arsenic, chromium, cadmium, and antimony. For ecological receptors, the most frequent metals of concern were lead, zinc, mercury, chromium, and selenium for birds, and arsenic for mammals.

For human receptors, three major areas of investigation were pursued: relative oral bioavailability of arsenic; relative oral bioavailability of cadmium; and percutaneous absorption of arsenic from soil. Briefly, the results showed that:

1. The mean RBA values for oral uptake of As from 10 soil samples from DoD sites varied from 5 to 31% (using a cynomolgus monkey model).
2. Of four soils tested using the juvenile swine model, three showed only slight decreases in the Cd RBA values (RBAs of 60 to 89%), while the fourth (a high-pH clayey soil with a unique form of Cd) had a much lower RBA of 18%.
3. There was virtually no dermal uptake of As from As-contaminated soils regardless of hydration levels (as measured using female Rhesus monkeys), although the dermal uptake of soluble As averaged 2.9%.

[4] http://www.serdp.org/Research/upload/CU-1165.pdf
[5] http://www.estcp.org/viewfile.cfm?Doc=ER%5F1165%5FFR%2E.pdf

The work on ecological receptors was designed to start development of a database. The oral bioavailabilities of arsenic, cadmium, chromium, and lead were measured in four test soils using *in vivo* shrew testing because ecological risk assessment models consistently indicate that small mammals represent the greatest level of potential exposure to metals in soil. In addition, *in vitro* research was initiated, using the physiologically-based extraction test (PBET) developed by the Solubility/Bioavailability Research Consortium.

A.4 ORAL BIOAVAILABILITY OF LEAD FROM SMALL ARMS RANGE SOILS (ER-0222[6])

This project (PI, Desmond Bannon) was designed to measure the relative oral bioavailability of lead in small-arms range soils by both *in vivo* and *in vitro* methods. The relative bioavailability of lead in soils from eight ranges across the United States was measured by the standard *in vivo* (swine) method. These results were compared to those from a proposed *in vitro* simulated GI tract method. Measured blood lead results from swine feeding tests were normalized to a lead acetate treatment group, giving the *in vivo* relative bioavailability. For the *in vitro* method, lead was extracted in a simulated gastric solution with a pH of 1.5, and results were normalized to the total lead to calculate the *in vitro* relative bioavailability.

The average relative bioavailability values for the eight soils were 102 ± 15% by the *in vivo* method and 95 ± 6% using the *in vitro* assay. In addition, x-ray fluorescence analysis of the eight soils showed a predominance of oxidized forms of lead, known to have high bioavailability. The high bioavailability found in these samples prompted screening of soils from an additional 20 sites using the *in vitro* method alone, and these also had measured bioavailability greater than 90%.

This project led to two major conclusions: 1) the bioavailability of lead at all small arms ranges tested was greater than the default value of 60% and in fact was close to 100% in all of the soils and 2) the *in vivo* and *in vitro* methods had a high degree of concurrence between them. The *in vitro* method was robust, but was only validated for a high-bioavailability form of lead. However, the high bioavailability of lead in all of the small-arms range soils suggests site-specific testing may be of little value for risk assessments.

A.5 QUANTIFYING METAL BIOAVAILABILITY IN SOIL (ER-1166[7])

The overall objective of this project (PIs, Mark Barnett, Phil Jardine and Scott Fendorf) was "to investigate the relative bioavailability of toxic metals in soils, primarily in relation to the human health risk posed by soil ingestion." Specific objectives included:

1. Measure changes in relative bioavailability over time in a wide range of soil types that may be encountered at DoD sites within the United States.

[6] http://www.estcp.org/Technology/ER-0222-VFS.cfm
[7] http://www.serdp.org/Research/upload/CU-1166.pdf

2. Develop a predictive ability to quantify toxic metal bioavailability on the basis of soil properties.
3. Investigate the fundamental relationship between molecular-level speciation and bioavailability of metals in soil.

As indicated, the project had a strong focus on understanding the factors that control bioavailability, particularly the impacts of the soil physical and chemical conditions. Bioavailability was assessed by the *in vitro* PBET, designed to estimate bioavailability in the human GI tract. Metals tested included Pb, As, Cr, and Cd, using 36 different soils from DoD sites. In addition, synchrotron-based x-ray absorption spectroscopy (XAS) was used to investigate the molecular-level speciation over time. Several hypotheses were developed prior to the research, including: 1) metal sequestration by soils will lower the relative bioavailability significantly; 2) key soil properties will be useful predictors of relative bioavailability; and 3) bioavailability is controlled by the molecular-level speciation.

The results presented in the final report[8] demonstrated that bioaccessibility of metals in soil can be significantly reduced, and this reduction can be caused strictly by soil-metal interactions (as opposed to site-specific metal speciation). Models were developed that successfully predicted As and Cr bioaccessibility based on soil properties. As(V) bioaccessibility correlated with the pH and Fe oxides, and Cr(III) bioaccessibility was strongly correlated with the clay content and the total inorganic and organic carbon content of the soils. These results have provided useful bioavailability models, as well as a better understanding of the soil properties that limit bioavailability.

Several fundamental studies were also performed to better understand the mechanisms by which bioavailability changes over time. For example, the fate of soluble As(III) added to soils was followed over time, and bioaccessibility decreased as an increasing fraction was oxidized to As(V) precipitates. Similarly, Cr bioaccessibility decreased with aging over a 200-day period, and chemical extraction methods and XAS revealed that Cr(VI) was reduced by soil organic matter, decreasing the bioaccessibility significantly (i.e., to ~10-20% soils with sufficient organic matter, as compared to ~60-70% in soils with lower organic matter contents). Interestingly, in some cases Pb and Cd were found to be highly bioaccessible even though they were effectively bound to soil mineral constituents because the weak surface bonds were disrupted in the acidic environment of the simulated GI tract. Other fundamental work with As and Pb has helped validate the important assumption that metal bioavailability in soils is independent of the metal concentrations.

This project largely provided the basis for an ongoing ESTCP project (ER-0517), which is designed to demonstrate and foster regulatory acceptance of a soil bioavailability screening tool. This project is described in Section A.5.

[8] http://www.estcp.org/viewfile.cfm?Doc=CU%2D1166%2DFR%2DOI%2E.pdf

A.6 VALIDATION OF A SOIL METAL BIOAVAILABILITY SCREENING TOOL (ER-0517[9])

This project, The Effect of Soil Properties on Decreasing Toxic Metal Bioavailability: Field Scale Validation to Support Regulatory Acceptance, is intended to demonstrate the screening approach developed in the prior SERDP projects. The screening approach is based on the use of soil properties and *in vitro* tests to estimate the human and ecological risks of metals in soil. The expected benefits include demonstrated tools to make better initial estimates of risk, which can be used to prioritize sites, to eliminate sites of portions of sites from further risk assessment or treatment, and/or to justify more definitive site-specific bioavailability studies.

The large team of PIs has emphasized gaining regulatory acceptance. As part of that effort, the project held a workshop with regulators, end users, and scientific experts to discuss the barriers to acceptance, as well as the outstanding technical issues and the path forward. The workshop white paper[10] yielded several relevant conclusions:

1. The regulatory barriers are complex and difficult to resolve.
2. Decisions will likely be on a case-by-case basis until there is greater comfort.
3. More data will be needed to link *in vitro* and *in vivo* results.
4. Standardized *in vitro* and *in vivo* methods should be developed.
5. An advisory panel would help guide the work and facilitate acceptance.

The advisory panel has been formed, and research is continuing to develop a larger and more robust database linking speciation, bioaccessibility, bioavailability, and toxicity of Pb, Cr, Cd, and As in soils from DoD sites. Comparisons of *in vitro* and *in vivo* metal bioavailability studies are being conducted for approximately 10 DoD soils using soil characterization, Physiologically-Based Extraction Test (PBET), swine feeding studies, and a suite of other ecological bioassays.

A.7 ECOLOGICAL SOIL SCREENING LEVELS (ER-1210[11], ER-1221[12], AND ER-1416[13])

ER-1210 (Development of EcoSSLs—Roman Lanno) is designed to investigate how chemical bioavailability and toxicity to soil invertebrates and plants is modified by soil physical/chemical properties and how bioavailability can be measured in soil systems for compounds of concern to terrestrial ecosystems, including PAHs, TNT, RDX, Pb, As, Cd, and Zn. The goal is to develop a model relating soil physical/chemical characteristics to the bioavailability, bioaccumulation, and toxicity of these compounds to soil invertebrates and plants. The resulting model should make it easier to incorporate bioavailability into the development of defensible Eco-SSLs, and speed up the initial screening of contaminated sites and the removal of low-risk sites from further ecological risk assessment. The project is ongoing.

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[9] http://www.estcp.org/Technology/ER-0517-FS.cfm
[10] http://www.esd.ornl.gov/research/earth_sciences/images/estcp_er-0517_white%20paper.pdf
[11] http://www.serdp.org/Research/upload/ER_FS_1210.pdf
[12] http://www.serdp.org/Research/upload/ER_FS_1221.pdf
[13] http://www.serdp.org/Research/upload/ER_FS_1416.pdf

ER-1222 (Development of Ecological Toxicity and Biomagnification Data for Explosives Contaminants in Soil—Roman Kuperman, Ron Checkai, and Geoffrey Sunahara) was focused on the measurement of the toxicity and potential for bioaccumulation of explosives-related contaminants in soil invertebrates and plants. The ultimate goal was to foster development of Eco-SSLs for ecotoxicological benchmarks. The final report[14] generated experimental data on the toxicity of RDX, HMX, 2,4-DNT, 2,6-DNT, and TNB to terrestrial plants and soil invertebrates. Ecotoxicological testing was specifically designed to meet the criteria for Eco-SSL derivation. Draft Eco-SSL values were derived for freshly amended and for weathered/aged amended soil using the effective concentration that caused a 20% reduction (EC20) level of the EM effects on plant growth or soil invertebrate reproduction. The team is continuing to work with the Ecological Soil Screening Level Workgroup to establish Eco-SSLs for explosives.

ER-1416 (Development of Toxicity Benchmarks and Bioaccumulation Data for N-Based Organic Explosives for Terrestrial Plants and Soil Invertebrates) is part of the continued effort to supply useful data to the EcoSSL Workgroup The overall objectives is to develop toxicity benchmark values, based on ecologically relevant soil biota, that are acceptable for derivation of Eco-SSLs for explosives contaminants. A portion of the work is explicitly designed to investigate and characterize the predominant soil physical and chemical parameters that may affect the bioavailability and resulting toxicity to soil invertebrates and terrestrial plants.

A.8 REDUCING METAL BIOAVAILABILITY IN SOIL (ER-1350[15], ER-1351[16], AND ER-1352[17])

ER-1350 (Novel Amendment Strategies—Phil Jardine) was intended to develop and test in situ chemical manipulation strategies to sequester metals and improve the understanding and predictability of the processes that "enhance long-term immobilization and decrease the bioaccessibility of the DoD priority metals." The project built on earlier SERDP work (ER-1166) by the same team and used similar methods to measure bioavailability and molecular speciation.

Metals were stabilized by changing the soil geochemistry in contaminant-appropriate ways (i.e., phosphate stabilization for Pb, reduction of Cr(VI) by organic matter additions oxidation of As(III) by addition of soluble Fe, and complexation of Cd by adding Ca-polysulfide. Metal bioaccessibility was measured using PBET, and molecular speciation was done to improve the mechanistic understanding of the processes involved. The project was completed in 2007, and the final report[18] shows that the treatments could be successful under appropriate conditions. Further, the results of the linked studies provided considerable insight into the conditions that are appropriate for effective treatment. Models were developed to better predict performance, including multiple regression and neural net models..

[14] http://estcp.org/viewfile.cfm?Doc=CU%2D1221%2DFR%2DOI%2E.pdf
[15] http://www.serdp.org/Research/ER_1350-CFS.cfm
[16] http://www.serdp.org/Research/upload/CU-1351.pdf
[17] http://www.serdp.org/Research/upload/CU-1352.pdf
[18] http://www.serdp.org/Research/upload/ER-1350-FR.pdf

ER-1351 (Soil Amendments to Reduce Bioavailability of Metals in Soils: Experimental Studies and Spectroscopic Verification—Katherine Banks*)* was designed to evaluate the "impact of adding phosphorus, sulfur-based compounds, iron-rich composted organic matter, and limestone (individually and combined) on the aqueous solubility and extractability of contaminant metals." The bioavailability of Cd, As, Cr, and Pb is being assessed using standard bioassays (including earthworms, lettuce germination and emergence, nematodes, and soil microorganisms). In addition, to provide a more mechanistic understanding of the bioavailability results, spectroscopic and x-ray analyses are being used to investigate the chemical bonding to soil surfaces, changes in speciation, and the chemical environment of the stabilized metals. The project is ongoing.

ER-1352 (Facilitated Immobilization of Heavy Metals in Soil by Manipulation with Plant Byproducts—Teresa Fan) was a one-year exploratory research project. The goals of this one-year proof-of-concept project were to explore the use of organic amendments for metal sequestration at the bench-scale and address the following two questions: (1) Can additions of organic materials, such as lignosulfonate (LS), and their subsequent humification help sequester heavy elements in soils and (2) Can the chemical sequestration mechanisms be understood? Humification was shown to reduce leaching, and a combination of NMR, pyrolysis gas chromatography-mass spectrometry, and 3-D fluorescence techniques was used to characterize the humified products. Bioavailability was not directly measured, although such work was suggested as a subsequent phase. The project was completed in 2005.

A.9 RELATED EFFORTS

Bioavailability in soil has been a minor component of a few other SERDP and ESTCP projects, generally as one measure of the effect of remediation technologies (such as metal stabilization technologies), or tangentially in studies designed to measure environmental toxicity or fate and transport. Such measurements have not been coordinated, and there has been no attempt to standardize bioassay methods, for example, so this information has not been addressed in this document. There is one recent workshop, however, that may be of interest for participants in this workshop (summarized briefly below).

A.9.1 Range Assessment Research Needs

SERDP and ESTCP recently convened a technical exchange meeting focused on range assessment and management. The meeting report noted that most of DoD's bioavailability research program has focused on a few metals and recommended that more research was needed to expand our understanding of the bioavailability of other contaminants of particular concern to DoD (SERDPand ESTCP, 2007). These included organic and inorganic munitions compounds (MC).

The report specifically recommended that one or more demonstration projects were needed and that these projects should focus on development of improved methods. The report also recommended that future work build on the existing and previous SERDP and ESTCP metal bioavailability projects (ER-1166 and ER-0517) and attempt to apply the lessons learned from

the work done on lead to develop models and/or procedures for other range-related MCs (e.g., tungsten).

The report also noted that there are clear data gaps in both chronic and acute human health toxicity data for several MCs and their by-products, and that such work needs to be done, particularly for military-unique compounds.

REFERENCES

SERDP and ESTCP. 2007. SERDP/ESTCP Technical Exchange Meeting on DoD Operational Range Assessment and Management Approaches. Arlington, VA. http://www.serdp.org/Reserch/upload/RAWorkshopRDTENeedsRpt.pdf.

RISK DRIVERS AT DoD SEDIMENT SITES

Katherine von Stackelberg, ScD, Tim Thompson, and Cara Patton
Background Paper, SERDP Workshop on Bioavailability Research Needs
20-21 August 2008, Westin Hotel, Annapolis, MD

1.0 INTRODUCTION

The U.S. Department of Defense (DoD) has significant liabilities associated with soil contamination, with thousands of sites awaiting cleanup. DoD therefore has a keen interest in understanding the actual risks posed by contaminants in soil. A better understanding would allow DoD to prioritize sites based on real risks and should also enable more effective and cost-efficient remediation.

As pointed out by the National Research Council (NRC) report on Bioavailability of Contaminants in Soils and Sediments (NRC, 2003), "chemicals in soils and sediments behave differently than when those chemicals are present in other media, notably water and air." The fact that these differences can strongly affect the potential for exposure has been known for well over a decade (e.g., Alexander, 1995), and regulatory frameworks explicitly recognize the influence of bioavailability on risks. However, bioavailability has rarely been used to date in risk assessments and regulatory decisions (particularly for soils), largely because of the uncertainties in our fundamental understanding in this area. Uncertainties include the nature and magnitude of the "bioavailability processes," the strengths and limitations of various methods used to measure bioavailability, and the appropriate uses of such data in risk assessment.

For these reasons, SERDP/ESTCP has funded several projects in recent years to better understand and measure bioavailability, but these projects have not been closely coordinated. Given the high importance of the area, the high costs associated with bioavailability testing and calibration studies, and the remaining significant uncertainties in this area, SERDP has convened a workshop to identify the key issues and research needs. This background paper for that workshop is intended to provide a brief summary of those contaminants, pathways, and receptors for which cleanup levels have been derived on the basis of potential human health and ecological risks at DoD sites. The paper will also present a brief overview of current or recent SERDP/ESTCP projects on sediment bioavailability. Having an understanding of risk drivers and current research will help to focus and prioritize research efforts with respect to how decisions are made currently.

2.0 EVALUATION OF SEDIMENT RECORDS OF DECISION

To evaluate the basis for decision making at sediment DoD sites, we developed a database that extracted summary information across a set of Records of Decision (ROD) published by US EPA. Identifying those contaminants, pathways, and receptors that most often lead to the development of cleanup goals will help to focus on where additional bioavailability research might be relevant. However, an important omission is to acknowledge that this would not include contaminants for which there are no toxicological data (either human health or ecological), thus precluding the development of a risk assessment and/or cleanup goals.

2.1 Methods

We identified 86 individual RODs at federal and state sites for which decision making was primarily based on contaminants in sediments. The RODs were all published between 1997 and 2007 and were obtained from the online US EPA RODs database.

We developed a database of the results of these RODs which includes the cleanup goal, the basis for the cleanup goal (human or ecological), the pathway, receptor, whether the goal is for tissue or sediment, and some indication of the basis for the cleanup goal (e.g., screening level, back calculated from the risk model using a bioaccumulation model, etc.).

2.2 Results

2.2.1 Risk Drivers

Table 1 presents a summary of the basis for decision making at individual OUs with respect to human and ecological risks and contaminants. Metals (Figure 1) showed the highest number of individual cleanup goals across sites and operable units. For ecological risk, the highest number of cleanup goals was based on lead, followed by zinc, copper and cadmium, and mercury. For human health, the highest number of cleanup goals was based on arsenic and manganese (4), followed by lead and mercury. All were for sediment—the only tissue-based cleanup numbers were for mercury (one each based on human and ecological risk). The highest three classes of compounds (metals, PAHs, and pesticides) all had more OUs for which cleanup goals were based on ecological rather than human health risks. The opposite was true for PCBs, chlorinated hydrocarbons, nitramines, and phthalates.

Table 1 Summary of Number of Operable Units with Cleanup Goals for Sediment and/or Fish Tissue and Their Basis

Class	Human Health	Ecological	Background	Total
Metals	23	70	5	98
PAHs	15	42		57
Pesticides	19	32		51
PCBs	24	9		33
Chlorinated Hydrocarbons	12	11		23
Nitramines	5	2		7
Phthalates	2	1		3
TPH	1			1
Dioxin	1			1
UXO		1		1
VOCs		1		1
Other	2	1		3

For ecological risk associated with exposure to pesticides, DDT showed the highest number of cleanup goals, followed by DDE, DDD, and total DDx (combined). All were sediment-based value (rather than tissue-based). Human health derived cleanup goals show a similar pattern,

with some values being for tissue rather than sediment. Two OUs derived cleanup goals for aldrin based on human exposures and none for sediment.

For PAHs, ecological risk-based cleanup goals were most often based on total PAHs rather than individual constituents, while for human health, an equal number of OU-derived cleanup goals was based on anthracene, fluorene, pyrene, benzo(a)pyrene equivalents, and total PAHs. These results are shown graphically in Figure 2.

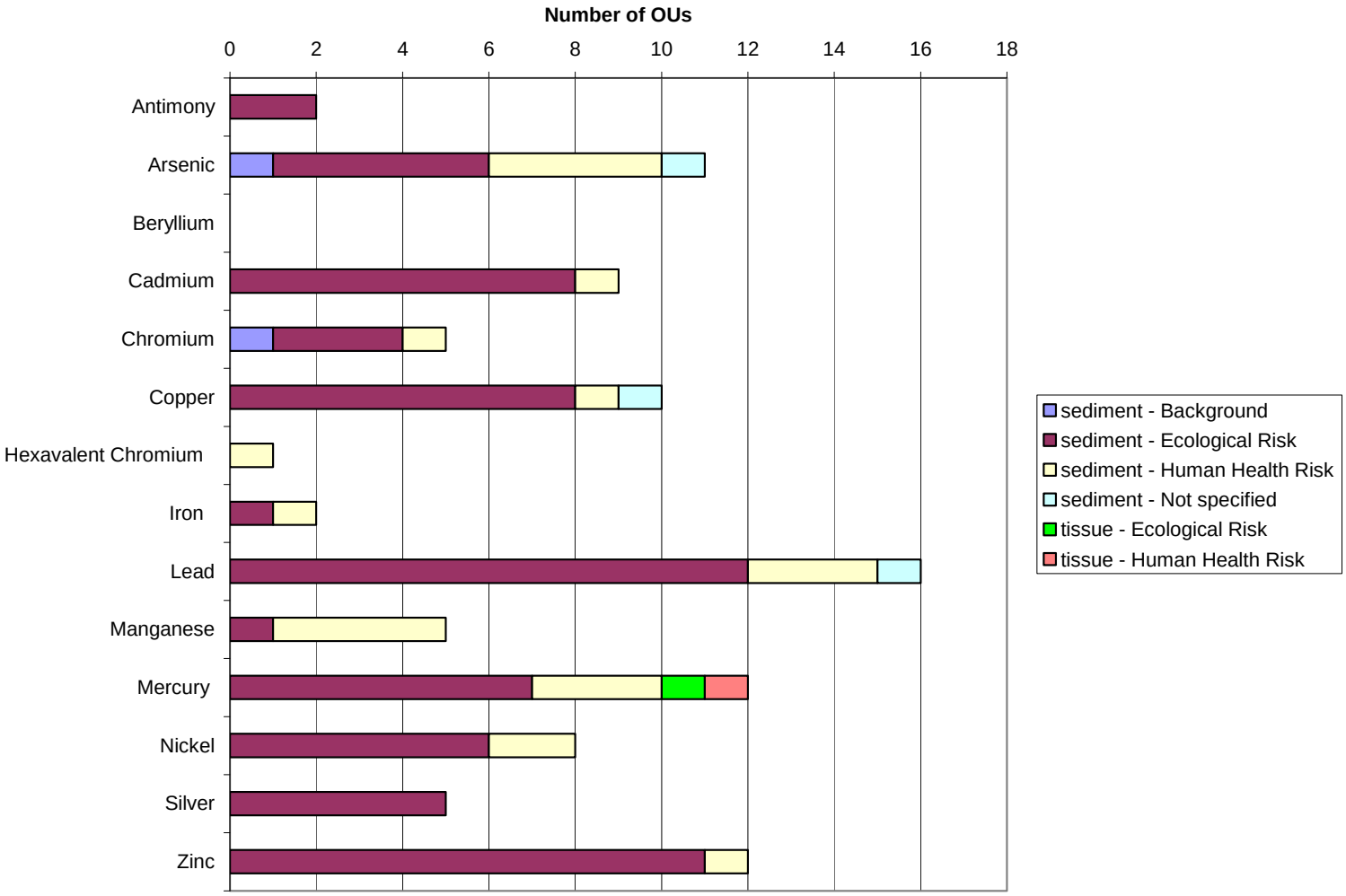

Figure 1: Number of OUs by Metal, Risk Type, and Pathway That Derived Cleanup Goals at DoD Sites

2.2.2 Cleanup Goals

Table 2 presents the range of derived cleanup goals across OUs. For metals, many of the ecological risk cleanup goals were based on NOAA ER-L or ER-M, or EPA (Region 4) screening levels. Human health cleanup goals across all contaminants tended to be derived from back-calculations of site-specific risk assessments, generally for subsistence angling. Some

contaminants show several of orders of magnitude difference in derived cleanup goals, including cadmium, copper, lead, mercury, PAHs, and PCBs.

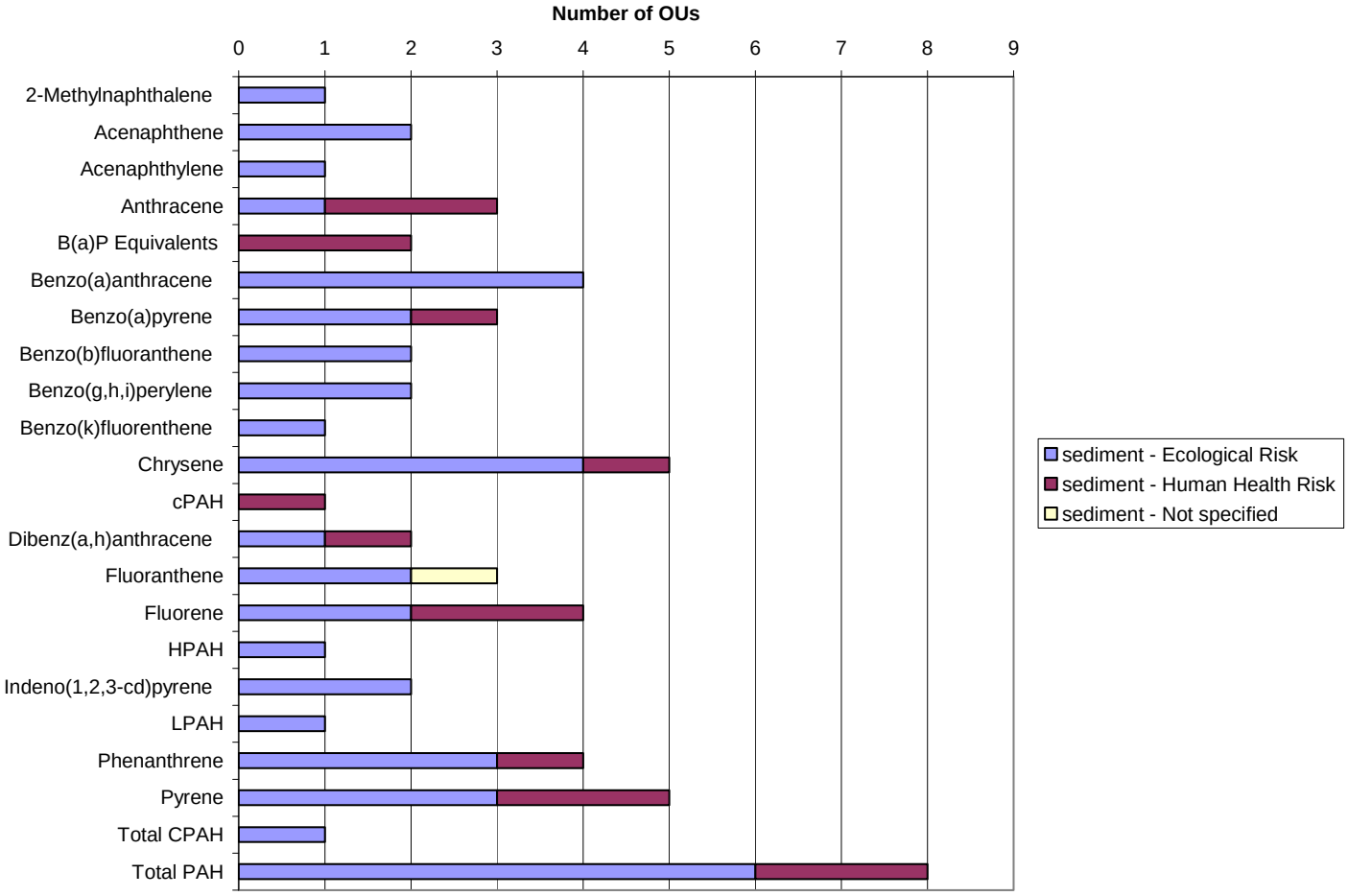

Figure 2. Number of OUs by PAH, Risk Type, and Pathway That Derived Cleanup Goals at DoD Sites

In the case of cadmium, cleanup goals represent EPA Region 4 screening levels, NOAA ER-Ls, and back-calculation from site-specific bioaccumulation modeling (the highest value) for the least tern. The screening level values are generally based on benthic invertebrate exposures. Copper, lead, and mercury follow a similar pattern. The lowest cleanup numbers are typically screening-level values from NOAA or EPA, while the highest values are based on the site-specific modeling incorporated in the risk assessments. By far the most common ecological receptors chosen as the modeling endpoint were benthic invertebrates (25 OUs). An equal number of cleanup goals was based on published screening values, and the remainder incorporated modeling for higher order receptors.

Table 2. Sediment Remedial Goals at DoD Sites

Contaminant[1]	Ecological Risk Range	Human Health Risk Range
Antimony	2 – 25 mg/kg	none
Arsenic	8.2 – 33 mg/kg	9.62 – 12.2 mg/kg
Cadmium	1.2 – 24.4 mg/kg	0.153 mg/kg
Chromium	6.8 – 80 mg/kg	none
Copper	34 – 390 mg/kg	none
Iron	20 mg/kg	23,000 mg/kg
Lead	46.7 – 580 mg/kg	42.1 mg/kg
Manganese	1,100 mg/kg	274 – 1,800 mg/kg
Mercury – sediment	0.15 – 0.59 mg/kg	3 mg/kg
Mercury – tissue	0.48 mg/kg	0.56 mg/kg
Nickel	20.9 – 52 mg/kg	none
Silver	1 to 6.1 mg/kg	none
Zinc	150 – 960 mg/kg	none
PCBs – sediment[2]	0.0227 – 1.13 mg/kg	0.0016 – 10 mg/kg
PCBs – tissue[2]	none	0.0022 – 0.042 mg/kg
DDD – sediment	0.00158 – 0.0336 mg/kg	102 mg/kg
DDD – tissue	none	0.018 mg/kg
DDE – sediment	0.0022 – 0.0316 mg/kg	8.58 mg/kg
DDE – tissue	none	0.013 mg/kg
DDT – sediment	0.001 – 5.1 mg/kg	2.11 mg/kg
DDT – tissue	none	0.013 mg/kg
DDx – sediment	0.033 – 2 mg/kg	5 mg/kg
DDx – tissue	none	none
Total PAH	1.684 – 44 mg/kg	8.94 mg/kg
Individual PAH	0.016 – 9.6 mg/kg	0.203 – 10 mg/kg
TPH	none	500 mg/kg
Ethylbenzene	10 mg/kg	none
Bis(2-ethylhexyl)phthalate	0.182 – 9 mg/kg	none
1,3,5-TNB	1.6 mg/kg	none
HMX	5.7 mg/kg	none
RDX	none	5 mg/kg
amino-DNTs	none	10 mg/kg
2,4,6-TNT	none	14 mg/kg
2,6-Dinitrotoluene	none	29 mg/kg
2,4-dinitrotoluene	none	60 mg/kg
2,4-Dimethylphenol	0.029 mg/kg	none
Pentachlorophenol	none	3 mg/kg
1,1,1-Trichloroethane – sediment	none	70,500 mg/kg
1,1,1-Trichloroethane – tissue	none	61 mg/kg
1,1-Dichloroethane – sediment	none	200,000 mg/kg
1,1-Dichloroethane – tissue	none	0.051 – 304 mg/kg
1,2-Dichloroethane	3.5 mg/kg	0.33 mg/kg (tissue)
cis-1,2-Dichloroethene	none	30 mg/kg (tissue)
Tetrachloroethene – sediment	none	31 mg/kg
Tetrachloroethene – tissue	none	0.51 mg/kg
trans-1,2-Dichloroethene	none	61 mg/kg (tissue)
Trichloroethene	1.6 mg/kg	2.8 mg/kg (tissue)
Vinyl chloride	none	0.016 mg/kg (tissue)

[1]Values shown are for sediment unless otherwise specified
[2]PCBs includes total PCBs and individual Aroclors

Figures 3 and 4 show the minimum and maximum derived cleanup goals for PAHs. There is a range evident in these values; for example, the lowest ecological risk based cleanup goal for acenapthylene is 0.016 mg/kg in sediment, while for HPAHs it is 9.6 mg/kg in sediment. The acenapthylene value is based on food chain modeling of terrestrial omnivorous mammals, while the HPAH value is also based on modeling of exposures to raccoon. Benthic invertebrates represented the most common ecological receptor-based cleanup goal (15 OUs) across all PAHs, followed by higher order mammals and birds (10 OUs). Twelve OUs were based on screening values (either NOAA, EPA Region 10, or EPA Region 4). For human health risks, values ranged from EPA Region 9 residential soil PRGs to site-specific modeling, generally for subsistence anglers or recreational shellfish consumption.

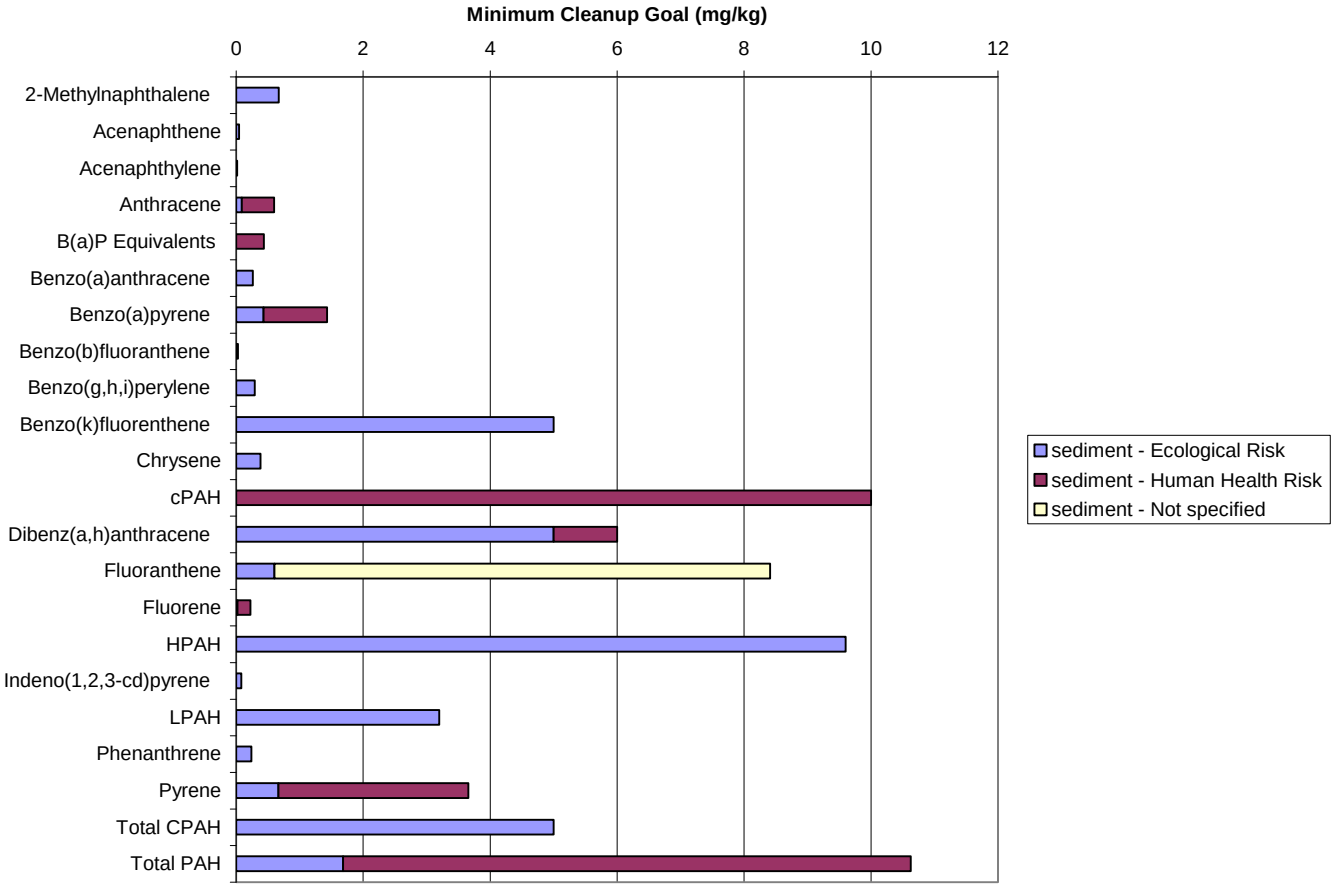

Figure 3. Minimum Sediment Cleanup Goals at DoD Sites.

There is somewhat greater consistency in the maximum derived cleanup goals across PAHs (see Figure 4), although one OU used the ER-M value (44 mg/kg), by far the highest value across all OUs for ecological risk-based cleanup levels.

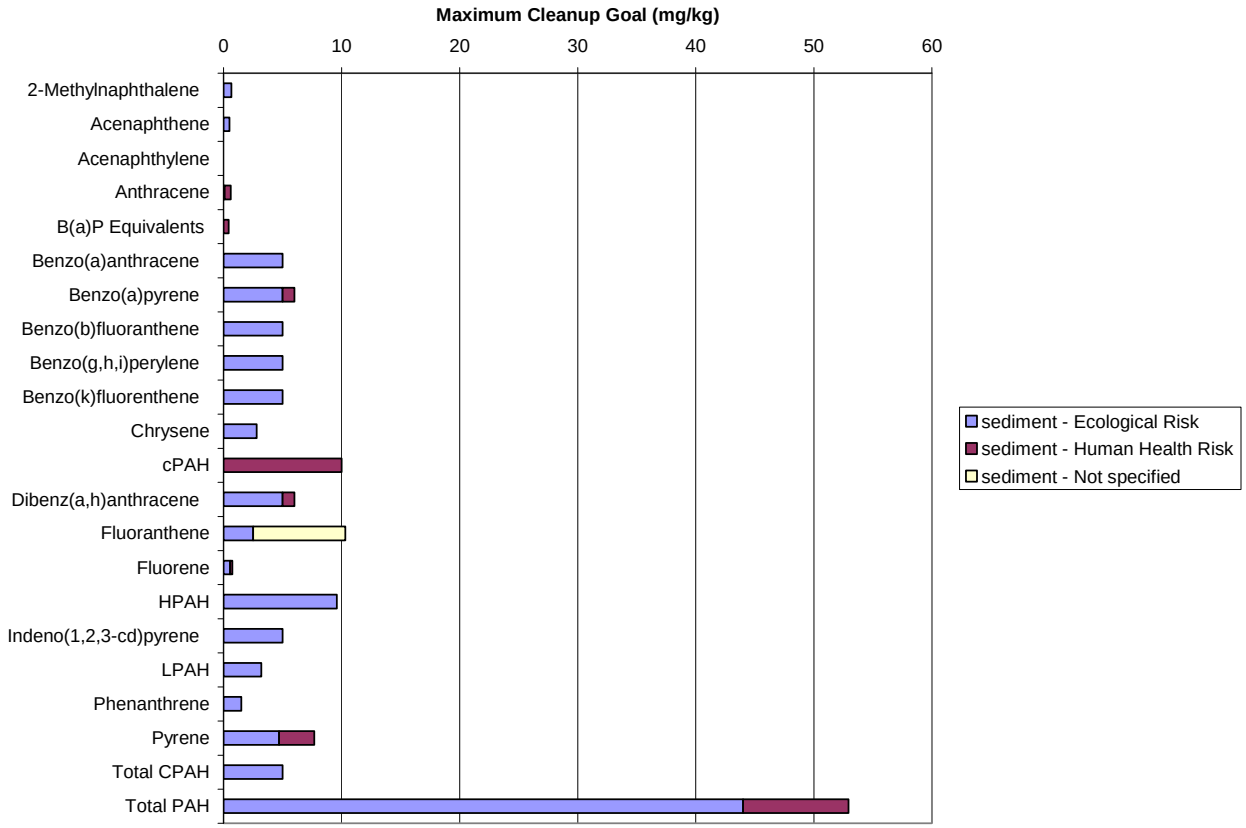

Figure 4. Maximum Cleanup Goals.

3.0 SERDP AND ESTCP BIOAVAILABILITY PROJECTS

SERDP/ESTC began proactively addressing the issue of contaminated sediments in 1999. It soon became evident that the magnitude of the problem was large, and that a systematic approach to developing tools to assess risk and remediation of contaminated sediments was necessary. SERDP/ESTCP convened an Expert Panel Workshop on Research and Development Needs for the In Situ Management of Contaminated Sediments in August 2004 to examine the state of the science and engineering (see table below) and to identify and prioritize research needs. The 2004 workshop carefully considered a range of research needs under the general categories of Capping, In Situ Remediation, Monitored Natural Recovery, Bioavailability, and Fate and Transport.

The convened expert panel and attendees identified 75 specific research needs across these categories; the prioritized research needs are described in the Workshop Final Report, which is available in the SERDP and ESTCP Online Library at http://docs.serdp-estcp.org . Of those, 21 priority research needs pertained to assessing bioavailability in pre- and post-remediated sediments (Table 3), and the Program currently is sponsoring 15 projects related to bioavailability.

Table 3. SERDP/ESTCP High Priority Research Needs.

Fate and Transport of Contaminants	
A1	Develop and validate tools and techniques to assess site-specific bioavailability
A2	Develop understanding of how sediment geochemical composition influences contaminant partitioning and bioavailability
A5	Develop protocols for building conceptual site models for in situ sediment remediation
Characterization of Contaminated Sediments	
A6	Develop, evaluate, and validate site characterization tools to measure the rates of important sediment chemical/physical/biological processes affecting the fate and transport of contaminants
A7	Develop, evaluate, and validate in situ measurement tools to efficiently monitor the effectiveness of a particular remediation strategy, assess the ecological risk, and assess the ecological recovery at contaminated sites
A8	Develop, evaluate, and validate tools to determine the bioavailability and bioaccumulation of contaminants at sites
A9	Improve methods for incorporating uncertainty into measurement of fundamental fate and transport processes, and into models for predictin and monitoring remedial alternatives
Capping Technologies	
A17	Develop and deomonstrate active cap amendments for contaminant sequestration and/or degradation
A18	Assess the ecological impacts of reactive caps
In Situ Treatment	
A22	Perform parallel field demonstrations of multiple in situ treatment technologies to provide performance comparison
A23	Refine and demonstrate tools and metrics to evaluate pre- and post-remedial impacts of in situ treatment
A24	Develop and assess innovative in situ amendments under a range of sediment conditions
Monitored Natural Recovery	
A27	Develop, evaluate, and/or validate a methodology to determine the desired end state that will yield environmentally acceptable sediment
A28	Develop, evaluate, and/or validate characterization tools to determine the fraction of the sediment-bound contaminants that will be “treated” or ‘transformed” during MNR
A31	Develop tools to measure contaminant availability to pore water and ecological and human receptors (i.e., bioavailability)
A32	Improve and/or develop ecological screening assays to predict ecological toxicity based on sediment chemistry in assessing the natural recovery of the impacted sediment over time during MNR
A33	Identify metabolites for contaminants of concern
A34	Determine the rates of attenuation of sediment-bound contaminants via microbiological action and/or abiotic reactions, including measurements of reaction byproducts
A35	Quantify the contaminant flux of sediment-bound contaminants into pore water and inot organisms and examine the impacts of weathering and the presence of anthropogenic carbon on these flux profiles
A36	Develop relationships between sediment chemistry, sediment organic carbon content, contaminant flux from sediments and organism uptake and toxicity
A37	Develop relationships between passive samplers and the results of both acute and chronic ecological assays

Table 4 SERDP/ESTCP Bioavailability Projects.

Project Title	Project #	Lead	Institution
SERDP Sediment Research Projects			http://www.serdp.org/Research/er-sediments.cfm
Rational Selection of Tailored Amendment Mixtures and Composites for In Situ Remediation of Contaminated Sediments	ER-1491	Dr. Upal Gosh	University of Maryland Baltimore County
Reactive Capping Mat Development and Evaluation for Sequestering Contaminants in Sediments	ER-1493	Ms. Amy Hawkins	Naval Facilities Engineering Service Center
An Integrated Field and Laboratory Study of the Bioavailability of Metal Contaminants in Sediments	ER-1494	Dr. Nicholas Fisher	Stony Brook University
Modeling and Decision Support Tools Based on the Effects of Sediment Geochemistry and Microbial Populations on Contaminant Reactions in Sediments	ER-1495	Dr. Jeanne Van Briesen	Carnegie Mellon University
Using Passive Polyethylene Samplers to Evaluate Chemical Activities Controlling Fluxes and Bioaccumulation of Organic Contaminants in Bed Sediments	ER-1496	Dr. Philip Gschwend	Massachusetts Institute of Technology
Sequestering Agents for Contaminants in Sediments – Application to the Development of Active Caps	ER-1501	Dr. Anna Sophia Knox	Savannah River National Laboratory
Application of Tools to Measure PCB Microbial Dechlorination and Flux into Water During In-Situ Treatment of Sediments	ER-1502	Dr. Joel Baker	University of Maryland
Biological Processes Affecting Bioaccumulation, Transfer, and Toxicity of Metal Contaminants in Estuarine Sediments	ER-1503	Dr. Celia Chen	Dartmouth College
Sediment Ecosystem Assessment Protocal (SEAP): An Accurate and Integrated Weight-of-Evidence Based System	ER-1550	Dr. Allan Burton	Wright State University
Bacterial and Benthic Community Response to Inorganic and Organic Sediment Amendments	ER-1551	Dr. Meriah Arias-Thode	SPAWARSYSCEN San Diego
Measurement and Modeling of Ecosystem Risk and Recovery for In Situ Treatment of Contaminated Sediments	ER-1552	Dr. Richard G. Luthy	Stanford University
ESTCP Sediment Projects			http://estcp.org/technology/ER-Sediments.cfm
Field Testing of Activated Carbon Mixing and In Situ Stabilization of PCBs in Sediment	ER-0510	Dr. Richard Luthy	Stanford University
Demonstration of an Integrated Compliance Model for Predicting Copper Fate and Effects in DoD Harbors	ER-0523	Dr. Bart Chadwick	SPAWAR Systems Center
SPME for In-Situ Assessment of Bioavailability	ER-0624	Der. Danny Reible	University of Texas
Determination of Sediment Polycyclic Aromatic Hydrocarbon Bioavailability Using Supercritical Fluid Extraction (SFE) and Ultra-Trace Porewater (UTP) Analysis	ER-0709	Dr. David Nakles	ENSR Corporation

4.0 CONCLUSIONS

Cleanup decisions at DoD sites have historically been made both on ecological and human health risks. Metals, PAHs, and pesticides dominate ecological risk-based cleanup goals—most are based on potential effects to benthic invertebrates, but they also include some food chain modeling to higher order mammals and birds. Metals, PCBs, and pesticides dominate human health risk based cleanup goals, generally based on subsistence or recreational angling.

Bioavailability appears to be infrequently considered in setting risk-based cleanup goals. Ecological remedial goals have been based principally on conservative screening values (such as NOAA ER-Ls and ER-Ms, EPA Region 4 screening levels, EPA Region 10). In some cases, the goals were developed based on site-specific back-calculations using the models and data from the risk assessment. Similarly, human health values range from screening level PRGs (e.g., EPA Region 9 for soils) to site-specific model back-calculations for either a subsistence or recreational angler scenario.

By definition, this analysis cannot consider those constituents which do not have toxicological values and/or dose response relationships, and therefore which cannot derive risk-based cleanup goals. It was not possible to identify all of those constituents, which might be present at risk-relevant exposure concentrations.

ELEMENT BIOAVAILABILITY AND BIOACCESSIBILITY IN SOILS: WHAT IS KNOWN NOW, AND WHAT ARE THE SIGNIFICANT DATA GAPS?

Rufus L. Chaney[1], Nicholas T. Basta[2], and James A. Ryan[3]

[1]USDA-ARS, Environmental Management and Byproduct Utilization Laboratory, Beltsville, MD.
[2]School of Environment and Natural Resources, The Ohio State University, Columbus, Ohio.
[3]US-EPA, Cincinnati, OH (retired).

ABSTRACT

Because the fraction of a soil element that can actually be absorbed by an organism to cause harm depends on the chemical forms present and physical and chemical properties of the soil, in both risk assessment and remediation evaluation, the fraction of a soil element that can actually cause harm must be identified. This fraction is ultimately defined as the bioavailable fraction, and because measurement of the bioavailable fraction is time-consuming and expensive, chemical methods are being developed to estimate the bioavailable fraction. In the case of ingestion of soil, the *in vitro* or chemical estimation method has been labeled "bioaccessible" to avoid confusion with "bioavailable." Extensive progress has been made in development of soil Pb and As bioavailability testing and bioaccessibility methods development. And great effort has been wasted in attempts to develop bioaccessibility methods that try to match all digestion processes. In the end, a bioaccessibility method only needs to be well correlated with an acceptable bioavailability method. Actually, the simpler and less expensive the bioaccessibility method can be made, the better, as long as the correlation with bioavailability is high. Further, for such methods to be relevant to testing of remediation methods, changes in bioavailability due to field treatments should be reflected in the bioaccessibility test results. In the case of soil Pb, *in situ* remediation using phosphate and other treatments have been proven to reduce bioavailability to pigs, rats and humans, but the bioaccessibility test conducted at pH 1.5 does not measure this 69% reduction in bioavailability to human adults, while testing at pH 2.2 or 2.5 does reflect the effectiveness of the soil treatment. Other simple chemical tests have been shown to suffer significant flaws in that the extraction causes changes in chemical speciation during the test, and they have not been shown to correlate with bioavailability changes due to soil treatments. Further, it is necessary to have a valid measure of why the bioavailability/bioaccessibility of samples are different and whether the changes are persistent. Soil As bioavailability testing has progressed to monkeys but not to humans; bioaccessibility methods have been reported.

For plants and soil organisms, where testing with the organism to be protected is more readily conducted, chemical methods have been developed that integrate potential toxicity across soil properties, including pH, which often strongly affects bioavailability. Mild neutral salt extractions are often found to be effective methods. However, assessment of potential toxicity by adding metal salts to uncontaminated soils substantially fails to mimic field contaminated soils because elements react with soils, and metal salt additions alter soil pH. Traditional toxicology approaches of adding element salts and immediately measuring toxicity are clearly inappropriate and can cause serious artifacts due to pH change resulting from the metal salt addition, or

formation of soluble metal complexes that temporarily increase or decrease element bioavailability. Thus, testing of potential toxicity has as many problems as testing of bioaccessibility. It seems clear that by taking present knowledge into account, effective toxicity testing, bioaccessibility evaluation, and risk assessment can provide massive savings to the public in dealing with contaminated soils.

INTRODUCTION: "BIOAVAILABILITY" AND SOIL ELEMENT RISKS:

Our focus is on the potential for adverse effects of soil elements to organisms, both soil organisms, plants, livestock, wildlife, and humans that ingest soils and crops grown on an element contaminated soil. The most common understanding of "bioavailability of a soil element" is the fraction of total soil element that can be absorbed into an organism and cause an adverse or beneficial effect in the exposed organism. In its concern with direct ingestion of soil, the US-EPA has defined bioavailability as "the fraction of an ingested dose that crosses the gastrointestinal epithelium and becomes available for distribution to internal target tissues and organs" (US-EPA, 2007a). From this definition, bioavailability can be divided into two kinetic steps—dissolution in gastrointestinal fluids and absorption across the GI epithelium into the blood stream—either of which can limit element bioavailability. Combining the variability of geochemical forms of elements in contaminated soils with dissolution chemistry and biological absorption processes in the GI tract is a complex system. We insist on further convoluting this complexity by recognizing that each element has its own specific environmental toxicology; by that term we mean the organism to which it can cause an adverse effect at the lowest environmental exposure and the interaction of other factors with that element such as Ca with Pb, Zn with Cd, and Cu with Mo. In some cases, the key interaction that affects element risk is related to dissolution from ingested soil, while in other cases, interaction during intestinal absorption is the key process that controls risk from an element. This understanding has come from assessment of the specific pathway from soil to organism for each element that can harm a sensitive, exposed organism. Often children are the most exposed and sensitive organisms exposed to contaminated soils in urban areas, but for remote DoD sites, wildlife, plants, or soil organisms are likely to be the most exposed and sensitive organisms. But each element has its specific chemistry in soils, potential for uptake by plants or soil organisms, and potential to affect consumers of plants or soils.

FORMS OF METALS IN SOILS

Each element has its own equilibrium chemistry in soils in relation to soil pH, soil sorbent phases, soil organic matter, soil redox potential, etc. A good summary of soluble element speciation in soils is provided by Langmuir et al. (2005). If the element is only weakly bound by a soil, it may be leached through the soil to contaminate groundwater. Considering pH and element chemistry, the monovalent anions and cations are usually leachable. Divalent anions such as sulfate are readily leached, while selenate, molybdate, tungstate, and some others are only leachable at alkaline pH; at acidic pH, these elements can be sorbed well by Fe and other sesquioxides.

Arsenate is sorbed well at acidic pH and precipitated as a Ca mineral at higher pH. Arsenic has become a subject of greater concern in recent years as the acceptable intake level for humans was lowered. Human As poisoning has been recognized from contaminated drinking water (millions of humans are exposed to excessive well water As in Bangladesh) but never observed in humans from ingested soil or crops. Crop accumulation of As is weak, and translocation to edible crop tissues even lower. In aerobic soils, As is present as arsenate, but upon soil reduction, arsenite is generated. Arsenite is much less strongly adsorbed by soil surfaces, so root uptake and phytotoxicity are greater in crops grown in anaerobic soil. That is essentially rice. Further, when rice is grown in flooded soils, accumulation of As and transport to grain is higher than when rice is grown in drained or upland soil conditions (Xu et al., 2008). It is believed that arsenate is absorbed by plants by a phosphate permease of the roots; further, added phosphate competes with arsenate for adsorption by soil oxides, and added phosphate can increase soluble arsenate temporarily to phytotoxic levels (Peryea, 1988).

Soil organic matter, pH, and clay content are soil chemical properties that influence metal bioavailability and toxicity to ecological receptors (i.e., earthworms, plants). A comprehensive study of 21 natural soil types, multiple contaminants, and multiple plant and earthworm endpoints was conducted to determine the simple and combined effects of soil chemical properties on metal bioavailability and toxicity (Lanno and Basta, 2003). Soils were selected to produce a combined range of soil pH, organic C content, CEC, reactive Al and Fe oxide, and clay content (Lanno and Basta, 2003).

In this novel approach, soil type, not contaminant concentration, was used to produce a range of metal bioavailability and exposure doses. Metal bioavailability and toxicity were determined through 28-day bioassays using mature earthworms (*Eisenia andrei*) and bioassays lettuce (*Lactuca sativa* cultivar Parris Island Cos). Soil properties greatly affected metal bioavailability (Lanno and Basta, 2003). Lettuce tissue Pb ranged from 3.22 to 233 mg Pb/kg and relative dry matter growth ranged from 2.5 to 88.5% of their respective controls (Figure 1) (Dayton et al., 2006). Similarly, soil type greatly affected metal bioavailability and toxicity to earthworms. Earthworm mortality ranged from 0 to 100% acute mortality following exposure to the same total concentration of Pb (2,000 mg/kg) in amended field soils. Internal Pb concentrations in earthworms ranged from 28.7 to 782 mg/kg, with a mean of 271 mg/kg. (Bradham et al., 2006).

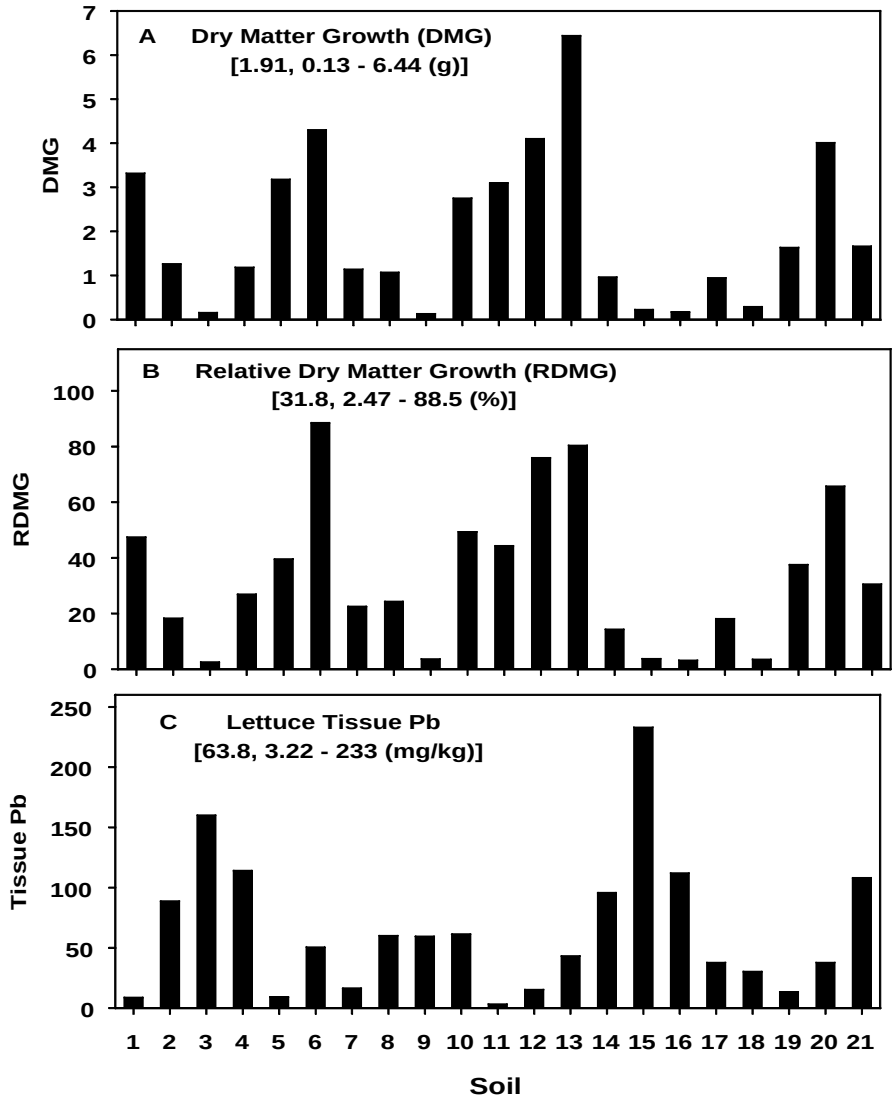

Figure 1. Range in Lettuce Biological Endpoints for Lettuce Grown in Pb Spiked (2,000 mg Pb/kg) Soils. Numerical Values in Figures are Means, Range (Units) (Dayton et al., 2006).

FOOD-CHAIN RISKS

Plant uptake is essentially the inverse of leaching, with further limitation by plant processes and tissue barriers to element transport. Chaney (1980) introduced the "Soil-Plant Barrier" concept to describe why nearly all animals are protected from food-chain transfer of nearly all elements in soils. Most elements are so insoluble or so strongly adsorbed in soils or in plants roots that they do not reach plant shoots in levels that comprise risk to highly exposed individuals. Examples include Au, Ag, Hg, Pb, Cr^{3+}, Ce, Sn, Ti, and Zr. Included in another group of elements does not

comprise food-chain risk because they are phytotoxic to plants before the concentration in the plant comprises risk to consumers are Zn, Cu, Ni, Mn, F, and As.

One key group—Mo and Se—does comprise potential risk to ruminant livestock consuming forages grown on alkaline soils. Both of these elements are less strongly adsorbed in alkaline soils, so that if the alkaline soil is Mo- or Se-enriched, plants may accumulate higher concentrations. Under worst case conditions, plants accumulate high levels without suffering phytotoxicity, and ruminant livestock are sensitive to Mo. Excessive Mo intake inhibits absorption or use of Cu in ruminants; Cu deficiency has commonly occurred when forages contained excessive Mo. The Mo case is focused on ruminants because monogastric animals are much less sensitive to dietary Mo. Plants are essentially insensitive to Mo at levels that are already toxic to ruminants. Soil and biosolids Mo risks were reviewed by O'Connor et al. (2001), and a limit of 40 mg Mo per kg dry biosolids was suggested as a regulatory limit. This suggested limit considered the mixture of grass and legume crops normally consumed by ruminants and the usual mixture of feedstuffs provided by producers, and the fact that forage production on an alkaline soil that promotes Mo uptake also promotes Mo leaching over time, which reduces Mo risks. McBride and Cherney (2004) considered this much Mo in biosolids to be a significant risk but focused on feeding legumes only, an impractical diet, and assumed that all feed was grown on alkaline soils enriched in Mo. Ruminants must be kept on the high Mo diet for some months to deplete body Cu reserves before an actual adverse effect occurs, and simple Cu supplementation counteracts the Mo toxic effect.

Se is potentially toxic to both monogastrics and ruminants, but because the leaves contain higher concentrations than grain or other storage tissues, grazing livestock are usually the most sensitive to excessive bioavailable soil Se. Under rare conditions, humans have suffered Se toxicity when normal crops could not be grown due to inadequate rainfall and the alternative food crops accumulated higher Se than the usual food crop, rice (Yang et al., 1983).

The principal exception to protection of humans by the Soil-Plant Barrier is Cd. Cd can be accumulated by plants to levels that harm animals that chronically ingest the crops. Longer-lived animals are at greater risk, and humans have experienced Cd disease from crops grown on contaminated soils (Reeves and Chaney, 2008). Another possible exception is Co, which can be accumulated to about 25 mg kg^{-1} before phytotoxicity is evident, but ruminant livestock can tolerate only about 10 mg kg^{-1} in chronic diets. No case of food-chain Co toxicity to cattle or sheep has been reported, perhaps because Co contamination is so rare.

Cd has caused renal tubular dysfunction and osteomalacia in farm families who ingested rice for decades from fields contaminated by mine and smelter discharges of Zn and Cd. The osteomalacia effect, "*itai-itai*" disease with repeated bone fractures, has occurred at several locations but in only a small fraction of the persons with severe renal tubular disease. Thus renal tubular dysfunction is the first adverse effect that must be prevented by regulatory controls. Other possible adverse effects of dietary Cd have been suspected but not observed. Chaney et al. (2004) and Reeves and Chaney (2008) have discussed the key role of Zn, Fe, and Ca deficiency in subsistence rice diets, which promote human absorption of Cd. These nutritional deficiencies due to subsistence rice diets are a significant international malnutrition problem for which

agronomists and nutritionists are seeking rice cultivars with improved grain bioavailable Fe and Zn to prevent widespread adverse effects (Graham et al., 2007). A paper by Reeves and Chaney (2004) showed that the kinetics of Cd movement thru the intestine was significantly altered in rats with marginal Fe, Zn, and Ca diets such that net Cd retention was increased 10-fold compared to rats with adequate nutrition. Growing rice in flooded soils, but draining the soil at flowering to improve yields allows CdS formed during flooding to be oxidized and Cd (but not Zn) to be readily absorbed and translocated to grain. In soils with the normal geogenic ratio of Cd to Zn (about 1 μg Cd per 200 μg Zn) and in crops other than rice, Zn inhibits Cd uptake by the crop and reduces the bioavailability of Cd in the crop. No adverse Cd effects have been shown for agricultural food-chains other than subsistence rice. Biosolids can increase both Cd and Zn in crops such that when Cd in Swiss chard was increased five-fold, no increase in kidney or liver Cd occurred in guinea pigs fed the chard (Chaney et al., 1978b) while high increase in lettuce Cd from a high Cd:Zn ratio biosolids caused a large increase in kidney Cd (Chaney et al., 1978a). Interestingly, Cd in spinach was significantly less bioavailable than Cd in lettuce to Japanese quail or rats consuming these foods (Buhler, 1985), and increased plant Zn significantly reduced retention of plant Cd by quail (McKenna et al., 1992).

Oysters accumulate high levels of Cd but also accumulate Zn and Fe, which reduce risk from Cd in shellfish. A few sources of Cd are of especially high potential risk—those without normal Zn co-contamination (Ni-Cd batteries, Cd-pigments, Cd plastic stabilizers, Cd plating wastes, Cd-Cu smelter emissions). Failure to find Cd-induced renal tubular dysfunction at a number of sites (the United Kingdom, United States, Germany, and France) where smelter emissions or mine wastes have caused garden soils to contain 100 mg Cd and 10,000 mg Zn kg^{-1}, while finding 80% incidence of renal disease in older persons ingesting home-grown rice, highlights the role of rice diets increasing dietary Cd bioavailability in human risk (reviewed in Chaney et al., 2004). Consuming three-fold normal daily Cd intakes from shellfish diets did not increase blood Cd in Swedish young women (Vahter et al., 1996), nor did consumption of high amounts of high Cd oysters by New Zealand residents cause Cd disease (Sharma et al., 1983; McKenzie-Parnell and Eynon, 1987).

Several northern European populations have been reported to possibly suffer adverse effect of dietary Cd at much lower dietary Cd, blood Cd, and urinary Cd (Buchet et al., 1990; Järup et al., 2000) than other populations without identified adverse Cd effects (Ikeda et al., 2003). These reports are not explicable in terms of known aspects of Cd metabolism, and remain debated among scientists.

ISSUE: How can bioavailability of Cd in different foods and diets be taken into account in risk assessment?

How can the presence of increased bioavailable Zn or Fe in a food be taken into account in risk assessment for Cd in crops?

PHYTOTOXICITY RISKS FROM SOIL ELEMENTS:

As noted above, the most sensitive adverse effect of some elements in soils is phytotoxicity. It seems clear that the first limiting effect of Zn, Ni, Cu, Mn, Al, and possibly some other elements are phytotoxicity to sensitive plants. Of course, plant species vary in tolerance of soil elements. And soil properties can strongly affect phytotoxicity. For cations, acidic soil pH strongly promotes element toxicity, and the elements react over time increasingly strongly to lower phytoavailable forms. In the case of Ni, it was shown by Singh and Jeng (1993) that Ni was about 10-fold less accumulated by perennial ryegrass over a three-year test period using experimental methods that are highly defensible. Initially, such results were explained in terms of adsorption and diffusion into micropores of the sesquioxides (e.g., Bruemmer et al., 1988). Since then, research has shown that new mineral phases may form in Ni-enriched soils, both Ni-Al layered double hydroxides and Ni-silicates (e.g., Scheckel and Sparks, 2001). And although Zn can also form such layered double hydroxide (LDH) species, the Zn forms are weaker than the Ni forms (Roberts et al., 2003). Cu and Cd apparently do not form the LDH species in soils, and Co may form them (Scheinost and Sparks, 2000).

Figure 2 summarizes known soil reactions of Ni in relation to plant uptake and Ni phytotoxicity. Some industrial compounds can land on soils and persist for long periods. For example, NiO dissolves very slowly, with a half life of 20.4 years at pH 7.25, and slower with larger particle size (Ludwig and Casey, 1996). A study of Ni species in a smelter-contaminated soil at Port Colborne, Ontario, found particles of NiO remaining in the soil more than 30 years after smelting ceased (McNear et al., 2007). They also found that Ni-LDH had formed in these soils over time, confirming the practical significance of Ni-LDH formation in contaminated soils. Ni-sulfides deposited on soils can be oxidized by microbes. Other Ni enters into equilibria with soil sorption surfaces and chelation surfaces. Much soluble soil Ni^{2+} is chelated or complexed, but the free ion shuttles among sites based on free energy and binding site specificity. As shown in Figure 3, grasses suffer an unusual symptom of Ni-induced Fe deficiency chlorosis in which the severity follows a diurnal pattern (banded chlorosis). Phytosiderophores (PSid) are secreted by young grass roots to dissolve soil Fe, and the Fe-phytosiderophore (FePSid) is absorbed by a transport protein specific to the Fe-PSid. At low pH, Ni fills the PSid and can push Fe out by competition, but during the morning pulse of PSid secretion, some Fe is dissolved and absorbed so part of the growing leaf blade receives Fe before it emerges from the culm. As pH is raised, Ni is bound increasingly strongly by soil sorbents, and forms new solids (Ni-LDH, Ni-silicates) such that insufficient Ni remains reactive to compete for filling the PS in the rhizosphere (see Kukier and Chaney, 2004). Simply making soils calcareous can remediate Ni phytotoxicity potential for species that are very sensitive at acidic pH (Siebielec et al., 2007). Interestingly, Cu is more bound by organic matter than Fe and Mn oxides, and it does not form LDH compounds in soils, so as pH is raised and Fe is less available for chelation by PSid, Cu inhibits Fe uptake in a simple Fe deficiency pattern (Michaud et al., 2007) rather than the banded chlorosis caused by Ni and Co. Zn forms LDH compounds and is readily converted to lower phytoavailability forms in soil, so making a high Zn soil calcareous with reasonable soil fertility remediated Zn phytotoxicity to sensitive plants (Li et al., 2000).

Others followed the toxicological approach to establish limits for soil Ni, adding Ni salts, cropping immediately, failing to correct for the metal salt-induced drop in soil pH, etc. (Oorts et al., 2006; Rooney et al., 2007; Thalaki et al., 2006). Or they studied nutrient solutions but did not understand metal chelate equilibria in nutrient solutions and observed apparently higher toxicity at higher pH (Weng et al., 2003), in strong contrast with the real world (Kukier and Chaney, 2004; Siebielec et al., 2007).

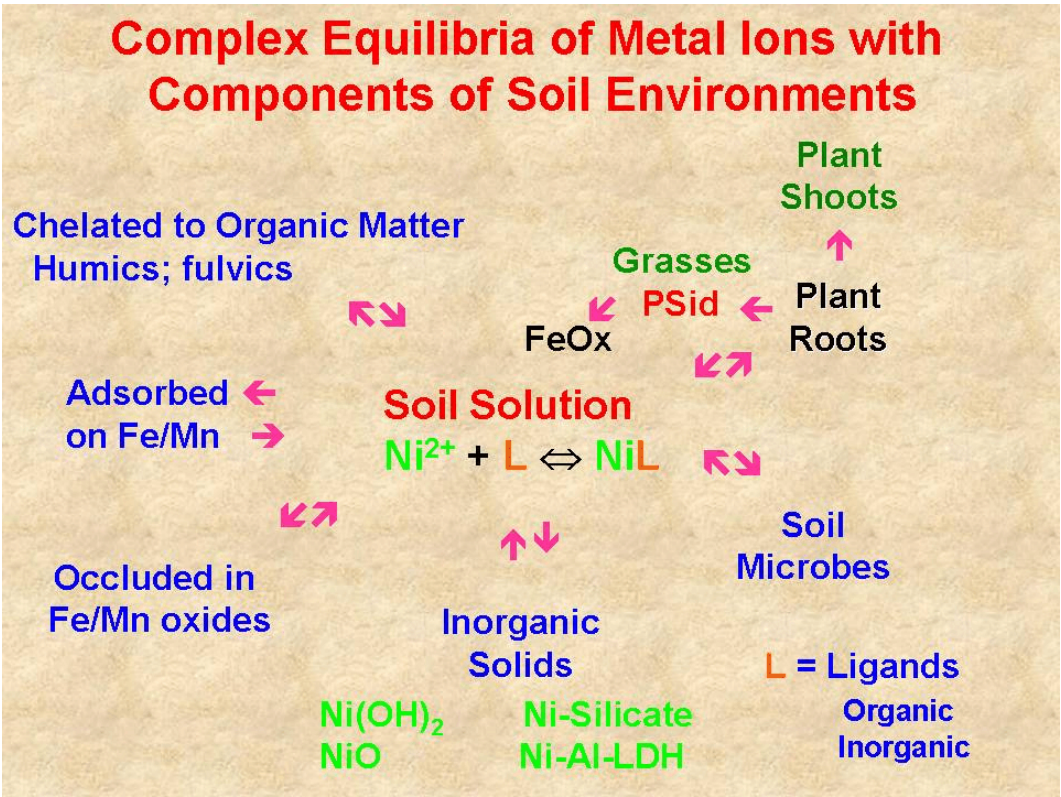

Figure 2. Equilibria of Ni in Soils in Relation to Uptake by Both Dicots and Grasses; Note Formation of Ni-Al-Layered Double Hydroxide (LDH) and Ni-Silicate Over Time, Which Reduces Ni Phytoavailability. PSid are Phytosiderophores Such as Deoxymugineic Acid Secreted by Wheat to Chelate Soil Fe.

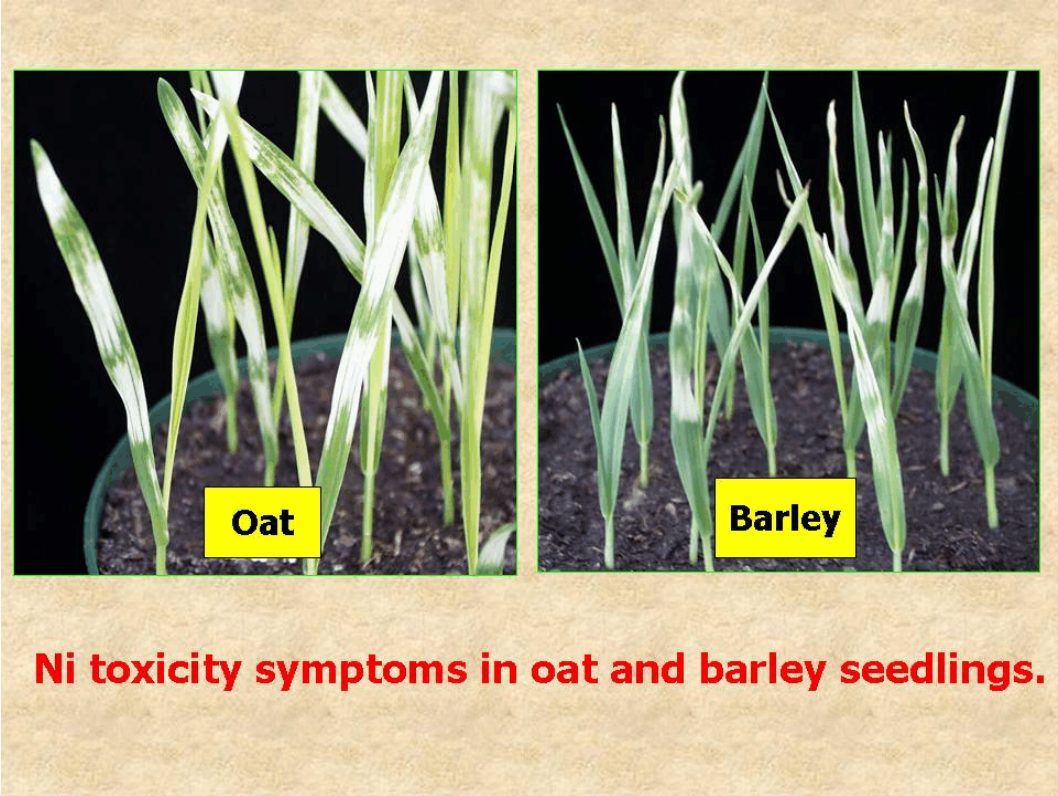

Figure 3. Unique Symptoms of Ni-Induced Fe Deficiency (Ni-Phytotoxicity) with Diurnal Variation in Severity, which Results from Ni Preventing Fe-Phytosiderophore Formation in the Rhizosphere Except During Morning Pulse Secretion of Phytosiderophore by Young Grass Roots.

COMMON SOIL EXTRACTIONS TO PREDICT RISK OF PHYTOTOXICITY OR FOOD-CHAIN RISK.

Many soil extraction tests have been developed to assess phytoavailability of soil elements, especially nutrients required for maximum plant yields. These tests are commonly conducted in most countries in usual farm production. The key factor in development of such tests was that the extraction result was highly correlated with the potential for economic yield response to fertilizer applications. In recent years, mechanistic tests are preferred for estimation of element uptake, but the key to adoption of any method is the correlation with the potential for phytotoxicity or excessive plant uptake, or correction of deficiency due to element levels in soils. Extractions such as the DTPA-TEA method (Lindsay and Norvell, 1978) have become widely adopted in its original form, or as modified for analysis of even more elements as the DTPA-NH_4-Bicarbonate extraction (Soltanpour, 1985).

Several authors have illustrated that chelation methods can become saturated and thus underestimate phytoavailable element levels in soils (Li et al., 2000; Kukier and Chaney, 2000). In our experience, neutral salt non-complexing solutions can predict plant-relevant Zn and Ni

uptake across soils and soil pH (e.g., 0.01 M $Sr(NO_3)_2$ at 10 g soil/20 mL, Siebielec et al., 2007). The presence of chloride rather than a non-complexing anion such as nitrate necessarily increases extractability of metals, which can be complexed by chloride; whether that is useful or a problem lies in the eye of the beholder. Using high levels of $CaCl_2$ in extractions increases dissolved metals and makes measurements easier, but may give a false picture of the relative phytoavailability of several elements in the soil sample.

In the last few years, a new soil testing strategy has been tested, the DGT (Diffusive Gradients in Thinfilms) method (e.g., Davison & Zhang, 1994; Letho et al., 2006). Although this may give significant correlations with plant uptake, it takes considerably longer and costs much more than simple neutral salt extraction methods. A problem with mild extraction methods is the low concentration of analyte present in the extract. If it takes an ICP-MS to be able to make useful measurements, a method is of lesser utility than a method that can use ICP-AES or Atomic Absorption methods. On the other hand, when a method integrates metal phytotoxicity over soils and soil pH levels so that the instantaneous phytotoxicity potential of that soil for a specific plant species can be estimated, it is a powerful method for risk assessment (Siebielec et al., 2007).

ISSUE: Remediation by liming metal phytotoxic soils may be highly effective in restoring vegetative cover and a safe ecosystem for wildlife, but the applied alkalinity can be consumed by acidic rainfall and acidifying soil amendments. Required maintenance of such sites needs to be established by field experiments.

RISKS TO SOIL ORGANISMS

Toxicity to soil microbes and fauna has received much study, but often the methods used suffered from serious artifacts much as noted above for phytotoxicity. The addition of metal salts to soils is even more inappropriate in the study of soil organisms because the organism receives the shock of soluble added elements rather than the metals equilibrated with the soil. Complexes of the metals with anions can cause persistence of soluble ions, and high rates of metal cations can drive pH several units lower, greatly increasing soil metal solubility. The effects of diverse soil properties on Pb toxicity to earthworms are considered in Bradham et al. (2006).

In addition, remediation of phytotoxicity is often successful for remediation of toxicity to soil microbes and fauna (e.g., Brown et al., 2004, 2005). As we have noted, when metals are present at phytotoxic levels, the recommended remediation treatment would be to make the soil calcareous to minimize metal phytoavailability and provide a persistent remediation. Because this treatment gives lower and lower metal bioavailability over time, it generally provides effective protection of soil organisms. And consumers of soil organisms appear to be protected except for soil ingestion risks (Pb, As, F) where earthworms can carry a high fraction of dietary soil into diets of earthworm consumers.

Risks from soil Cd to earthworms and earthworm consumers have often been over-estimated (Brown et al., 2000a, 2000b). In estimating bioaccumulation ratios, one needs to take into account that the ratios are 10-fold higher for background uncontaminated soils than for contaminated soils. Prediction of risks to earthworm consumers has not been confirmed except

for the case of a Cu-Cd smelter at Prescott, UK. Because Zn was not present with the Cd, earthworms accumulated high body burdens of Cd without injury that would have occurred from Zn in most contamination cases. In mine waste studies, Cd bioaccumulation was clearly limited by the presence of Zn (Andrews et al., 1984).

Tolerance of soil microbes to metals is very complex, and traditional methods of study by adding metal salts to soils clearly confound the tests. Soils with deficient Zn have microbes which are less resistant to Zn additions than found in soils with Zn contamination. These findings led McLaughlin et al. to introduce the concept of "metalloregion" to suggest that some soils may be much more resistant to additions of Zn than other soils; that is, it would be an error to apply results from the most sensitive soil to all soils (McLaughlin and Smolders, 2001). Although it is clear that white clover rhizobium is relatively sensitive to excessive soil Zn, it is also very sensitive to simple soil acidity; causation in selection of ineffective nodulating strains was more affected by low soil pH than by soil Cd or Zn levels (Ibekwe et al., 1997). In our experience, sensitive plants are less resistant to excessive bioavailable soil metals than are the microbes in the soil, such that protection against phytotoxicity protects soil function.

RISKS THROUGH SOIL INGESTION

For selected elements, the element in ingested soil can comprise a risk to animals or humans and is especially well studied for Pb and As, but also considered important for F, Hg, and possibly other elements. Soil ingestion circumvents the Soil-Plant Barrier whereby limited plant uptake limits significant exposure. In soil ingestion, an element must have sufficient bioavailability/solubility that it can be absorbed in the intestine to a greater extent than if garden foods growing on the soil were consumed.

It has been recognized for decades that Pb deposited on the outside of forages can cause adverse effects in grazing livestock. Then, as risks from Pb in the urban environment was studied in more detail, it became apparent that Pb-rich exterior soil and dust can be carried into homes and provide exposure to young children who do not play outdoors. And that Pb-paint dust ingested by hand-to-mouth transfer could be the important pathway for Pb exposure. Additional research eventually showed that interior paint Pb comprised far greater risk than soil Pb (Lanphear et al., 1998). But a key learning was that soil Pb was a greater risk through soil ingestion than through uptake by garden food crops (Chaney and Ryan, 1994). Pb uptake by plants can occur, but uptake of equilibrated soil Pb is small; soil adhering on low-growing crops is a more important source of Pb risk than in Pb uptake by plants. Gardening in urban soils is a difficult issue; if gardeners avoid growing low-growing leafy and root vegetables and take care to exclude soil from their homes, gardening can be a safe practice until soils exceed levels which comprise a clear risk by soil/dust ingestion.

Soil Pb became a worrisome source of risk to children because Pb has become widely dispersed in urban soils (Mielke et al., 1983, 2007) as well as at industrial and DoD sites. Paint, building demolition dispersing interior paint (Farfel et al., 2005a and Farfel et a., 2005b), stack emissions, and automotive exhaust emissions contributed to urban soil Pb loadings. Center city soils are considerably more contaminated than suburban soils, although exterior Pb paint scrapped to soil

can cause massive soil contamination wherever it occurs, easily causing soil to exceed 10,000 mg Pb kg^{-1}.

HOW MUCH SOIL DO CHILDREN INGEST?

Several studies have been conducted to estimate soil ingestion by young children. Some investigators measured soil on hands of children and how long after starting play it took for their hands to become contaminated. The most widely accepted estimate of chronic soil ingestion by young children was reported by the team of Calabrese, Barnes, and Stanek at University of Massachusetts. They used ICP-AES and later ICP-MS to measure tracer elements in feces of children recovered from diapers. They analyzed diets to allow correction for dietary intake of elements and provided toothpaste low in Ti so that fecal Ti might measure soil. Over time, they discovered that some of the elements they originally used as tracers were present at lower levels in the fine soil fraction (<250 μm) than in bulk soil (< 2 mm), and thus they had to reassess their whole calculation method (Calabrese et al., 1996; Stanek et al., 1999). In the end, the data for two populations they investigated are reported in Stanek et al. (2001). These final estimates of the distribution of soil ingestion by young children are considerably lower than the original estimates (final median = 24 mg d^{-1}; SD = 16 mg d^{-1}; 95th percentile = 91 mg d^{-1}. These data were the original source of information for the development of the 200 mg soil d^{-1} assumed soil ingestion by children used in Superfund Risk Assessment. The original estimate (based on 2 mm soil and a different set of elements than those used in later estimates) is now known to be an overestimate of high end normal soil ingestion by exposed children.

HOW MUCH SOIL PB IS TOO MUCH?

Greatest risk from soil Pb depends on getting the soil into the area where it can be ingested by hand-to-mouth play and exploration by children. Growing children are very sensitive to excessive absorbed Pb and absorb a higher fraction of dietary Pb than do adults. Epidemiologic studies in Pb-dust-contaminated housing show that peak blood Pb in childhood occurs at about 18-24 months age, but that is still before children are allowed to play unsupervised in soil. So, interior dust, paint dust, and soil/dust brought into the house must provide the Pb exposure that causes the bulk of excessive soil-Pb absorption by children. This process was first proven when the clothing of Pb workers raised Pb levels in house dust and caused Pb poisoning of their children even though their housing did not have high Pb paints (Dolcourt et al., 1978).

Although the focus here is on soil Pb, it must be recognized that paint Pb in a home is the much more likely source of high Pb levels in house dust and excessive Pb absorption in children. In several smelter town studies, for at least some of the children the majority of blood Pb came from paint rather than from soil or industrial dusts (Gulson et al., 2004). By the same token, industrial dusts emitted from smelters, or resuspended Pb-contaminated dusts in an arid community readily recontaminate household dust and remain key sources of excessive blood Pb. In Trail, British Columbia, it was found that blood Pb dropped substantially when a new flash smelting technology was introduced, which caused much lower Pb emissions, with a corresponding drop in house dust Pb (Hilts, 2003).

For Pb absorption to occur, the chemical forms of Pb in the soil/dust must be absorbable when the soil is ingested. Research has shown that some Pb minerals are poorly absorbed by humans (PbS, chloropyromorphite), while some others are readily absorbed ($PbCO_3$). Perhaps the most important factor in Pb absorption is the presence of food in the stomach/intestine when the Pb source is present. Several research teams evaluated Pb isotope absorption by human volunteers fed Pb with meals or specific foods, or on fasting. On fasting, soluble Pb is absorbed at 50-80%, usually assumed by EPA to be 50% for Pb acetate. But when the Pb is ingested with a meal, one hr before a meal, or up to 4 hr after a meal, absorption falls to the range of 2-5% of dose (James et al., 1985; Heard and Chamberlain, 1982; Heard et al., 1983). Particular food ingredients ingested with Pb can greatly reduce Pb absorption, especially Ca (Blake and Mann, 1983); Ca is believed to compete with Pb absorption by a Ca-transport protein in the small intestine and to form co-precipitates with phosphate and Pb. Pb incorporated in kidney or spinach had quite low bioavailability to adults (Heard et al., 1983).

One key learning in this area of science came from a test of soil removal and replacement. The US-EPA conducted a congressionally-supported test in three cities of whether removal and replacement of soil would cause a reduction in blood Pb in the children who lived there. The biokinetics of blood Pb in children versus exposure was considered, and it was believed that if soil Pb absorption by children was reduced for a year by the soil replacement, blood Pb should decline significantly if soil were contributing to the Pb that was being absorbed. Tests were conducted in three cities. Children who lived in areas where soils around houses contained at least 500 mg Pb kg^{-1} were identified, and volunteers were assigned to early replacement and late replacement (at the end of one year, the second half of the population would have their soil replaced). Blood Pb was sampled before any changes were made, after the first half were replaced and several more times until the end of the test. The children were randomly (of the general area where they lived) assigned to early or late replacement so it was a randomized test. In Baltimore (Farrell et al., 1998) and Cincinnati, soils that were replaced contained only about 500 mg Pb kg^{-1}, and there was no significant reduction in blood Pb in the children. In Boston, children were assigned to early or late replacement as they joined the study; the soils replaced contained between 1,800 and 2,000 mg Pb kg^{-1}; soil replacement included dust control post soil replacement to assure full removal of the exposure source that may have been stirred up during replacement; replacement plus dust control was compared with dust control alone versus absolute control, and soil replacement gave a small significant reduction in blood Pb at this high soil Pb level (Weitzmann et al., 1993). The "late" replacement also gave a small significant reduction in blood Pb (Aschengrau et al., 1994): "The combined results from both phases suggest that a soil lead reduction of 2,060 ppm is associated with a 2.25 to 2.70 μg dL^{-1} decline in blood lead levels." (from original mean level 12.8 μg dL^{-1}). The most important finding, however, was that other sources (paint) had more important impact on blood Pb than did exterior soil. There was some evidence that the biokinetics of reduction of blood-Pb were slower than anticipated, with the second year of reduced exposure yielding somewhat lower blood Pb than one year of reduction. As noted above, a meta-analysis of the contribution of soil versus house dust to blood Pb of urban children has shown that house dust was considerably more important (Lanphear et al., 1998). It was suggested that the proportion of exposure from soil versus house dust in the IEUBK model needed to be changed to reflect this improved knowledge, but that has not yet occurred.

BIOAVAILABILITY OF SOIL/DUST PB

The earliest tests were conducted with rats (Stara et al., 1973; Chaney et al., 1984, 1989) and urban dust or garden soil samples with varied levels of Pb from the Baltimore, MD, area. An ARCO Coal Company led team investigated chemical speciation of Pb in Superfund soils and tested the bioavailability to rats and rabbits. Several groups noted that Pb in mining site soils caused less increase in blood Pb than did Pb in smelter site soils (e.g., Steele et al, 1990). Davis et al. (1993) found galena and anglesite ($PbSO_4$) with rinding in mine waste soils at Butte, MT. The dissolution of $PbSO_4$ was found to be inherently slow compared to the time needed for clearance of the stomach and intestine of children, helping to explain why this form of Pb caused less uptake into blood. Mineral PbS or chemical PbS both had low bioavailability to rats (Dieter et al., 1993) (Figure 4), while extremely fine PbS formed by adding sulfide to a solution of Pb-isotope was somewhat more bioavailable in fasting human tests (Rabinowitz et al., 1980). Thus part of the lower risk of mining waste PbS has to do with particle size; very fine PbS in cosmetics is apparently more dangerous than PbS in soils. Freeman et al. (1993) conducted tests of methods to assess Pb bioavailability and found that the usual one dose, area under the curve approach was not workable for environmental levels of Pb exposure. Gavage Pb acetate was absorbed very quickly and disappeared from blood quickly, while soil Pb caused only a small increase in blood Pb over several days. So they moved to a chronic feeding approach using purified diets. It had already been shown that using ordinary rat chow greatly reduced Pb bioavailability, but using the American Institute of Nutrition (AIN) purified diets for rats promoted Pb bioavailability (Mylroie et al., 1978). They fed several levels of two soils compared to Pb-acetate (Figure 5).

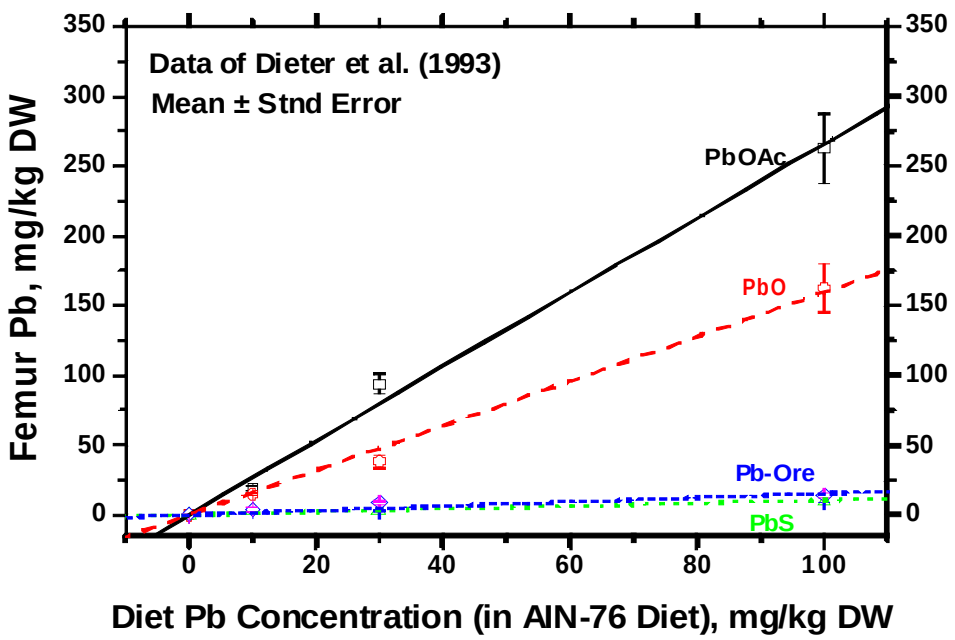

Figure 4. Absorption of Pb From Different Pb Compounds Added to the AIN-76 Purified Diet (Dieter et al., 1993.)

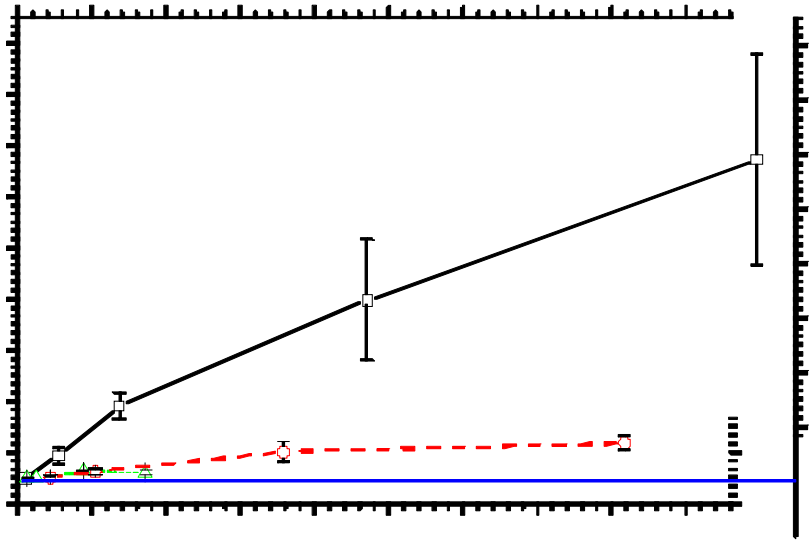

Figure 5. Effect of Soil Dose and Mining Waste Soil Pb Concentration on Pb in Bone of Rats Fed the Test Soils in AIN Diets for 35 Days (Freeman et al., 1992).

A number of years later, Superfund researchers decided to assess relative bioavailability so that more precise decisions about soil treatment could be generated. The lead scientist in that project asserted that juvenile swine were the only animals that could be used to conduct such tests, even if rat tests were conducted to prevent the problems with rat feeding experiments (Weis and Lavelle, 1991). After years of research, that team kept asserting that it might be appropriate to use relative bioavailability measured using the swine bioassay to adjust soil Pb cleanup levels,

but that the IEUBK computer program had to be used and that treatment of soils could not achieve reduction in risk. Over this decade extensive research showed that the bioavailability of soil Pb could be reduced by treatment with biosolids or with phosphate sources (Ryan et al., 2004; Brown et al., 2003). A summary of that progress is reported by Ryan et al. (2004) regarding a large, multi-year field test of soil Pb remediation at Joplin, MO.

Eventually, the EPA Region-8 team (Casteel et al., 1996, 1997; Drexler and Brattin, 2007; US-EPA, 2007) worked to develop their own bioaccessibility test (see below).

How to conduct relative soil Pb bioavailability tests has been debated for many years. Some felt that one had to follow the usual toxicological approach and use fasting animals. However, comparison feeding tests of Pb on fasting or to persons consuming small meals showed that for some time before and after consumption of a meal, a remarkable reduction in Pb absorption occurred in humans (James et al., 1985). It was common for water soluble Pb to be absorbed between 60-80% on fasting, but only 1-5% with food (James et al., 1985; Heard and Chamberlain, 1982; Heard et al., 1983). Many have noted this critical effect and wondered how animal testing should be conducted. Is all soil/dust ingested by children between meals such that only the fasting condition is representative? The juvenile swine test compromised and has fed soil mixed with a ball of the purified "dough" AIN feed used in the test; one can only gavage a young pig so many times before it become too difficult to continue gavage dosing. Thus one part is fed after long fasting, and the second part is fed after a short fast. So the actual test is a hybrid or confounded method (Casteel et al., 1997, 2006; U.S. EPA, 2007b). One issue seldom discussed is the need for testing soils with high Pb concentration in order to make significant measurements in animal tissues during bioavailability evaluation. Nearly all of the soils fed were on the order of 10-50 times higher in Pb than the current limit for Pb in bare soils of homes under Housing and Urban Development (HUD) rules (400 mg kg_{-1} for bare soil). It is possible that the soil and diet factors that interact with soil Pb bioavailability are different for such highly contaminated test soil materials than in soils to which children are commonly exposed.

Ultimately, human tests of soil Pb bioavailability were conducted, and these should be the gold standard for soil Pb biovailability. Maddaloni et al (1998) fed human volunteers soil on fasting or with a meal using Pb stable isotopes ($^{206}Pb/^{207}Pb$ ratio) to measure the absolute Pb absorption from the test dose. By selecting subjects with quite different isotope ratios than the soil to be tested, a very sensitive assay was constructed. The soil from Bunker Hill, ID, contained 2,240 mg Pb kg^{-1} whole soil and 2,924 mg Pb kg^{-1} in the <250 µm sieve fraction. It was found that the humans fed about 225 µg Pb in 80 mg soil absorbed 26.2% of the soil Pb on fasting, but only 2.52% when they ingested the soil with a light breakfast meal. The interpretation of the stable Pb isotope based bioassay is based on the normal distribution of IV-injected Pb after 24 hr, with 55% remaining in whole blood (Maddaloni et al., 1998). Additional consideration suggests that individuals who consume much soil are breaking their fast due to the soil ingestion itself. Other work has shown that higher dietary Ca (and to some extent phosphate) inhibit Pb absorption considerably (e.g., Blake and Mann, 1983). The apparent reason that Ca has the stronger effect is that phosphate is recirculated in the digestive system, so that diet Ca has plenty of phosphate with which to co-precipitate dietary Pb. The effect of dietary Ca cannot be attributed to a role in formation of chloropyromorphite (CP) (a very low solubility Pb compound with low

bioavailability). The first mention of the possible formation of chloropyromorphite in soil that we know of was by Nriagu (1974). Subsequently Cotter-Howells and Thornton (1991) reported formation of CP in Pb mineralized soils of an old English village. And then Ryan, Logan, Ma, and Traina examined formation of CP with Pb compounds and soil Pb, and their work suggested this could be an effective soil Pb remediation technology (Ma et al., 1993).

In our view, the ultimate question about soil Pb bioavailability is "Can you remediate soil Pb to persistently reduce Pb bioavailability?" This question was the goal of the IINERT Action Team (of the US-EPA Remediation Technology Development Forum) led by Ryan and Berti (Ryan et al., 2004). A large team applied different promising soil Pb remediation methods to an urban soil contaminated with Pb, Zn, and Cd from smelter emissions in Joplin, MO. Treatments included phosphoric acid, triple superphosphate (TSP), rock phosphate, biosolids compost ± TSP and iron oxide ± phosphate. The amendments were incorporated in replicated randomized plots and incubated for several months at the pH of the mixture, then limed to about pH 7 and seeded with tall fescue. The soils and grass were sampled periodically over the next few years for soil Pb bioaccessibility and bioavailability (Ryan et al., 2004) testing, and analysis of plant uptake (Brown et al., 2004). Phosphoric acid treated and control soils were fed to rats, juvenile swine, and human volunteers. The results of feeding the soil about 1.5 years post field treatment showed a reduction of bioavailability of about 69% (42.2 versus 13.1% ABA) to fasting adults, about 38% to juvenile swine and 38% to rats. The Ruby et al. (1993, 1996, 1999) SBRC Pb bioaccessibility test showed a reduction of 38% when conducted at pH 2.2 or 2.5, but no change when conducted at pH 1.5, the level specified by Drexler and Brattin (2007).

In addition to measurement of Pb bioavailability and bioaccessibility, study of Pb speciation was undertaken by Scheckel and Ryan (2004). Using nondestructive EXAFS, they were able to measure the fraction of total soil Pb in several chemical forms and found that phosphate applications caused most of the soil Pb to be changed to CP. This finding is very important because CP has very low bioavailability and is stable under normal soil environmental conditions, becoming less and less bioavailable as the solid becomes larger and more ordered over time (Scheckel and Ryan, 2002). Although acidic pH favors the reactions of various P additions with soil Pb species, CP is formed from most Pb compounds, under most normal soil conditions (Ryan et al., 2001; Zhang and Ryan, 1998, 1999a, 199b; Zhang et al., 1997, 1998), and if the mixture of phosphate with soil has occurred, the CP formation may occur rapidly in the stomach if it had not already occurred in the soil before ingestion (Scheckel et al., 2003). Actually, this latter publication shows that sequential extraction procedures cause the formation of new Pb compounds during the procedure and show another failing of sequential extractions in trying to understand forms of metals in the environment. Various P amendments are effective in formation of CP over time including phosphoric acid, triple superphosphate, diammonium phosphate, rock phosphate, composts and biosolids (Brown et al., 2003), bone meal (Hodson et al., 2000), etc. (Hettiarachchi et al., 2001; Knox et al., 2006; Yoon et al., 2007; Cao et al., 2008). Rhizosphere soil conditions or soil microbes may promote formation of CP in amended soils (e.g., Cotter-Howells et al., 1999).

ISSUE: Human soil feeding tests with soil with a range of Pb levels and sources of Pb contamination, without and with remediation treatments, are needed to establish

the reduction in bioavailability due to promising soil treatments. Other methods of measurement of bioavailability as well as methods to verify effectiveness of remediation treatment should be performed on these samples.

BIOACCESSIBILITY OF SOIL PB:

When feeding studies were being conducted to characterize the relative and absolute bioavailability of soil Pb, it was intended to develop a chemical extraction test for soils that correlated well with the relative bioavailability determined by feeding. Ruby et al. (1993) reported the initial study and introduced the term "bioaccessibility" for chemical assessment of relative bioavailability. There has been a lot of effort to improve this test and to make it simpler or less expensive to conduct since the original paper, and important progress has been made. On the other hand, numerous authors have conducted tests of variation of the extraction method, adding different digestion factors from the human digestive system assuming that the more life-like the method, the better the reliability would be (e.g., Oomen et al., 2002, 2003a, 2003b). Some authors have simply used dilute HCl ignoring the buffering aspect of stomach secretions (Thums et al., 2008). In our view the only relevant issue is the relationship of the bioaccessibility test and an acceptable bioavailability measure.

Ruby et al. (1996, 1999) extended the development of their extraction method and called it the Physiologically-Based Extraction Test (PBET). The test was more complicated but seemed well correlated with results of some feeding studies.

Drexler and Brattin (2007) reported their Relative Bioavailability Leaching Procedure (RBALP) using the simplified stomach phase only. They had access to the diverse soil materials from Superfund sites, which had been fed to juvenile swine using the Casteel et al. (2006) procedure. The test uses 0.4 M glycine with enough HCl to buffer the solution at pH 1.5 to mimic fasting stomach pH; the extraction is conducted at 37°C for 1 hr, using 1 g dry soil/dust per 100 mL extraction fluid. They suggest that if the pH of the extraction fluid is raised by the soil under test that the pH should be manually adjusted to 1.5 until it stays at that pH for the extraction period. The correlation with swine RBA results was found to be R^2=0.82; the correlation was R^2=0.75 when conducted at pH 2.5. But as noted above, conducting the extraction at pH 1.5 left it insensitive to the highly effective soil remediation treatments using phosphate tested at Joplin, which were proven to have lower bioavailability by feeding to swine, rats, and humans. Thus we believe this method should be conducted at pH 2.5 so that the results have relevance to soil remediation.

Further, the extraction test result gave a smaller reduction in soil Pb bioavailability (38%) than found with human volunteers fed the Joplin soil on fasting (69%), as did the pig and rat feeding tests. This is clearly evidence that more soil Pb remediation test materials should be fed to humans to provide the definition of remediation of risk that seems to be obtainable with inexpensive technologies (Ryan et al., 2004). Another attempt to validate an extraction procedure was reported by Schroder et al. (2004). They fed 18 soils to swine following the Casteel et al. (2006) procedure and tested stomach and intestinal phases on an *in vitro g*astrointestinal (IVG) extraction method. The presence of the dough used to dose the soil/dust Pb to swine significantly

reduced IVG Pb perhaps due to the presence of phytate. Their method used pH 1.8 and added porcine enzymes. Strong correlation was obtained between IVG and RBA results.

Further, research has indicated that highly effective remediation could be achieved by application of a mixture of soil amendments to revitalize soils that had been severely injured by metal contamination from smelter and mine wastes (Allen et al., 2007). Combinations of biosolids, composts, manures, alkaline byproducts, wood ash, fly ash, limestone, etc., can generate calcareous soil amendment mixtures at low cost and yield remediated soils that protect humans, wildlife, and other ecosystem components. This approach has now been applied at several Superfund and similar sites with persistent success (Li et al, 2000; Basta et al., 2001; Brown et al., 2003, 2004; Condor et al., 2001; Farfel et al., 2005a, 2005b; Stuczynski et al., 2007).

ISSUE: Validation of bioaccessibility testing methods that correlate with effects of remediation treatments on human bioavailability of soil Pb is needed.

The effect of soil Pb concentration and soil dose on relative bioavailability to humans needs to be established experimentally rather than assumed to be linear.

SOIL AS BIOAVAILABILITY IN RISK ASSESSMENT

The underlying assumption in quantifying metal intake toxicological evaluation is that all of the As measured by the total metal analysis is related to the absorbed dose. However, there is an inherent problem with the above assumption as the forms of As found in soils and waste produces a wide range of As solubility in contaminated media. Most metal and metalloid sulfides, for example, are less soluble than their respective oxidized compounds; for As, the solubility of As_2S_3 in water is 0.005 g L^{-1}, while the solubility of As_2O_3 is 37 g L^{-1}. These differences may have a significant impact on the dose absorbed from ingestion of contaminated soil. Other elements or soil chemical factors may influence As dissolution and As absorption in the intestine

Recently reviewed *in vivo* models used to measure bioavailable As include juvenile swine, monkey, rabbit, and dog (Ruby et al., 1999; Valberg et al., 1997; Roberts et al., 2002, 2007). In these *in vivo* dosing trials, soil As bioavailability was evaluated by measuring As in urine, blood, feces, and/or storage tissues (bone, skin, nails, hair) of some species. The monkey tests used urine As collection to measure the absorbed dose so that animals are not sacrificed during the tests (Freeman et al., 1995; Roberts et al., 2002). Juvenile swine and monkey are the animal models used most often to obtain site-specific bioavailability of soil As for use in risk assessment at Superfund sites. Both monkey and swine are remarkably similar to humans with respect to their digestive tract, nutritional requirements, bone development, and mineral metabolism (Dodds, 1982). Juvenile swine are commonly used because of several factors, including the economics of husbandry, ease of dose delivery, and the concern of animal rights' groups regarding animal model selection. Young swine are considered to be a good physiological model for gastrointestinal absorption in children (Casteel et al., 1996; Weis and Levelle, 1991). The swine model for bioavailability determinations has gained acceptance as a method to determine

soil Pb RBA at US-EPA (US-EPA, 2007b). However, dosing trials using primates and swine are expensive. Recently, new findings using laboratory mice, a less expensive animal model, for measuring bioavailable As have been reported (Thomas et al., 2007).

FACTORS SHOWN TO AFFECT SOIL AS BIOAVAILABILITY

Co-ingestion of food and contaminated soil has been shown to decrease bioavailable Pb compared to soil ingestion without food to humans (Maddaloni et al., 1998); therefore, fasted conditions are considered conservative estimates of Pb RBA. However, fasted conditions may not be conservative estimates for As RBA because phosphate associated with diets may increase As bioaccessibility and perhaps RBA (Basta et al., 2007a).

ISSUE:

1. Soil As RBA research, using animal models, is needed to (1) obtain less expensive animal models and (2) achieve interspecies RBA comparisons for field soils.
2. Research on the effect of food on As bioavailability and bioaccessibility is needed.

To overcome the difficulty and expense associated with *in vivo* trials, research effort has been directed toward the development of *in vitro* methods to simulate human gastrointestinal conditions. Several of these methods have been reviewed (Oomen et al., 2002; Rodriguez et al., 1999; Ruby et al., 1999). More recent IVG methods for measuring bioaccessible As have been described (Basta et al., 2007a; Lowney et al., 2007). Regardless of the method, bioaccessible As measured by an *in vitro* method must be well correlated with bioavailable As. According to EPA Guidance (USEPA, 2007a): "In the case that a validated *in vitro* method is used to estimate bioavailability, it is recommended that the protocol specified in the methodology be followed for making the extrapolation from *in vitro* data to *in vivo* values. That is, there is no *a priori* assumption that all validated *in vitro* methods must yield results that are identical to *in vivo* values. Rather, it is assumed that a mathematical equation will exist such that the *in vitro* result (entered as input) will yield an estimate of the *in vivo* value (as output)."

At a minimum, the *in vitro* method must be correlated with As RBA measured by an "acceptable" animal model. However, *in vitro* methods that are able to predict bioavailable As, with an estimate of uncertainty, are highly desirable. Because of the cost of animal dosing trials, few studies comparing IVG methods with animal models have been conducted. Basta et al. (2001) and Rodriguez et al. (1999) reported a strong correlation ($r = 0.91$, $P<0.01$) of bioaccessible As measured by the OSU IVG method with As RBA determined by immature swine for 14 contaminated soils (Figure 6). Juhasz et al. (2007) reported a strong correlation ($r = 0.96$, $P<0.01$) of bioaccessible As measured by SBET with RBA As determined using swine for 12 contaminated soils. Lowney et al. (2007) reported correlation between bioaccessible As and RBA As determined using Cynomolgus monkey. Ruby et al. (1996) reported comparison of bioaccessible As measured using PBET with RBA As using rabbit and Cynomolgus monkey for three contaminated soils. Bioaccessible As (i.e., PBET) over-predicted RBA As. The small number of soils prevented a thorough comparison of As-PBET with As-RBA.

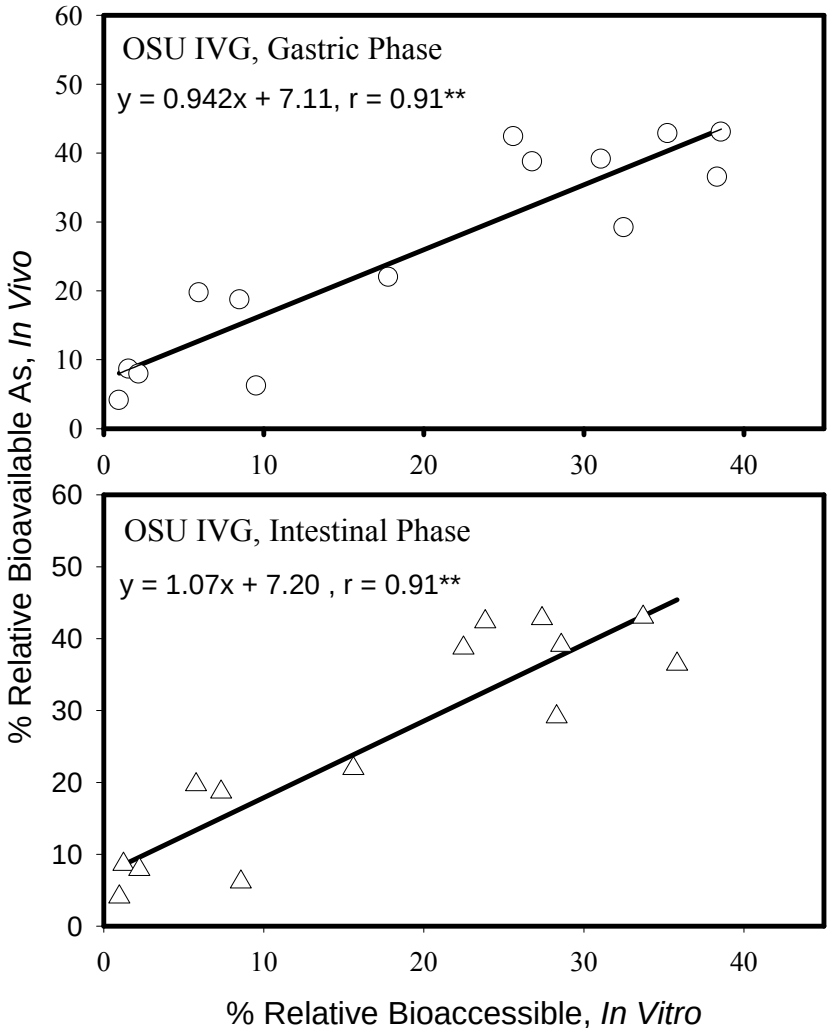

Figure 6. *In Vivo* RBA As versus OSU IVG Relative Bioaccessible As. Data Re-Graphed from Basta et al. (2001).

USEPA (2007a) recommends validation of IVG methods described by the Interagency Coordinating Committee for Validation of Alternative Methods (ICCVAM). ICCVAM's validation criteria for test methods include inter-laboratory and intra-laboratory round robin studies. To our knowledge, round robin studies of IVG methods for As have not been conducted in the United States. Round robin studies should be limited to IVG methods that have been shown to be well correlated with bioavailable As from animal dosing trials.

ISSUE: Round robin studies that evaluate inter-laboratory and intra-laboratory bioaccessible As that have been shown to be predictive of bioavailable As in animal models are needed. Soils with established RBA As should be used in the study including soils treated to reduce As bioavailability.

CHEMICAL FORMS OF AS IN SOILS VERSUS BIOAVAILABILITY/BIOACCESSIBILITY:

Most studies show that As bioavailability in contaminated soil is much lower than the bioavailability of soluble inorganic As (i.e., sodium arsenate) used for assessing risk from As in drinking water (Ruby et al., 1999). Bioavailability of As in contaminated soil relative to sodium arsenate (i.e., relative bioavailability, RBA) ranged from 0 to 98% with a median value of 35.5% for 16 contaminated soils and media fed to rabbits (Ruby et al., 1999), from 4.07 to 42.9% with a median value of 25.5% for 14 contaminated soils and media fed to swine (Basta et al., 2001), and 17% (range 5-31%) with most in the 10-20% range for 14 soils fed to monkeys (Roberts et al., 2007). Most contaminated soils have RBA of <50% showing clearly that As was less bioavailable in soil than when dissolved in water. Addition of soluble Na arsenate to soil gave 95% RBA, while addition of arsenopyrite gave 1% RBA. Ng et al. (1998) fed soils to rats and found low bioavailability which they attributed to the chemical speciation of As in their test soils. Another important finding regarding soil As risk was that dermal absorption of As from soil was negligible, much lower than the default USA-EPA assumption of 3% dermal absorption based on study of solutions (Lowney et al., 2007).

Studies measuring bioaccessible As have been conducted on a limited number of soils and contaminant sources. Soil properties have a great influence on As bioaccessibility (Yang et al., 2002). It is unclear whether these methods can be extrapolated to other soils/contaminant sources. Do IVG bioaccessible As versus *in vivo* RBA As studies have to be conducted for every soil and contaminant source studied? The expense would be huge. A better approach may be to determine the form of arsenic that is bioavailable (i.e., contaminant speciation). Solid phase As species, measured by spectroscopic methods, have been shown to be related to bioavailable As (Basta et al., 2007b). Available pools, measured by traditional soil extraction methods, can also be used to provide information on bioavailable As pools (Rodriguez et al., 2003). However, care must be used when applying these extractions to estimate As chemical speciation of soils or other media (Scheckel et al., 2003).

Knowledge of the relationships between As speciation and As bioavailability could allow extrapolation of IVG methods to new soils with *similar* solid phase As species as the bioavailable arsenic source term.

ISSUE: Research is needed to document the relationship between As speciation, bioaccessibility, and bioavailability. The primate feeding test based on dietary As reaching urine should be considered the best approach for measurement of relative bioavailability.

MODIFICATION OF SOIL AS CHEMICAL FORM TO REDUCE BIOAVAILABILITY/RISK:

Much study has been conducted on the remediation of Pb by using soil amendments to modify the chemical form of Pb and reducing its bioavailability (Hettiarachchi and Pierzynski, 2004; Ryan et al., 2004; Allen et al. 2007). However, studies on the use of soil amendments to reduce As bioavailability or bioaccessibility are limited. Rodriguez et al. (2003) and Yang et al. (2002) reported most arsenic in contaminated soil that was likely associated with amorphous (i.e., reactive) Fe oxide minerals was not bioavailable. Beak et al. (2006) found Fe oxide surfaces in ferrihydrite greatly reduced As bioaccessibility to < 5% relative bioaccessibility. The speciation of As, determined using extended X-ray absorption, fine structure near-edge spectroscopy was determined to be strong binuclear bidentate bonding with the Fe oxide surface. Although the ability of Fe to sorb As(V) from water is well known, little research is available on the ability of Fe and other soil amendments to reduce bioavailable or bioaccessible As in soil.

ISSUE: Although the ability of Fe to sorb As(V) from water is well known, research is needed to evaluate the ability of Fe and other soil amendments to reduce bioavailable or bioaccessible soil As.

Field testing of promising soil remediation treatments followed by feeding to appropriate test species is needed to support adoption of remediation technologies.

ASSESSMENT ACROSS CONTAMINATED SOILS

Cancer risk can be expressed by the following equation: Risk = CDI x SF, where CDI is the chemical daily intake and SF is the cancer slope factor. Non-cancer risk can be calculated as CDI/RfD, where RfD is the reference dose. The effect of contaminant bioavailability from soil ingestion to human receptors can be evaluated by making adjustments to the dose using the following equation: $CDI_{adjusted}$ = CDI x RBA, Alternately, RBA can be used to make site-specific risk adjustments for cancer risk by using the following equation: $SF_{adjusted} = SF_{IRIS}$ x RBA, where SF is the slope factor. Site-specific adjustment for non-cancer risk can be calculated by the following equation: $RfD_{adjusted} = RfD_{IRIS}$ / RBA. However, the usefulness and/or ability to adjust CDI for bioavailability depends on many issues, including (1) the contaminant concentration in the soil and (2) the chemical properties of the soil/geomedia. Because animal models and IVG methods have inherent uncertainty in RBA, CDI adjustments will be less likely used on highly contaminated (>1,000 mg kg^{-1} As) than moderately contaminated soils (<500 mg kg^{-1} As). Often, the highly contaminated area is much less than the moderately contaminated area of soil on a site. Excavation and replacement of the highly contaminated area may be feasible but is less feasible for large areas of moderately contaminated soil. Thus, RBA adjustments are needed for moderately contaminated soils. Cleanup of many sites is often considered at <50 mg kg^{-1} soil As. It may not be possible to obtain RBA values for As using animal models for some moderately contaminated soils that contain < 200 mg kg^{-1} As. Arsenic in urine or blood, used to determine RBA from animal diets in dosing studies may determine the soil As detection limit. A strong advantage of IVG methods is the ability to estimate RBA at very low soil As concentrations

including background levels of <10 mg kg^{-1} As. IVG methods are not limited by background arsenic from food as *in vivo* animal models. However, IVG methods that incorporate a variety of foodstuffs and/or biochemicals that result in high background As in the *in vitro* solution may suffer poor detection limits for As contaminated soil.

Arsenic bioavailability and bioaccessibility are affected by soil type. Sorbent solid phases (i.e., Fe oxides), organic C, and soil pH have been shown to affect bioaccessible As. It is more likely that CDI adjustment for RBA As for soils with properties likely to sequester As and decrease its bioavailability. Soil properties that affect As bioavailability and bioaccessibility to humans should be considered in human risk assessment of contaminated soil.

ISSUE: Research is needed to establish a decision-based framework for site-specific adjustments of CDI for As bioavailability and bioaccessibility based on soil type.

ASSESSMENT FOR REDUCTION IS SOIL AS RBA AT REMEDIATED SITES:

Studies are available that focus on the ability of soil remediation to reduce As solubility and mobility, including plant uptake. However, comprehensive research to evaluate the effect of soil remediation on As bioavailability to animals has not been conducted. Several studies have shown using Fe oxide amendments can reduce As bioaccessibility. Animal dosing trials are needed to confirm the ability of these soil treatments to reduce As bioavailability. IVG methods may be predictive of bioavailable contaminant in untreated soil but not in treated soil. Research is needed to confirm the ability of IVG methods for measuring bioaccessible As are capable of predicting RBA As of remediated soil.

ISSUE: Research is needed to confirm the ability of *in vitro* methods to measure bioaccessible As that are capable of measuring changes in As RBA for remediated soil.

Risk from soil As is complex. It is assumed that soil and dust ingestion by children gives the highest exposures, just as for Pb. In the case of As, actual absorbed doses can be reliably measured by measuring speciated As in urine. Two Superfund sites have had extensive evaluation of urine As in children in relation to As in soil and dust (Hwang et al., 1997; Tsuji et al., 2005). These studies seem to indicate that at least up to 40 mg As kg^{-1}, no significant increase in absorbed dose occurred, and perhaps even up to 100 mg As kg^{-1}. Presently most locations consider that any soil As of 20 mg kg^{-1} or higher require further detailed risk assessment.

But the Soil Screening Level for Superfund is 0.429 mg As kg^{-1} based on the cancer slope factor and assumptions about soil ingestion and 100% bioavailability of the ingested soil As. One newer aspect of the US-EPA estimate is a further assumption that dietary inorganic As has a 10-fold higher slope factor for children than adults, In light of the low As bioavailability seen in relatively low As concentration soils fed to monkeys and swine, some reconsideration of this risk may be appropriate (adjust soil dose assumption and soil As bioavailability assumption). It seems remarkable that anyone would suggest a lower Soil Screening Level for As than occurs in background uncontaminated soils. As reported by Smith et al. (2005), a recent U.S. Geological

Survey sampling of 254 soils in two transcontinental transects of North America yielded a soil As mean±S.D. = 5.74±2.96 mg kg^{-1}, geometric mean 4.94 mg kg^{-1}, and 5th-95th percentile range of 2-12 mg As kg^{-1}.

ISSUE: From the above discussions on risks of Pb and As from direct soil ingestion, it is apparent that many ways to measure bioavailability and bioaccessibility exist, but there are inadequate comparisons between the two measures or, for that matter, within either of the measurements to support policy changes. Further understanding for why two samples provide different RBA is often lacking because definitive characterization of the matrix to allow more than speculative conclusions has not been done. These concerns can only be resolved by obtaining results for all tests (bioavailability, bioaccessibility, chemical speciation, soil characterization) on the same matrix. A number of different matrix samples must be included in order to better understand the variability that occurs in order to support policy change in risk assessment and remediation decisions.

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Bioavailability of Chemicals in Sediments and Soils: Toxicological and Chemical Interactions

Dominic M. Di Toro

Edward C. Davis Professor of Civil and Environmental Engineering
Department of Civil and Environmental Engineering
University of Delaware
Newark, DE

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I. INTRODUCTION AND BACKGROUND

It has been found experimentally that the toxicity of chemicals in sediments and soils is highly variable. The same chemical tested using the same organism will exhibit quite different toxicity in different sediments or soils depending on the chemical state of the toxicant in that sediment or soil. Fig.1 presents two examples of dose response curves for kepone and cadmium tested in three different sediments. The LC50s differ by more than an order of magnitude. This variation is attributed to the differing bioavailability of the chemical in each of the sediments.

Field collected sediments also exhibit this effect. The total concentration of a chemical in units of weight of chemical/unit weight of dry sediment or soil, e.g., mg chemical/kg dry wt., correlates only weakly with the observed toxicity of that chemical. An example is shown in Fig. 2 for total PAH concentrations in various sediments for both laboratory-spiked and field-collected sediments. The situation is much worse for metals in sediments, as shown subsequently.

II. SUMMARY OF TECHNICAL FINDINGS AND ISSUES

BIOAVAILABILITY AND THE FREE METAL CONCENTRATION

The toxicity of metals in water only exposures was initially understood using the Free Metal Ion Activity Model (FIAM) (Campbell, 1995; Sunda and Guillard, 1976; Sunda et al., 1978). Fig. 3 presents the original data supporting the hypothesis. Algal growth was measured at varying copper concentrations with differing concentrations of a complexing ligand (Tris) and pHs. Whereas the toxicity of copper to algal growth is only weakly related to the total copper concentration (top)—note the two circled data at the same total Cu with markedly differing toxicity—the data collapses to a single dose response curve as a function of divalent Cu (or as it is called, the "free" copper) concentration. Actually the divalent copper ion activity is used, which is the concentration corrected for ionic strength. The FIAM and its organic chemical analog—that toxicity is due to only the uncomplexed fraction of the total dissolved chemical—is the basis for understanding the effects of aqueous phase chemistry on the toxicity of dissolved chemicals.

The most recent generalization of this model—the Biotic Ligand Model (BLM) —accounts for competition of major cations and protons for binding at the site of action, the biotic ligand (Di Toro et al., 2001; Santore et al., 2001). Fig. 4 presents the model schematic. The LC50 occurs when the concentration of metal bound to the biotic ligand exceeds the critical body burden for that metal and organism. The metal cation (M^{2+}) competes with other cations (Ca^{2+}, Na^{+}, …) and protons for biotic ligand binding sites. This is the mechanism that accounts for hardness cations affecting toxicity (Pagenkopf, 1983). In addition, the metal cation complexes to inorganic anions (OH^{-}, HCO^{3-}…) and dissolved organic carbon (DOC). These latter reactions account for toxicity variations due to changes in alkalinity, pH, and organic matter. Hence the BLM accounts for the varying bioavailability of metals as a function of varying water chemistry. Fig. 4 (right) presents comparisons of BLM predictions and observations for Cu and Zn toxicity to *Daphnia magna*.

The observed LC50s span two (Zn) to three (Cu) orders of magnitude, which is the extent to which bioavailability affects metal toxicity. The BLM predictions are, for the most part, within a factor of two (the dashed lines). This is the extent to which bioavailability is understood in aqueous exposures.

The BLM has been the subject of intensive research by many groups, e.g. (De Schamphelaere et al., 2002; De Schamphelaere and Janssen, 2002; Heijerick et al., 2005; Keithly et al., 2004; Playle, 2004; SETAC, 2007). It is publically available (HydroQual, 2002). It has been accepted by the USEPA for application to metal water quality criteria. The freshwater copper criteria uses the BLM as the basis for determining the criteria concentrations as a function of the water chemistry parameters (USEPA, 2007). Its application to sediments and soils is discussed subsequently.

BIOAVAILABILITY IN SEDIMENTS – THE EQUILIBRIUM PARTITIONING MODEL (EQP)

The presence of particles in sediments complicates the chemistry and also the exposure routes by which chemicals can interact with the benthic biota. This complicates the situation and gives rise to the varying toxicity exhibited by different sediments (Fig. 1). The Equilibrium Partitioning (EqP) model of sediment toxicity is an attempt to solve this problem. The method was first suggested by Pavlou and Weston (1983). The first critical data set that demonstrated the principle was presented by Adams et al. (1985). A systematic presentation of the EqP model for nonionic hydrophobic chemicals, with larger and more diverse sets of supporting data, was presented subsequently by Di Toro et al. (1991).

Fig. 5 presents the initial data. The dose-response curves for kepone toxicity to *C. tentans* are different for the three sediments tested (Fig. 5 left). However, the dose-responses collapse to a single curve when toxicity is compared to the pore water kepone concentrations (Fig. 5 right). In addition, the LC50 based on pore water concentration is essentially equal to that found in exposures of *C. tentans* to kepone in water only tests, i.e., tests conducted without sediment present. This remarkable finding spurred a concerted effort to test whether this was a generally applicable result. Fig. 6 presents the results of tests for six chemicals using three sediments each, Mortality is plotted versus the ratio of pore water concentration to independently determined water-only LC50. The EqP prediction is that 50% mortality should occur at a ratio = 1. The experimental results are within approximately a factor or two of the predictions. Fig. 7 presents the results for Cd toxicity to *Amplescia abdita*. The pore water Cd^{2+} activity was measured with a specific ion electrode and compared to water-only data (Fig. 6 right). Sediment copper toxicity was also tested (Ankley et al., 1993) with similar results.

The EqP model schematic is presented in Fig. 8. Toxicity predictions are derived from effects concentrations measured in water-only exposures (Fig. 8 left). In sediment exposures, the effect is predicted to occur at the same concentration or, more precisely, at the same chemical activity or fugacity in the pore water of the sediment. The equivalent sediment concentrations are derived from partitioning theory applied to the pore water-sediment particle system, which is assumed to be at equilibrium, hence the name "Equilibrium Partitioning," or EqP. Note that the organisms

are not assumed to be at equilibrium—the arrows to the biota are one way. Only the pore water and sediment particles are assumed to be at equilibrium. Further it is assumed that the exposure from both pore water and sediment ingestion is equivalent. The reason is that the chemical activity of the pore water-sediment particle system is the same at equilibrium, and therefore exposure from either or both media exerts the same "chemical pressure" or fugacity on the organism. An issue with deposit feeding organisms is whether conditions in the gut of the organism modify the chemistry sufficiently so that ingested sediment cannot be assumed to be in equilibrium with pore water. This issue can only be addressed by examining the experimental data presented below.

The prediction of the sediment concentration that causes toxicity is based on a partitioning model that relates the toxic pore water concentration to the equivalent sediment concentration. In the EqP model, the observed variation in sediment toxicity is ascribed to the variations in the partitioning between pore water and sediment particles. For nonionic hydrophobic organic chemicals, the partitioning is assumed to be to sediment organic carbon. Fig. 9 presents the same data as Fig. 8. However, in Fig. 9 the pore water concentration, C_W, is predicted from the measured sediment concentration, C_S, using the partitioning equation

$$C_S = f_{OC} K_{OC} C_W \tag{1}$$

where f_{OC} is the fraction organic carbon of the sediment, and K_{OC} is the partition coefficient to organic carbon, which is computed from the octanol-water partition coefficient of the chemical. The predicted LC50s are more scattered than in Fig. 8 since the uncertainty in the partitioning model adds to that of EqP. The predicted results are roughly within a factor of three of observations (Fig. 10).

METAL BIOAVAILABILITY IN SEDIMENTS—SEM-AVS

The EqP model requires a prediction of the pore water concentration based on the measured sediment concentration. This requires a partitioning model that applies to the class of chemicals being considered. For nonionic hydrophobic organic chemicals, a model that considers only partitioning to organic carbon has been found to be reasonably satisfactory. For metals, however, there is a much stronger binding phase in sediments that must first be taken into account.

Anoxic sediments contain amorphous iron monosulfides (FeS) that can react rapidly with metal cations M^{2+} and form insoluble metal sulfides (MS)

$$M^{2+} + FeS \rightarrow MS + Fe^{2+} \tag{2}$$

Thus the quantity of FeS is a critical component of sediments that greatly affects metal bioavailability (Di Toro et al., 1990). The amorphous iron sulfide is measured as acid volatile sulfide (AVS). The metal in sediments that is potentially bioavailable is measured in the same extract as is used to extract the AVS and called simultaneously extracted metal (SEM) (Allen et al., 1993; Di Toro et al., 1992). There are two reasons for this procedure. Certain metal sulfides

(e.g. CuS) are not very soluble in the AVS extraction. Therefore it is assumed that these insoluble metal sulfides are not bioavailable. The AVS extraction extracts the metals associated with the fraction of the MS that dissolves. This is the fraction for which the sulfide is also extracted. Additionally SEM extracts the metal that is sorbed to various other sediment phases.

If the SEM is less than or equal to the AVS, then all the extracted metal is present as MS, and the pore water activity of M^{2+} is very low due to the insolubility of MS. Therefore, no toxicity would be predicted. Fig. 11 presents a compilation of data from multiple investigations that compare percent mortality (top) and presence or absence of chronic effects (bottom) versus SEM – AVS. For the cases for which SEM < AVS, no mortality or chronic effects have been reported. The data include laboratory spiked sediment, field collected sediments tested in the laboratory, and field experiments using in situ colonization tests. Both epibenthic and benthic organism with various feeding modes, including deposit feeding organisms, have been tested. These results conclusively demonstrate that if AVS exceeds SEM, no toxicity is expected. However, if SEM exceeds AVS, then toxicity may or may not occur.

The SEM – AVS method considers only AVS as a metal binding phase. However, it is known that metals bind to organic carbon. If the excess SEM_x = SEM – AVS is assumed to be bound only to organic carbon, then the partitioning equation would be

$$SEM - AVS = K_{POC}\, f_{OC}\, [M^{2+}] \tag{3}$$

where K_{POC} would be the partition coefficient of the metal to particulate organic carbon. The proper normalization of the sediment concentration would be

$$(SEM - AVS) / f_{OC} = K_{POC}\, [M^{2+}] \tag{4}$$

It might be expected that toxicity would correlate to organic carbon normalized excess SEM ($SEM_{x,OC}$ = (SEM – AVS) / f_{OC}). The data in Fig. 12 demonstrates that this is indeed the case. There appears to be a boundary between toxic and non-toxic sediments at $SEM_{x,OC}$ = 100 umol/gOC.

This result motivated a more quantitative although still preliminary investigation of a model that combines AVS and organic carbon as partitioning phases (Di Toro et al., 2005b). It uses the BLM and the WHAM V speciation model to determine the partitioning to particulate organic carbon. The schematic is shown in Fig. 13. Sediment organic carbon is modeled as humic acid. The predictions (Fig. 14) are made using the critical body burdens for *D. magna.* The vertical lines are pH = 6 to 9. The data are for amphipod toxicity tests. There is better than order of magnitude agreement between the predictions and observations. This application is meant only to demonstrate the feasibility of developing a sediment BLM. It would be useful for sediments where the AVS concentration is low and the toxicity is controlled by partitioning to other phases.

METAL BIOAVAILABILITY IN SOILS—THE TBLM

For metal partitioning to soils, organic matter is the primary partitioning phase for soils with organic matter greater than approximately one percent. The development of a terrestrial BLM (TBLM) is based on the schematic in Fig. 15. WHAM VI is used for the partition calculations (Tipping, 1998). Soil organic matter is modeled as humic acid. The activities of Fe and Al cations, which are strong competing cations, are determined by assuming equilibrium with $Fe(OH)_3$ and $Al(OH)_3$.

The TBLM has been applied to various toxicity tests conducted using seven non-calcium-containing soils (Thakali et al., 2006a; Thakali et al., 2006b). The dose response curves for barley root elongation as the test endpoint are shown in Fig. 16. There is over an order of magnitude variation in EC50 based on total Ni concentration (Fig 16. left), whereas the dose response based on the fraction of the biotic ligand sites occupied collapse to a single curve (Fig. 16 right). Predicted versus observed EC50 for Cu and Ni for the various endpoints are shown in Fig. 17. The dashed lines represent factors of two uncertainty bounds. Essentially all the Ni data and almost all Cu data are within these bounds.

MIXTURE TOXICITY

The evaluation of risk associated with contaminated sediments and soils from field settings usually requires that mixtures of toxicants be evaluated. The appropriate model for assessing the toxicity of mixtures depends on the individual chemicals' modes of action. For chemicals with similar modes of actions, the toxic unit model of additive toxicity is appropriate. A toxic unit TU_X is defined as (Sprague and Ramsay, 1965)

$$TU_X = C_X/LC50_X \tag{5}$$

where C_X is the concentration and $LC50_X$ is the LC50 concentration in the same medium: X = W for water and X = S for sediment. The toxic unit concentration of the mixture is found by addition of toxic units

$$TU = \sum_j TU_{X,j} = \sum_j C_{X,j}/LC50_{X,j} \tag{6}$$

The most studied class of compounds for which additivity has been found are the narcotic chemicals (Hermens, 1989). Fig. 18 presents the results of a number of mixture toxicity experiments using aqueous exposures. The number of chemicals tested in the mixture is presented as well as the observed toxic unit concentration. The predicted TU = 1 for a 50% effect. The mixtures are made up of equally toxic fractions ($TU_{W,j}/N$) of each of the N chemicals using the measured individual chemical $LC50_{W,j}$'s. The results (Fig. 18) support the use of the additive toxic unit model for the classes of chemicals tested.

TOXICITY MODELS—APPLICATION TO MIXTURES IN WATER COLUM AND SEDIMENT EXPOSURES

The use of the toxic unit model requires measurements or estimates of the LC50 for all chemicals in the mixture. For complex mixtures with many chemicals, e.g. PAHs, the experimental data are not available and estimates are required. Quantitative structure activity relationship (QSAR) models have been developed for this purpose for narcotic chemicals (McCarty, 1986; Veith et al., 1983). The critical body burden $C^*_{L,j}$ is used to determine the $LC50_{i,j}$.

$$C^*_{L,j} = K_{LW\ i,j}\ LC50_{i,j} \tag{7}$$

where $K_{LW\ i,j}$ is the lipid-water partition coefficient for the ith chemical and j^{th} species. The octanol-water partition coefficient is used to estimate the lipid-water partition coefficient

$$K_{LW} = a_0 + a_1\ K_{OW} \tag{8}$$

The critical assumption for these models is that the critical body burden (umol/g lipid) is the same for all narcotic chemicals, i.e. $C^*_{L,j}$ is not a function of i. A recently developed model (the Target Lipid Model -- TLM) (Di Toro and McGrath, 2000; Di Toro et al., 2000) makes the further assumption that the lipid-water partition coefficient $K_{LW\ i,j}$ (Eq 8) is the same for all organisms so that $K_{LW\ i,j} = K_{LW,i}$, and is a function of only the chemical via K_{OW}. Thus the coefficients in Eq 8 are universal. They are determined from the entire set of narcotic toxicity data, together with the organism-specific critical body burdens $C^*_{L,j}$ The model can be applied to organisms for which only a few chemicals have been tested since the parameters for $K_{LW,i}$ are globally estimated (Eq 8) and the LC50 measurements are used to determine the critical body burden $C^*_{L,j}$. The model has been applied to a large set of narcotic chemicals, including PAHs. Comparisons to single PAH toxicity experiments in water column and sediment exposures are shown in Fig. 19. The uncertainty is approximately a factor of three.

This model can be used to predict the results of mixture experiments (McGrath et al., 2005). The results for a series of gasolines are shown in Fig. 20. There is at least an order of magnitude variation in toxicity for various gasolines if the total concentration of hydrocarbons is used to quantify the exposure (Fig. 20 left). The results using the toxic unit model, for which the individual LC50s are predicted using the target lipid model (Fig. 20 right) are more consistent.

The application to sediments uses EqP to quantify the toxic unit concentrations of the components of the mixture.

$$TU_{S,j} = C_{S,j}/C^*_{S,j} \tag{9}$$

where $C^*_{S,j}$ is the sediment LC50 concentration. It is computed from the EqP relation

$$C^*_{S,j} = f_{OC}\ K_{OC}\ LC50_{W,j} \tag{10}$$

where $LC50_{W,j}$ is the LC50 for water column exposure predicted from the target lipid model. The results are shown in Fig. 21 for a laboratory spiked sediment experiment (left) and for field collected sediments from an oil spill (right).

TOXICITY MODELS—APPLICATION TO POLAR COMPOUNDS

Recently we have proposed the polyparameter TLM (pp-TLM) (Kipka and Di Toro, 2008) that replaces octanol as the basis for estimating log K_{LW} with a polyparameter estimation equation. The motivation is to predict the toxicity of more polar organic chemicals, the type II narcotic chemicals, as well as the type I narcotics and PAHs. The target lipid-water partition coefficient is estimated using a polyparameter linear free energy relationship (LFER). The LFER was first presented in its current form for general solvent partitioning in 1991 (Abraham et al., 1991). It has been used to predict air-water partitioning of a number of solutes in various solvents (Satoshi and Schmidt, 2006), tadpole narcosis (Abraham and Rafols, 1995), partitioning of contaminants from water into organic matter (Nguyen et al., 2005), and predicting LC50s for specific organisms (Hoover et al., 2005).

In the pp-TLM, polyparameter LFER is used to estimate solute partitioning between target lipid and water. The partition coefficient, log K_{LW}, is represented as a sum of solvent (lower case)- and solute (upper case)-specific variables.

$$\log K_{LW} = c + eE + sS + aA + bB + vV \tag{11}$$

The parameters E, S, A, B, and V are a set of solute descriptors that represent the effect of the solute properties on the solute-solvent interactions. The corresponding parameters e, s, a, b and v are coefficients representing the solvent influences. The parameter c carries the units of log K_{LW}. For the solute descriptors E is the excess molar refractivity of the solute, and S represents the (di)polarizability. Hydrogen bond formation is parameterized by A, the hydrogen bond acidity, the ability to donate a hydrogen bond, and B, the hydrogen bond basicity, the ability to accept a hydrogen bond. V is the molar volume of the solute. These parameters completely characterize the solute. The solvent descriptors parallel the solute descriptors and represent the solvent-water differences: e = the ability to polarize the solute; s = interaction through dipole-dipole and induced dipole forces; a and b = accepting or donating a hydrogen bond from the solute; and v = cavity formation energy for accommodating the solute.

The solute parameters are either available experimentally (Abraham et al., 1994) or can be estimated (Pharma Algorithms, 2006). The solvent parameters are estimated from toxicity data together with the critical body burdens, as in the original TLM. The predicted versus observed LC50s for the original TLM (Eq 8) are shown in Fig. 22 (left). When the type II polar compounds are included as well, the results are less satisfactory (Fig. 22 right). If the polyparameter QSAR is used (Eq 11) the results are much improved (Fig. 23). The prediction errors are similar for type I and type II chemicals (log LC50 RMSE = 0.449 and 0.501).

The pp-TLM is a significant improvement since it is applicable to a much broader class of compounds. In particular, for the explosives RDX, HMX, and TNT, two of the four descriptors

(E and V) are within the range of values found for nonpolar chemicals, but S and B are outside the range. They strongly accept hydrogen bonds (B) and are strongly polarized (S). We would expect that estimates of environmental parameters for these chemicals that are based on K_{OW}, e.g. K_{OC}, would not be reliable.

BIOAVAILABILITY AND TOXICITY PREDICTIONS IN SOILS

There are, at present, no predictive models for estimating bioavailability and toxicity of organic chemicals to a wide range of soils. It is likely, however, that the same methods that have proven successful in developing models for sediments (EqP and TLM) can be applied to soil toxicity data. Fig. 24 presents a very preliminary test of this hypothesis. The soil toxicity data are observed EC10 concentrations for four PAHs and three organisms in a single test soil. The predictions are based on the soil organic carbon and the average log K_{OW}s of the chemicals. They are compared to the chronic sediment HC5—the concentration that is chronically protective of the lower 5th percentile of the species distribution (McGrath et al., 2005). It is expected that the HC5 should be below the observed endpoints for individual organisms, as is the case (Fig. 24). This encouraging result suggests that applying the EqP and TLM methodology will produce useful models for chemical bioavailability and toxicity in soils.

RELATIONSHIP OF EQP AND EMPIRICAL SEDIMENT QUALITY GUIDELINES (SQG)—FIELD CONTAMINATED SEDIMENTS[19]

It should be pointed out that EqP-based predictions for field-contaminated sediments are bound to fail if the cause of toxicity is not among the measured chemicals. This can be the case in situations where many chemicals are present and only a few are quantified, for example, in oil-contaminated sediment where only 13 PAHs are measured. Additionally, the partitioning theory can fail. The EqP model requires a partition coefficient to predict the sediment concentration corresponding to the toxic concentrations established in water-only exposures (Eq 1). The presence of significant quantities of unusual partitioning phases (Luthy et al., 1997), e.g., soot or wood particles that are not properly taken into account, would invalidate the predictions. However, the data presented above suggests that these are relatively rare occurrences and for the many sediment samples employed in laboratory-spiked experiments and for the field-collected sediments that are heavily contaminated, the EqP predictions are consistently within the error bounds presented above. The exception to this appears to be the results from the large data sets for which the EqP SQGs are overprotective in approximately 50% of the cases (O'Connor, 2002).

One final comment on the relationship between mechanistic and empirical SQGs is worth mentioning. The use of mechanistically based SQGs derived from the EqP method is warranted for situations in which the chemical cause of the toxicity is in question, i.e.: What is the

[19] This section is reproduced from Di Toro D. M., Berry W. J., Burgess R. M., Mount D. R., O'Connor T. P., and Swartz R. C. (2005a) The Predictive Ability of Sediment Quality Guidelines Derived Using Equilibrium Partitioning. In *Use of Sediment Quality Guidelines and Related Tools for the Assessment of Contaminated Sediments* (ed. R. J. Wenning and C. G. Ingersoll). SETAC Press.

concentration C of chemical X in sediment Y that will cause an adverse effect to organism Z? The empirical SQGs do not answer that question. Rather they make a probability estimate of whether a field collected sediment with concentrations C's of chemicals X's will cause an adverse effect to organism Z (Field et al., 2002; Long et al., 1998). That is, they would predict that there is a P% chance that that particular sediment will cause an adverse effect if tested. But the identity of the chemical or chemicals causing the adverse effect is unknown. In fact, it may be an unmeasured chemical that covaries with the measured chemicals. Thus the two methods are complimentary. Mechanistic EqP SQGs seek to establish cause and effect using partitioning models. Empirical SQGs seek to make predictions based on empirical correlations. Each has its uses, and each has its limitations. Perhaps the most useful outcome of the Pellston Conference devoted to this topic (Wenning et al., 2005) was this clarification, and the resulting cessation of hostilities between the proponents of mechanistic and empirical SQGs.

III. FUTURE RESEARCH ISSUES

Research areas can be usefully divided into those applying to soils or sediments. Further divisions by chemical classes are also useful. One general requirement follows from application of EqP to either soils or sediments. A partitioning model is required for the sediment/soil and chemical/chemical class being considered. Also a mixture toxicity model is required for evaluating sites with multiple chemical contamination. The state of the science for partitioning and toxicity models is presented in Table I. Soils and sediments are divided into those for which organic carbon is the primary binding phase (f_{OC} > 1%) and those for which other binding phases, e.g. metal oxides, are important (f_{OC} < 1%). One percent is an order of magnitude estimate of the dividing line.

PARTITIONING MODELS

For low organic matter soils and sediment, there are virtually no available models for organic chemicals with general applicability. For metals there is a framework for soils—WHAM VI (Tipping, 1998)—that can address partitioning but not precipitation. For high organic matter soils and sediments, there are partitioning model of various sorts for nonpolar organic chemicals and, in soils, for metals. The more advanced models consider kinetics as well as equilibrium (Delle Site, 2001). For polar organics, the polyparameter models are a framework that has been applied to K_{OC} (Nguyen et al., 2005). For ionic and metallo-organics, there are no models available.

TOXICITY MODELS

For single chemicals, toxicity models exits for non-polar and polar narcotic organics and certain metals. No generally applicable models are available for ionic and metallo-organics. For mixtures, the toxic unit model for nonpolar narcotics is likely applicable to polar narcotics as is using the pp-TLM as discussed above (Kipka and Di Toro, 2008). The BLM and the TBLM are probably applicable to metals that bind to the same biotic ligand (Playle, 2004).

REGULATORY ACCEPTANCE

The use of bioavailability models for risk assessment and in regulatory practice has proceeded with the development of scientifically sound methods. The most expeditious path to regulatory approval is to proceed jointly with the agency involved. The EqP model was developed in cooperation with personal from the EPA Criteria and Standards Division and the EPA Research Laboratories. Of critical importance during this process were reviews by the EPA Science Advisory Board (e.g., USEPA, 1992, 1994). The methods were published in the peer reviewed literature (Di Toro et al., 1991) and later as EPA reports (USEPA, 2003a, 2003b, 2003c, 2005, 2006). The most prominent application is the recently issued "Aquatic Life Ambient Freshwater Quality Criteria - Copper. 2007 Revision," which uses the biotic ligand model to compute the criteria for the appropriate water chemistry (USEPA, 2007). The acceptance of these methods in Europe has also been proceeding. The technical guidelines for chemical risk assessment (EU, 1996, 2003) support the use of EqP as the basis for evaluating toxicity in sediments.

However, this is not the case for soils. There are no criteria for soils in regulatory use that correct for bioavailability. The TBLM has been developed for this purpose but it is yet to be incorporated into regulatory practice.

It should be noted that the use of sediment quality guidelines that are not corrected for bioavailability, e.g., ERLs and ERMs (Long et al., 1995; Long and Morgan, 1991) or TELs and PELs (MacDonald et al., 1996) and various other similar SQGs (MacDonald et al., 2000) is still prevalent. However, it is generally agreed that these empirical SQGs cannot be used by themselves to establish the chemicals causing the toxicity. Mechanistic SQGs are the only appropriate choice (Wenning et al., 2005).

IV. CONCLUSIONS

The use of bioavailability and toxicity models to assess ecological risk in sediments is well established, both as sound science and as regulatory practice. However, the equivalent models for soils have either not yet, or only recently, been developed. The application of bioavailability and toxicity models to soils would greatly improve the risk assessment at DoD facilities. It is a fertile area for future research and development.

Table I. State of the Science.

Partitioning Model				
	Soils		Sediments	
	foc > 1%	foc < 1%	foc > 1%	foc < 1%
Nonpolar organic	Y	N	Y	N
Polar organic	?	N	?	N
Ionic organic	N	N	N	N
Organo-metallic	N	N	N	N
Metals	Y	?	?	N

Toxicity Model				
	Single Chemical		**Mixtures**	
Nonpolar organic	Y		Y	
Polar organic	Y		?	
Ionic organic	?		N	
Organo-metallic	?		N	
Metals	Y		?	

Y = Well developed, ? = Framework exists, N = Neither

FIGURES

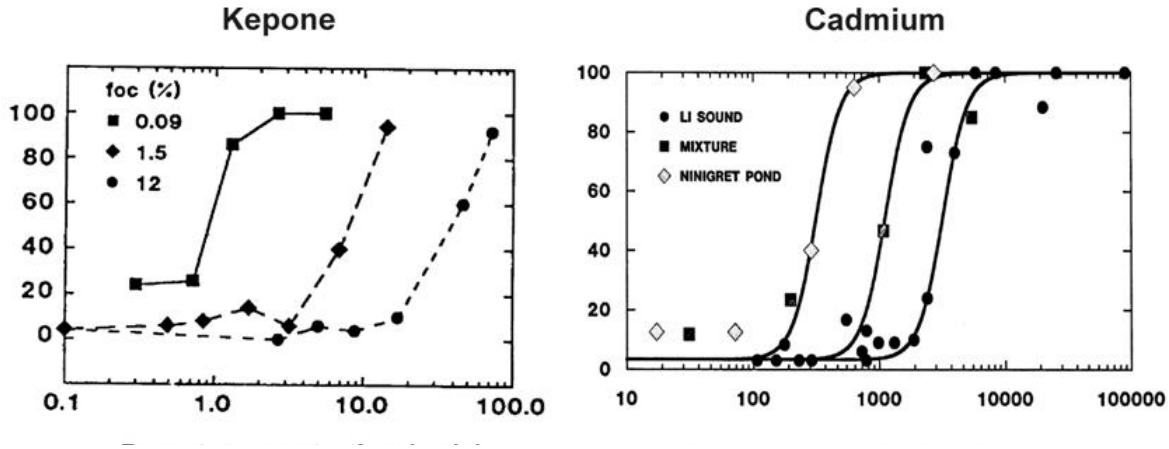


Figure 1. Organism Mortality (%) Versus Sediment Concentrations (mg/kg dry wt of sediment) for Three Sediments: (Di Toro et al., 1990; Di Toro et al., 1991)

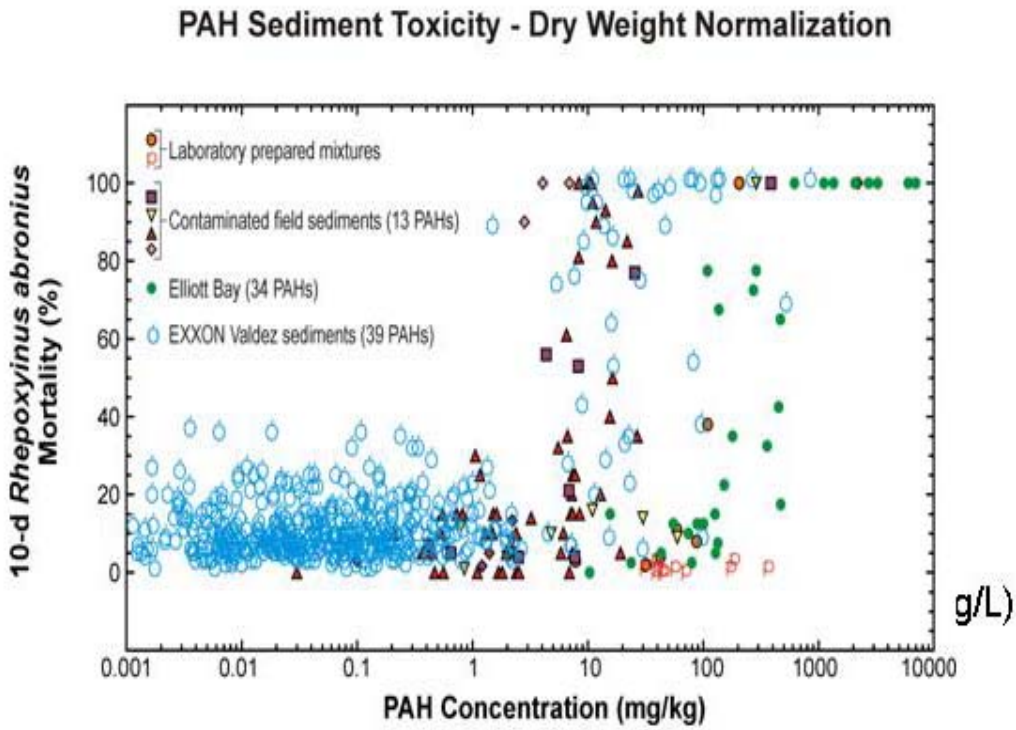
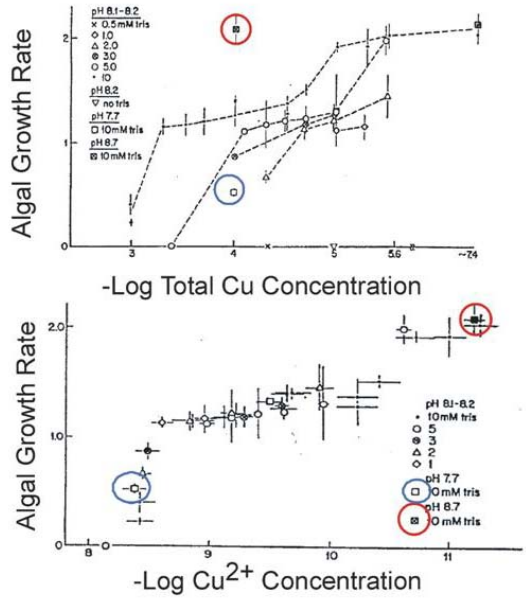


Figure 2. Percent Mortality versus Total PAH in Sediments (McGrath and Di Toro, 2006)



Sunda, W., & Guillard, R. R. L. (1976).J. Mar. Res., 34, 511-529.

Figure 3. Variation in Algal Growth Rate (divisions/day) Versus Total Cu Concentration (top) and Divalent Copper Concentration (bottom) (Sunda and Guillard, 1976)

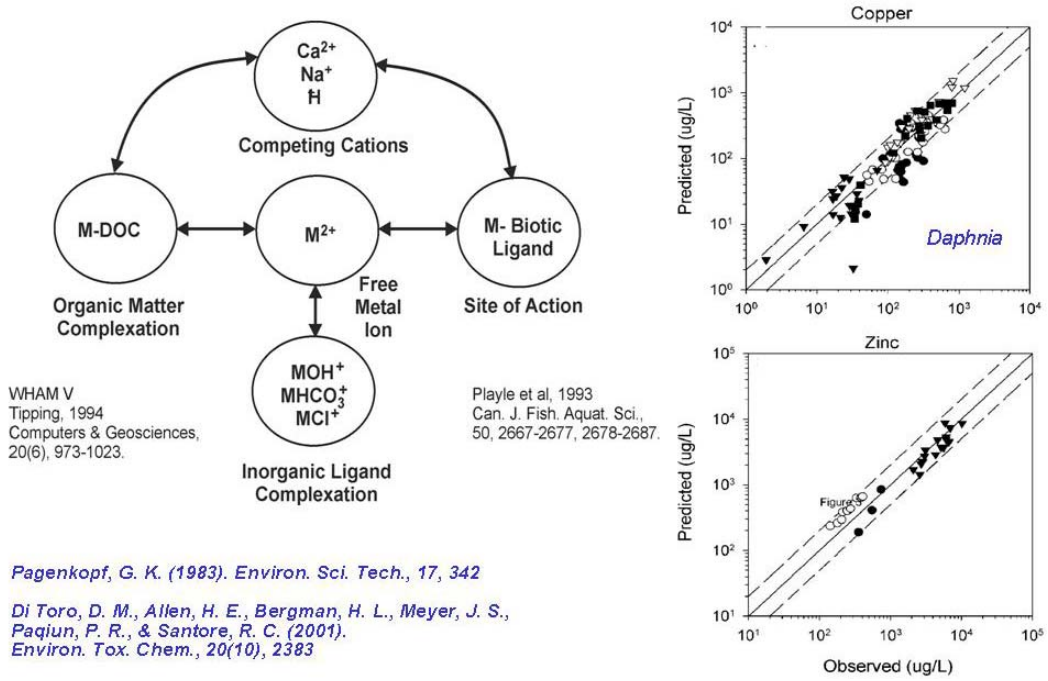


Figure 4. Schematic of the Biotic Ligand Model (left) (Di Toro et al., 2001; Santore et al., 2001). Application of the BLM to *D. magna* for Cu and Zn (right) (Di Toro et al., 2005b).

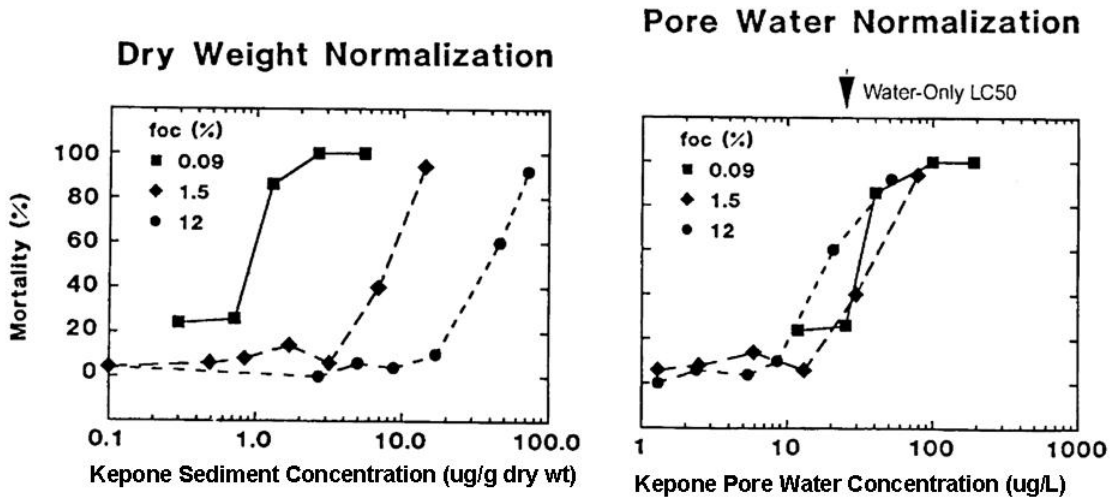


Figure 5 Toxicity of Kepone to *C. tentans* in Three Sediments with f_{OC} as Indicated (left). Same Data Versus Pore Water Concentrations (right). Water Only LC50 Also Indicated (right) (Adams et al., 1985; Di Toro et al., 1991)

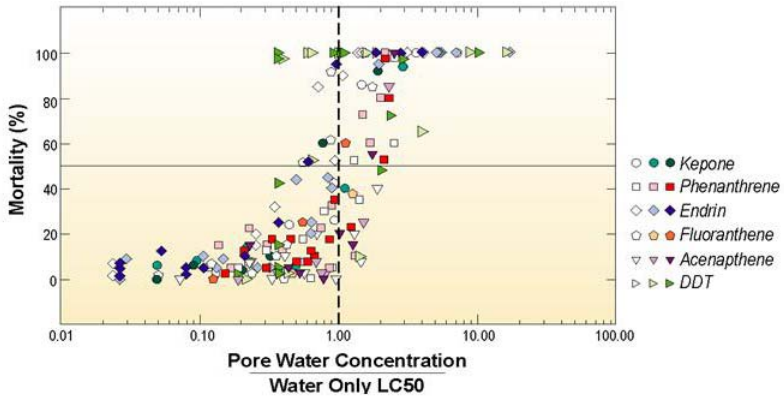


Figure 6. EqP Validation. Organism Mortality Versus the Ratio of Pore Water Concentration to Independently Determined LC50 in Water Only Exposures. EqP Prediction is that 50% Mortality Should Occur at a Ratio = 1. Data from USEPA, 2000

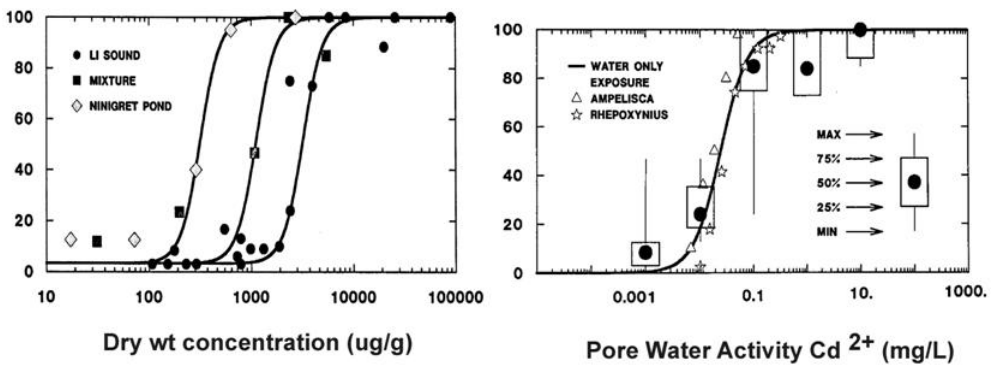


Figure 7. Organism Mortality (%) Versus Sediment Cadmium Concentration on a Dry Wt Basis (left) for Three Sediments. Organism Mortality (%) Versus Pore Water Cadmium Activity for the Same Three Sediments and for Water Only Exposures (right) (Di Toro et al., 1990).

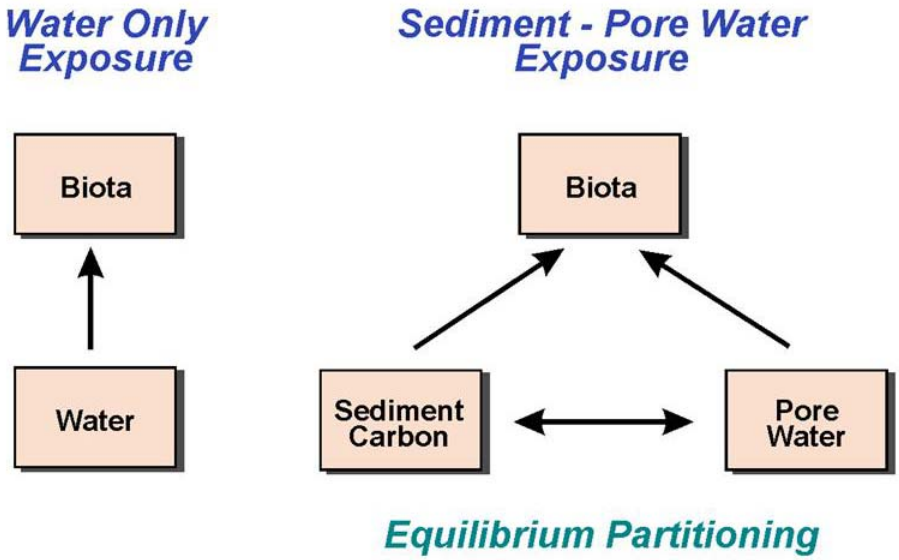


Figure 8. Schematic of the Equilibrium Partitioning (EqP) Model (Di Toro et al., 1991).

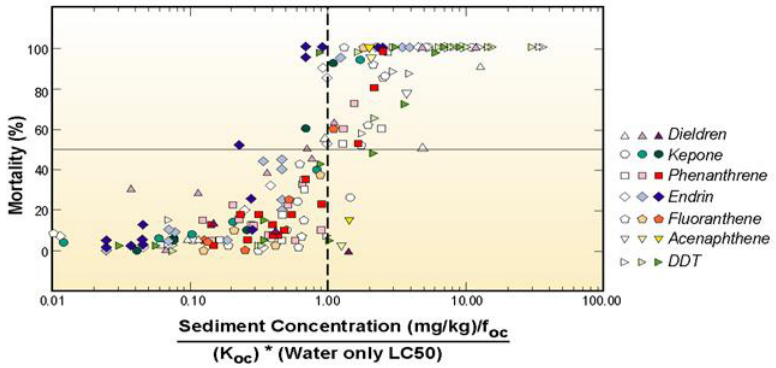


Figure 9. Predicting Organism Mortality Using EqP and the Organic Carbon Partitioning Model. Mortality (%) Versus Ratio of Predicted Pore Water Concentration (Eq 1) to Measured Water Only LC50 (USEPA, 2000).

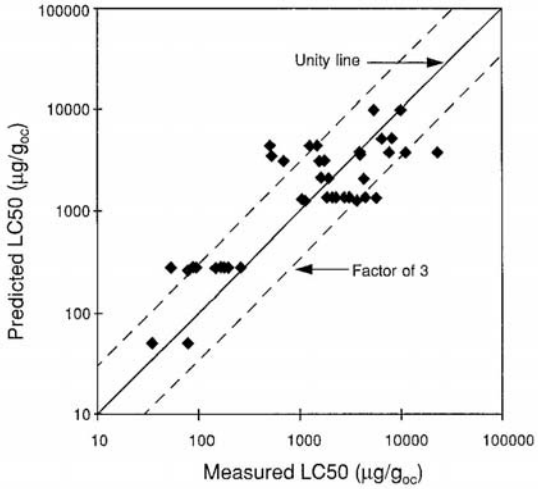


Figure 10. Predicted Versus Observed LC50s Using EqP. Data from Ankley et al., 1996.

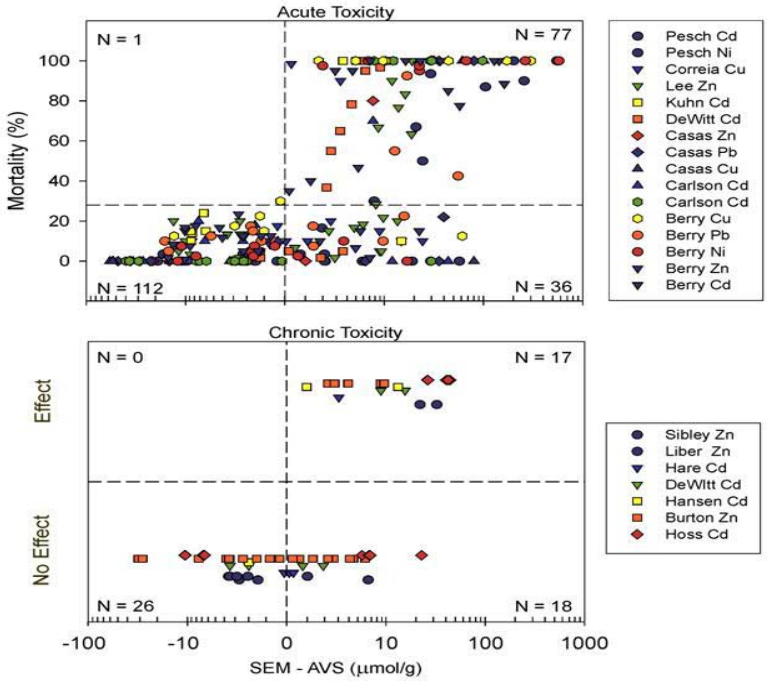


Figure 11. Validation of the SEM-AVS Model of Metal Toxicity in Sediments—Mortality (top) and Chronic Effects (bottom). For Chronic Effects, the Points are Jittered for Clarity of Display. Each Point Represents Either an Observed Effect or No Effect (Di Toro et al., 2005b)

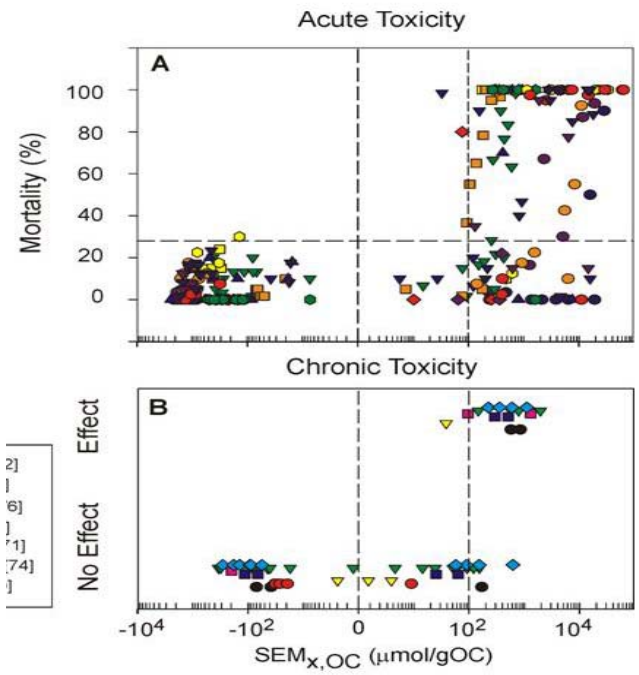


Figure 12. The Data in Fig. 11 Versus Organic Carbon Normalized Excess $SEM_{X,OC}$ = (SEM – AVS) / f_{OC} (Eq. 4) (Di Toro et al., 2005b)

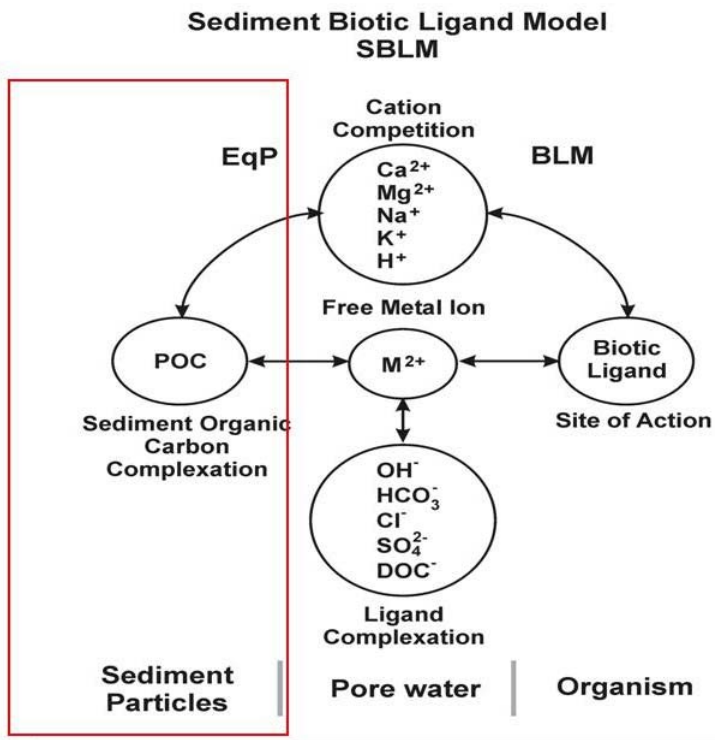


Figure 13. Schematic of the Sediment BLM (Di Toro et al., 2005b)

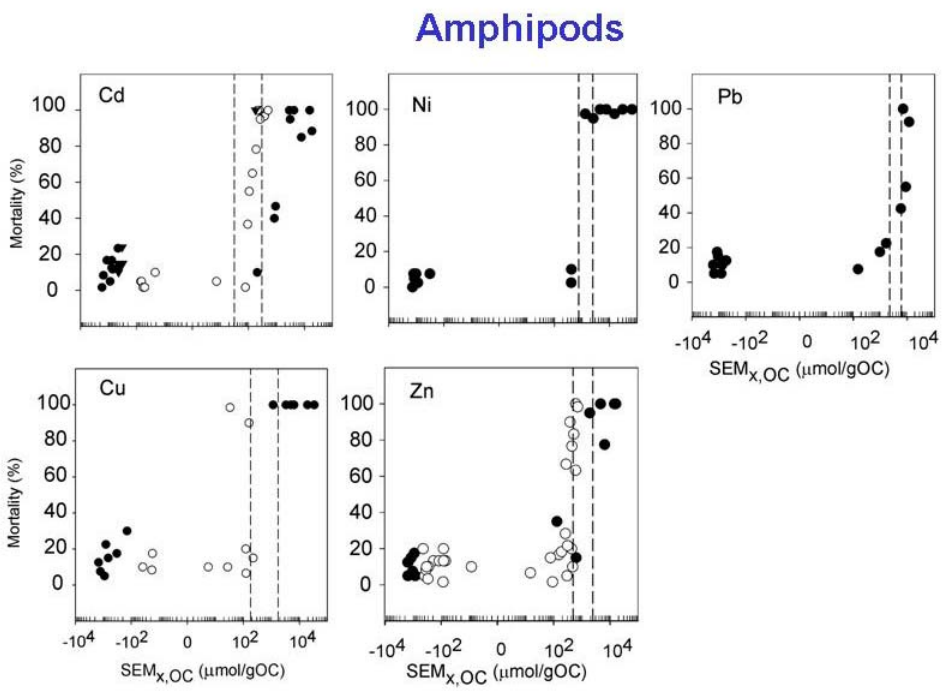


Figure 14. Comparison of Predicted and Observed Amphipod Mortality. The Dashed Lines are the Predicted *D. magna* LC50s for pH = 6 and pH = 9. The Data are Amphipod Mortality Versus Organic Carbon Normalized Excess $SEM_{X,OC}$ = (SEM – AVS) / f_{OC} (Eq. 4) (Di Toro et al., 2005b)

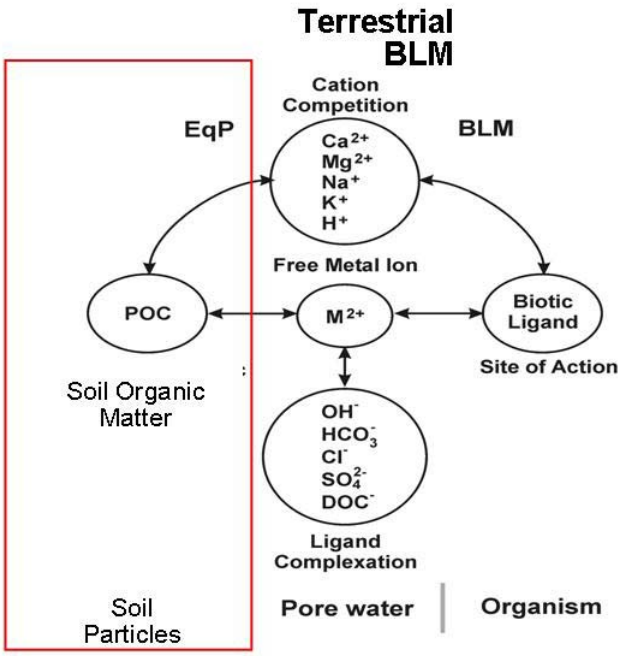


Figure 15. Schematic of the Terrestrial BLM (Thakali et al., 2006a).

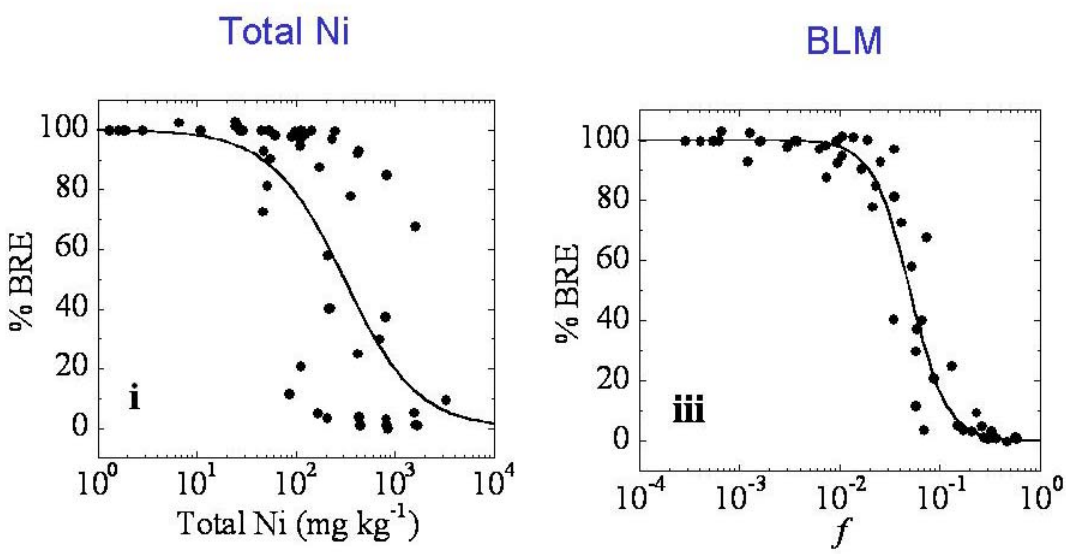


Figure 16. Reduction in Barley Root Elongation Relative to Controls Versus Total Ni in Soil (left) and Fraction of the Biotic Ligand Occupied (right) (Thakali et al., 2006a).

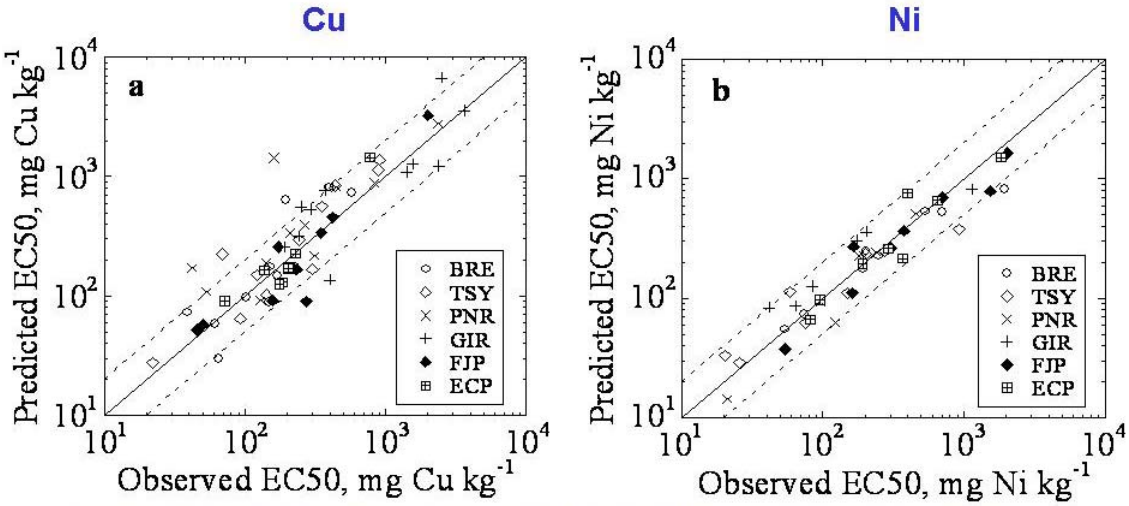


Figure 17. Predicted Versus Observed EC50s for Various Soil Toxicity Tests for Cu (left) and Ni (right) (Thakali et al., 2006b).

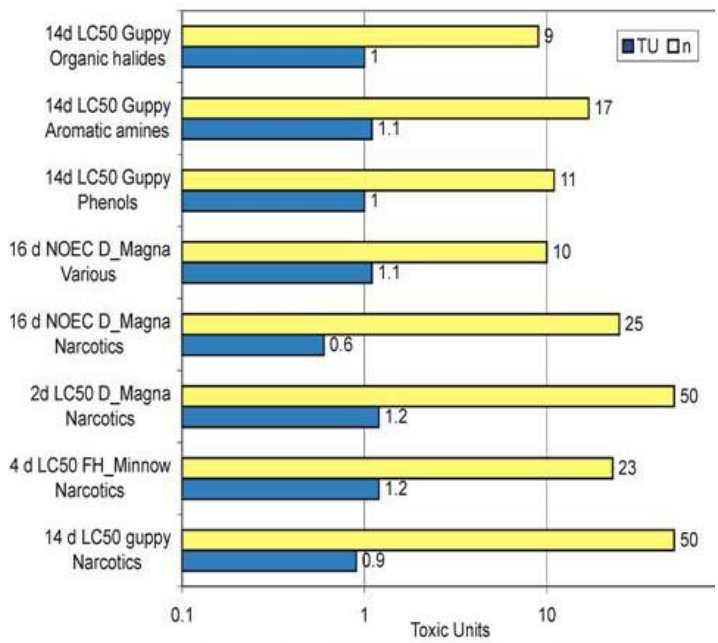


Figure 18. Summary of Mixture Additivity Data. Observed Toxic Units (TU) and Number of Chemicals in the Mixture (n). Compare to Predicted TU = 1 (Hermens, 1989; Sprague and Ramsay, 1965).

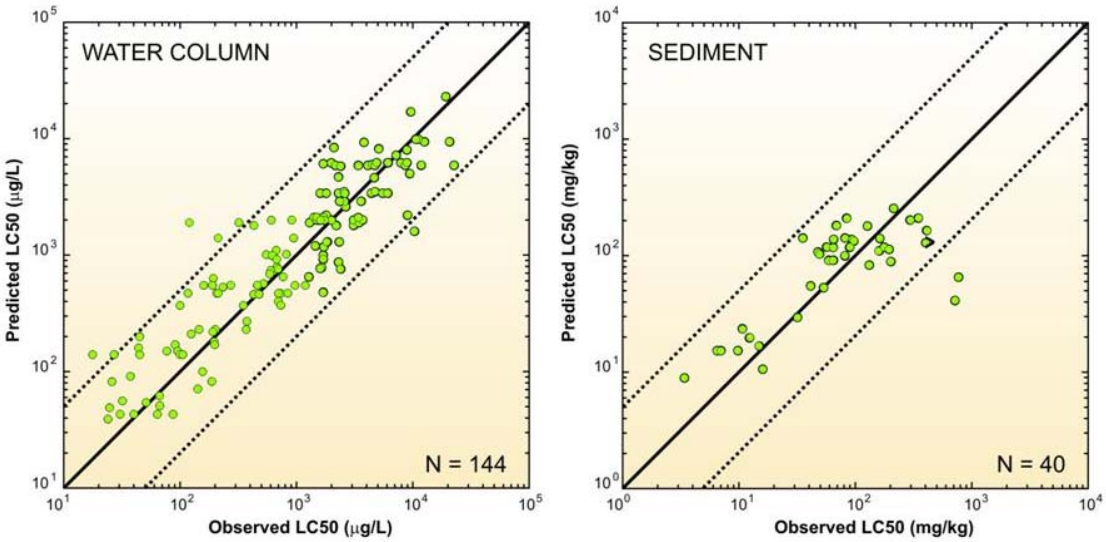


Figure 19. Predicted Versus Observed LC50s for Single PAH Exposures in Water (left) and Sediment (right). TLM (left) and TLM + EqP (right) Predictions (McGrath et al., 2005).

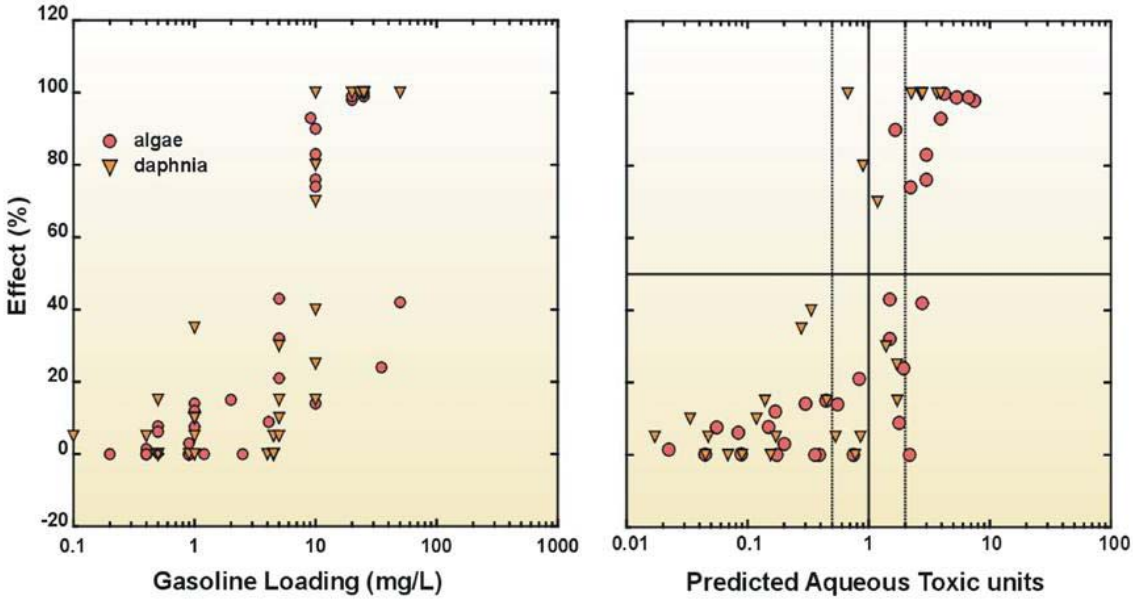


Figure 20. Observed Effects of Various Gasolines Versus Total Gasoline Concentration (left) and Toxic Units (right). Predicted 50% Effect at TU = 1 with Factor of Two Uncertainty Indicated (McGrath et al., 2005).

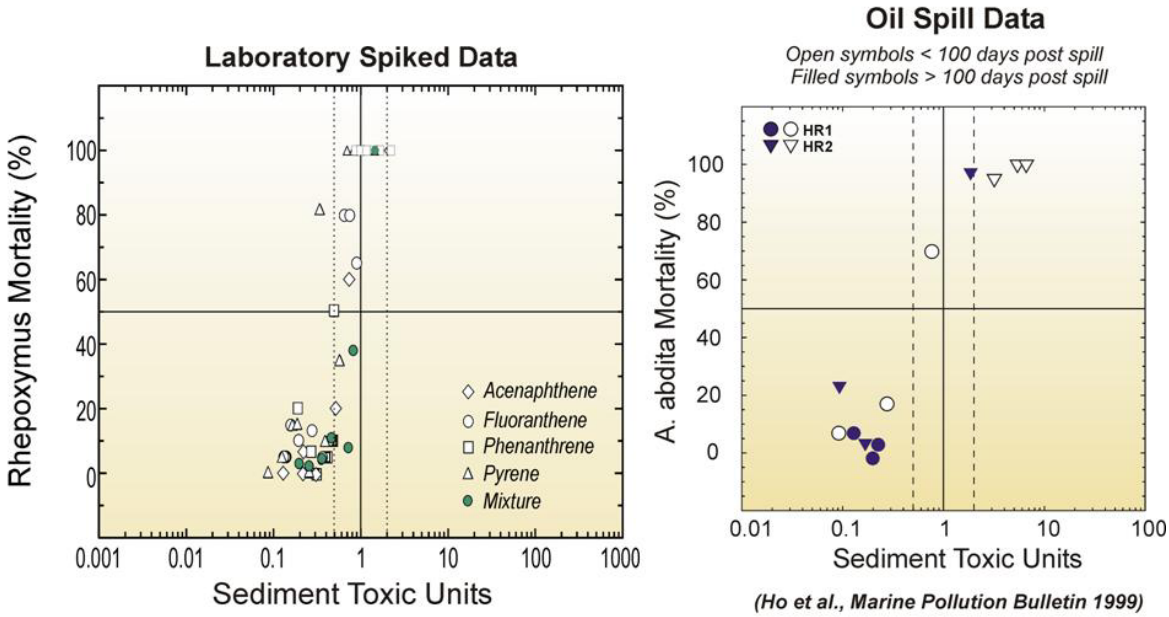


Figure 21 Observed *R abronius* Mortality Versus Sediment Toxic Units (TLM + EqP) for Laboratory-Spiked Single and an Equi-Toxic Mixture of the Four PAHs (left). Observed *A. abdita* Mortality Versus Sediment TUs for Sediment Samples Contaminated from an Oil Spill—Two Stations Sampled at Two Times (right) (Di Toro and McGrath, 2000)

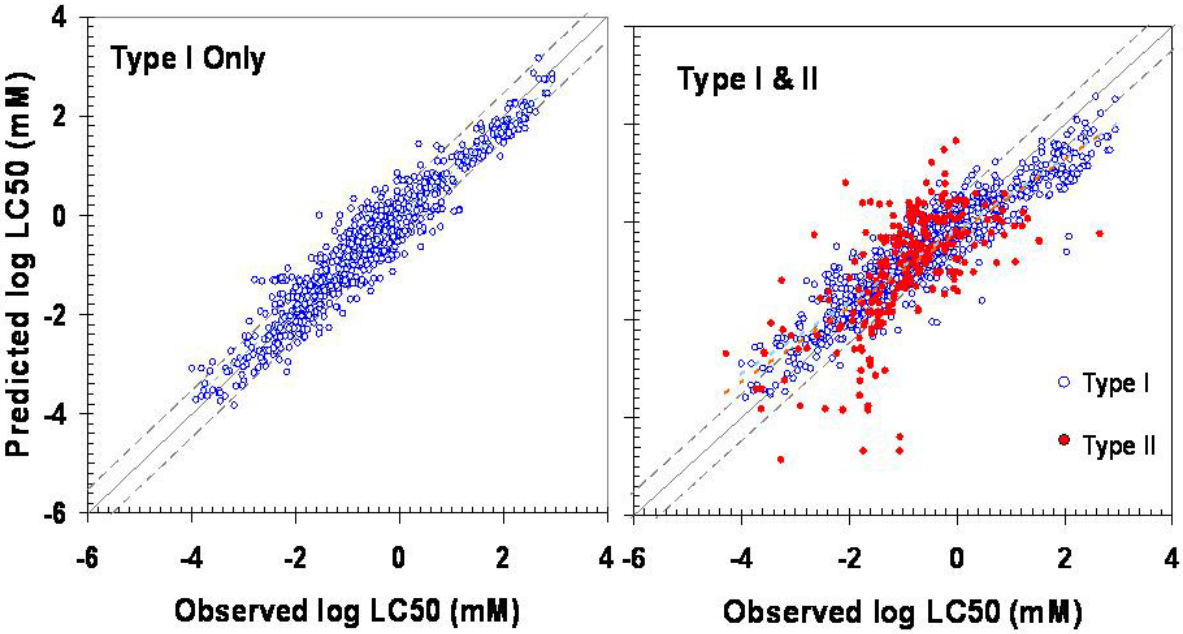


Figure 22. Predicted Versus Observed LC50s for TLM Using K_{OW} (Eq 8): Type I Chemicals (left) and Type I and II (right) (Kipka and Di Toro, 2008).

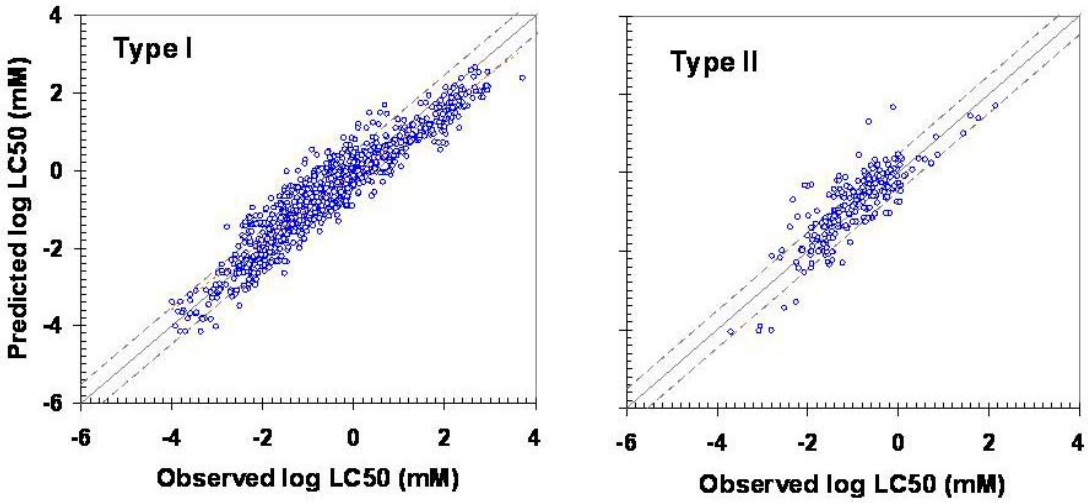


Figure 23. Predicted Versus Observed LC50s for TLM Using the Polyparameter Estimate for K_{LW} (Eq 11)—Type I Chemicals (left) and Type II (right) (Kipka and Di Toro, 2008).

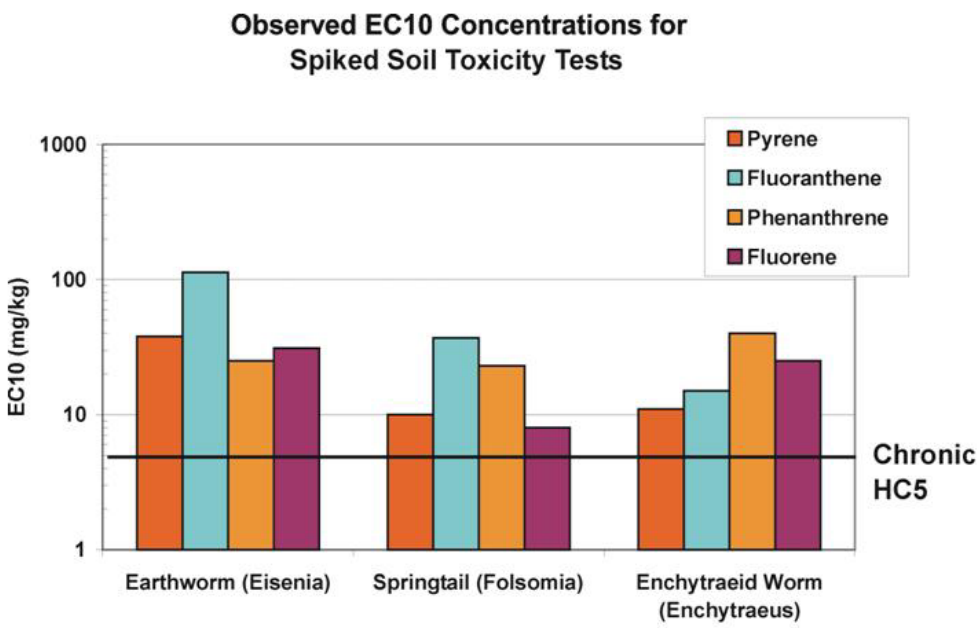


Figure 24. Comparison of PAH Chronic HC5 (McGrath et al., 2005) to Observed EC10 Concentrations in a Soil for Four PAHs and Three Organisms. Data from Sverdrup et al., 2002a, 2002b, 2001.

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APPENDIX C: WORKSHOP AGENDA

Workshop on Research and Development Needs for Understanding and Assessing the Bioavailability of Contaminants in Soils and Sediments

Wednesday, August 20, 2008

0800	Registration/Continental Breakfast	
0830	**Workshop Objectives and Structure**	Jeffrey Marqusee SERDP/ESTCP Director
	Workshop Objectives and Structure	Andrea Leeson SERDP/ESTCP Environmental Restoration Program Manager
DoD Risk Pathways and Drivers		
0845	Soils	Yvette Lowney Exponent, Inc.
0915	Sediments	Katherine von Stackelberg Harvard Center for Risk Analysis
State of the Science		
0945	Bioavailability Issues in Soils	Rufus Chaney USDA
1015	Bioavailability Issues in Sediments	Dominic DiToro University of Delaware
1045	Break	
1100	**Breakout Session I Discussions** • **Breakout Group 1 (Dick Luthy) Filibuster Room** • **Breakout Group 2 (Charlie Menzie) Senate B Room** • **Breakout Group 3 (Danny Reible) Senate A Room** • **Breakout Group 4 (Todd Bridges) Capitol A Room** • **Breakout Group 5 (Steve Roberts) Capitol B Room** • **Breakout Group 6 (Roman Lanno) Capitol C Room**	Breakout Groups
1200	Working Lunch	
1230	**Breakout Groups Continue**	
1530	Break	
1545	**Reconvene General Session: Recap of Day/Overview for Next Day**	
1615	**Reception with Poster Session Highlighting Relevant Projects**	
1830	Adjourn	

Workshop on Research and Development Needs for Understanding and Assessing the Bioavailability of Contaminants in Soils and Sediments

Thursday, August 21, 2008

0800	Continental Breakfast	
0830	Reports from Breakout Session I	Breakout Session Chairs
Bioavailability Use in the Decision-Making Process		
0930	Soils	Susan Griffin U.S. EPA
1000	Sediments	Marc Greenberg U.S. EPA
1030	Break/Convene to Breakout Sessions	
1045	**Breakout Session II Discussions** • **Breakout Group A (Dick Luthy) Filibuster Room** • **Breakout Group B (Charlie Menzie) Senate B Room** • **Breakout Group C (Danny Reible) Senate A Room** • **Breakout Group D (Todd Bridges) Capitol A Room** • **Breakout Group E (Steve Roberts) Capitol B Room** • **Breakout Group F (Roman Lanno) Capitol C Room**	Breakout Groups
1200	Working Lunch	
1230	Continue Breakout Session II	Breakout Groups
1445	Break	
1530	Reports from Breakout Session II	
1700	Discussion and Q&A	
1830	Adjourn	

Friday, August 22, 2008

Working Group Convenes (Steering Committee and Breakout Session Chairs/Scribes Only)		
0900	**Discuss Results and Preparation of Summary Report**	Breakout Session Chairs/Scribes
	• **Senate A Room**	
1200	Adjourn	

APPENDIX D: BREAKOUT SESSION CHARGES

Breakout Session Charge A

Workshop Objective: SERDP and ESTCP must determine how their limited research, development, and demonstration funds can best be invested to improve the Department of Defense's (DoD) ability to effectively address its environmental requirements to remediate contaminated sites. To strategically guide future investments in support of defining risk-based remedial endpoints, this workshop will (1) examine the current state of the science and technology for understanding and assessing bioavailability processes in soils and sediments that may impact risk-based remedial action decisions, (2) evaluate current and potential future applications of bioavailability concepts and assess barriers to their implementation, and (3) identify and prioritize research and demonstration opportunities that, if addressed, can facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites.

Breakout Session I: State of the Science and Technology
In the first breakout session, participants will identify knowledge or data gaps in addition to technology needs where additional research and development or field demonstrations would improve the understanding and assessment of bioavailability processes. Specific areas to be addressed by the breakout group follow:

<u>Fate and Transport</u>

- For what contaminants and conditions can bioavailability research make a significant impact on DoD's environmental liabilities?
- Identify the key scientific issues and current state of understanding of the processes that control fate and transport of organic and inorganic contaminants of concern in soils (or sediments) at DoD sites.
- What tools (biological, chemical and physical) are available to measure and characterize the fate and transport of the potentially bioavailable pool of contaminants, and what new tools are needed?

Breakout Session Charge B

Workshop Objective: SERDP and ESTCP must determine how their limited research, development, and demonstration funds can best be invested to improve the Department of Defense's (DoD) ability to effectively address its environmental requirements to remediate contaminated sites. To strategically guide future investments in support of defining risk-based remedial endpoints, this workshop will (1) examine the current state of the science and technology for understanding and assessing bioavailability processes in soils and sediments that may impact risk-based remedial action decisions, (2) evaluate current and potential future applications of bioavailability concepts and assess barriers to their implementation, and (3) identify and prioritize research and demonstration opportunities that, if addressed, can facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites.

Breakout Session I: State of the Science and Technology

In the first breakout session, participants will identify knowledge or data gaps in addition to technology needs where additional research and development or field demonstrations would improve the understanding and assessment of bioavailability processes. Specific areas to be addressed by the breakout group follow:

<u>Risk Assessment</u>

- For what contaminants and conditions can bioavailability research make a significant impact on DoD's environmental liabilities?
- What scientific understanding is missing that would provide confidence in the use of bioavailability factors in risk assessment?
- What mechanistic models are available to predict organism uptake or exposure (including defining representative suites of organisms, assessing the kinetics of processes controlling bioavailability, and understanding the inherent uncertainties), and what improvements to these models are needed?

Breakout Session Charge C

Workshop Objective: SERDP and ESTCP must determine how their limited research, development, and demonstration funds can best be invested to improve the Department of Defense's (DoD) ability to effectively address its environmental requirements to remediate contaminated sites. To strategically guide future investments in support of defining risk-based remedial endpoints, this workshop will (1) examine the current state of the science and technology for understanding and assessing bioavailability processes in soils and sediments that may impact risk-based remedial action decisions, (2) evaluate current and potential future applications of bioavailability concepts and assess barriers to their implementation, and (3) identify and prioritize research and demonstration opportunities that, if addressed, can facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites.

Breakout Session II: State of the Practice and Associated RDT&E Needs
In the second breakout session, participants will discuss current applications of bioavailability concepts and barriers to their implementation as well as research, development, test, and evaluation (RDT&E) needs building on the results of Breakout Session I. Topics to be addressed by all groups are as follows:

- How are bioavailability concepts currently used as part of risk assessments and associated remedial action decisions in the field?
- What barriers need to be overcome in implementing bioavailability concepts?
- Identify and prioritize the research and development needs that will have the greatest impact on our understanding and use of bioavailability.
- Identify and prioritize the demonstration and technology transfer efforts needed to increase the use of and confidence in bioavailability.

Criteria for Prioritizing RDT&E Needs

	Critical	High
Research	Research that potentially could have a significant impact on field implementation of bioavailability concepts to support risk assessments at DoD sites	Research that is of high priority but may not be able to be initiated until critical research needs are addressed or may be more clearly defined after critical research needs are addressed
Demonstration	Field demonstrations or assessments that can impact field implementation of bioavailability concepts to support risk assessments at DoD sites	Field demonstrations or assessments that are of high priority but may not be able to be implemented until critical demonstrations or assessments are completed

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14. ABSTRACT

The DoD is responsible for the management of thousands of sites with organic compounds and metals contamination in soils and sediments. SERDP and ESTCP convened a Expert Panel Workshop on Research and Development Needs for Understanding and Assessing the Bioavailability of Contaminants in Soils and Sediments in August 2008 to (1) examine the current state of the science and technology for understanding and assessing bioavailability processes in soils and sediments that may impact risk-based remedial action decisions, (2) evaluate current and potential future applications of bioavailability concepts and assess barriers to their implementation, and (3) identify and prioritize research and demonstration opportunities that, if addressed, can facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites. Two breakout sessions facilitated discussions of the current state of the science and identified data gaps that could be addressed through additional research, development, testing, and evaluation (RDT&E) activities. Specific research paths and demonstrations were identified and prioritized.

15. SUBJECT TERMS

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Soils
Sediments

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