WHITE PAPER

Bioavailability of Contaminants in Soils and Sediments: Status and Recommendations

SERDP/ESTCP White Paper

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LIST OF ACRONYMS

AC	activated carbon
As	arsenic
BaP	benzo(a)pyrene
Cd	cadmium
COC	contaminant of concern
Cr	chromium
CTC	cost to complete
DNA	deoxyribonucleic acid
DoD	U.S. Department of Defense
Eco-SSL	Ecological Soil Screening Level
EMNR	enhanced monitored natural recovery
ESTCP	Environmental Security Technology Certification Program
Fe	iron
HOC	hydrophobic organic compound
ITRC	Interstate Technology & Regulatory Council
MC	munitions constituents
MNR	monitored natural recovery
NAPL	non-aqueous phase liquid
NAVFAC	Naval Facilities Engineering Command
NELAP	National Environmental Laboratory Accreditation Program
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PE	polyethylene
PI	principal investigator
POCIS	Polar Organic Chemical Integrative Sampler
POM	polyoxymethylene
PSM	passive sampling method
PSR	Pacific Sound Resources
QA/QC	quality assurance/quality control

RAL	remedial action levels
RBA	relative bioavailability
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
RPM	Remedial Project Manager
Sb	antimony
SBAT	Soil Bioaccessibility Tool
SEA	Sediment Ecotoxicity Assessment
SERDP	Strategic Environmental Research and Development Program
SETAC	Society of Environmental Toxicology and Chemistry
SOP	Standard Operating Procedure
SPAWAR	Space and Naval Warfare Systems Command
SPME	solid phase microextraction
SQG	Sediment Quality Guideline
TNT	trinitrotoluene
TU	Toxic Unit
Zn	zinc

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EXECUTIVE SUMMARY

Bioavailability can be important to consider when assessing or mitigating the risks of contamination because not all of the contaminants present in a soil or sediment pose the same risks. However, incorporating bioavailability into risk assessments has proven difficult. Validated and cost-effective methods to measure bioavailability are needed, but the development and adoption of such methods has been challenging. Several interrelated processes must be considered, bioavailability is affected by numerous site-specific characteristics, and developing tests that accurately measure the potential exposure to organisms is understandably difficult, controversial, and time-consuming. The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) (the Programs) have invested in research on contaminant bioavailability for over a decade. This document represents a summary of the accomplishments over that period and the challenges that still remain.

For soils, SERDP's bioavailability research has focused primarily on development of *in vitro* tests to measure the bioavailability of lead (Pb) and arsenic (As), and to a lesser extent, polycyclic aromatic hydrocarbons (PAHs), munitions, and antimony (Sb). For sediments, the research has focused primarily on the polychlorinated biphenyls (PCBs). In particular, the objectives have been to develop and demonstrate both passive samplers capable of measuring the freely-dissolved porewater concentrations cost-effectively, and remediation technologies based on reducing bioavailability.

The current use of bioavailability in soils is limited. A validated *in vitro* assay for human oral exposure to Pb has been developed, and similar tests for As have been developed and are near validation. In addition, work is ongoing to develop site-specific tests for measuring the oral bioavailability of PAHs to humans. Finally, methods have been developed to measure bioavailability in soils for PAHs, munitions (trinitrotoluene [TNT] and hexahydro-1,3,5-trinitro-1,3,5-triazine [RDX]), and some metals (cadmium [Cd], Pb, As, and zinc [Zn]), and these results have been used to establish Ecological Soil Screening Levels (Eco-SSLs).

Bioavailability has had somewhat more impact in sediment assessment and remediation. SERDP and ESTCP have been instrumental in the development and field testing of several passive samplers designed to measure the bioavailable fraction of the total contaminant mass. These samplers are being adopted for sediment site characterization, and there has been a scientific consensus that passive samplers work, and that the use of these samplers can improve sediment management. Remediation of sediments through the addition of organic carbon amendments to reduce bioavailability has proven effective as well. Finally, bioavailability information is an important component of monitored natural recovery (MNR), and MNR guidance funded by the Programs has become an accepted strategy for managing sediment contamination. The Interstate Technology and Regulatory Council (ITRC) has developed a technical and regulatory guidance document on sediment bioavailability, an effort that has drawn heavily on Program-funded research.

This document includes recommendations for future research and technology transfer. For soils, the key remaining research needs include: (1) validation of the current *in vitro* assays for Pb and As in untreated soils for use in soils that have been treated to reduce bioavailability; and (2) development of dose-response relationships for dermal exposure, particularly to carcinogenic

PAHs. The technology transfer recommendations include: (1) development of soil bioavailability decision guidance, preferably through the ITRC team; and (2) fostering use of the relatively inexpensive mouse model for *in vivo* testing for As and possibly other metals.

For sediments, the highest-priority research needs include: (1) a better understanding of passive sampling techniques to evaluate bioavailability; (2) extension of passive samplers to a broader range of contaminants; and (3) demonstration of the long-term efficacy of amendments designed to contain or treat the bioavailable contaminants. The technology transfer recommendations include: (1) gaining acceptance of the use of passive samplers in assessing risk and setting remedial goals; (2) demonstrating the long-term effectiveness of *in situ* amendments such as activated carbon that can sequester contaminants in unavailable forms; and (3) developing a state of the science compendium on the use of activated carbon to reduce bioavailability.

In summary, SERDP and ESTCP have made considerable progress in extending the fundamental science of bioavailability into risk assessment and site management. This work has improved assessments of Pb- and As-contaminated soils, and of sediments contaminated with hydrophobic organics, notably PCBs. However, the adoption of this knowledge has been relatively slow. Fostering this adoption, as well as extending the research to other contaminants and pathways, could improve management of contaminated soils and sediments by ensuring that remediation efforts target the materials that truly pose risks to human health and the environment, and by developing cost-effective *in situ* technologies to reduce contaminant bioavailability.

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) are the U.S. Department of Defense's (DoD) environmental research programs (herein referred to as "the Programs"), harnessing the latest science and technology to improve DoD's environmental performance, reduce costs, and enhance and sustain mission capabilities. The Programs fund basic and applied research as well as field demonstration and validation efforts. For additional information, refer to www.serdp-estcp.org.

Soil and sediment contamination remain significant environmental liabilities for the DoD. The DoD maintains responsibility for thousands of sites contaminated with a wide variety of compounds: polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), various metals and metalloids, and military-unique compounds such as munitions constituents. Most of these contaminants are persistent, remaining onsite with long-term exposure to ecological and human receptors. Environmental restoration and closure of these contaminated sites is a top priority for DoD.

The DoD is committed to protecting human health and the environment in its environmental restoration of the inventory of upland and in-water sites. Through more than a decade of investment by the Programs in the Environmental Restoration Program Area, ESTCP and SERDP researchers have developed cost effective technologies for the characterization, remediation, and monitoring of contaminated soils, groundwater, and sediments. The persistent challenge to the Programs is to foster new and innovative science and technology for environmental restoration, while engaging in an effective transfer of these technologies into the hands of DoD, Federal, and state remedial site managers.

Bioavailability has been one of the key initiatives undertaken by the Programs. There is a substantive body of scientific evidence that supports making environmental restoration decisions not simply on the basis of presence of a specific contaminant in soil or sediments, but whether the contaminant(s) are biologically available to cause harm to humans or ecological receptors. Since the seminal treatise by the National Research Council (NRC), *Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications* (NRC, 2003), the Programs have invested in research and demonstration efforts to improve the understanding and assessment of contaminant bioavailability. The objective of the Bioavailability Initiative has been to foster improvements in understanding, which could establish more technically defensible cleanup goals and more realistic cleanup priorities, while also ensuring protection of human health and the environment. Additional information can be found at https://www.serdp-estcp.org/Featured-Initiatives/Cleanup-Initiatives/Bioavailability.

Bioavailability can be important to consider when assessing or mitigating the risks of contamination, because not all of the contaminant mass present in a soil or sediment may pose the same risks to human health and the environment. Bioavailability is the "state of being capable of being absorbed and available to interact with the metabolic processes of an organism" (USEPA, 1992). To cause harm to an organism, a chemical must (1) be released from the soil or sediment (either in the natural environment [desorption] or after ingestion [bioaccessibility]), (2) come in

contact with a membrane (e.g., stomach, intestine, lung, or skin), and (3) be distributed to an organ or cell. Several individual processes control a chemical's bioavailability. The NRC (2003) defined these bioavailability processes as the "physical, chemical and biological interactions that determine the exposure of plants and animals to chemicals associated with soils and sediments" (Figure 1). Bioavailability assessment tools measure these processes, and therefore can aid in assessing the potential for human and ecological exposure and in developing site-specific remedial action objectives.

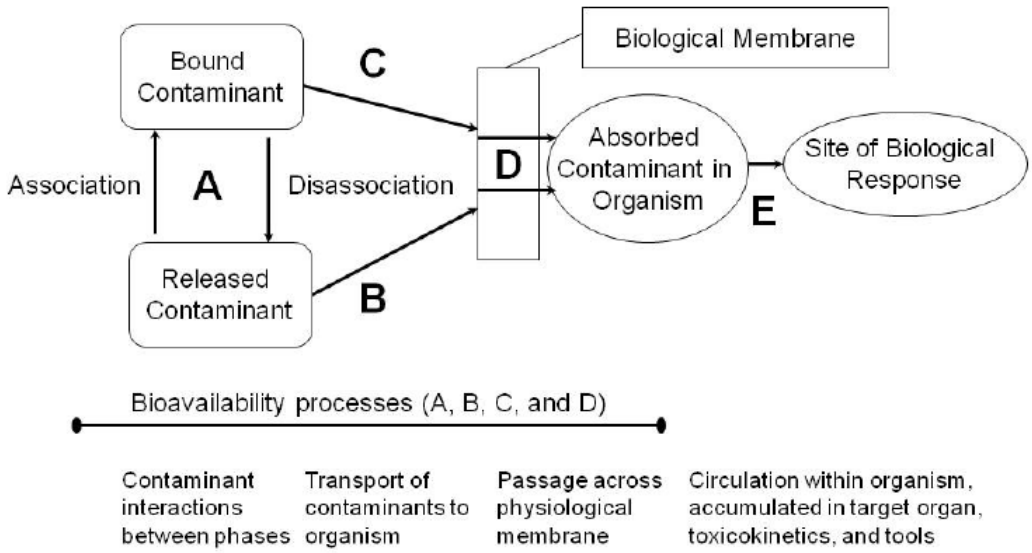

Figure 1. Bioavailability Processes in Soil or Sediment (NRC, 2003)

This white paper represents a review for the Programs of the accomplishments of the bioavailability research investment portfolio to date, and an evaluation of what additional investments might be made in research, demonstration, and technology transfer to further foster the use of bioavailability in remedial decision-making. It is intended to provide background on the SERDP and ESTCP bioavailability research conducted to date, and recommendations for future research and technology transfer to foster the appropriate uses of bioavailability information and related tools and techniques for evaluating bioavailability at specific sites.

Other groups have also funded contaminant bioavailability research over the last 20–30 years, within the United States and internationally. The USEPA has supported considerable internal and external research (http://www.epa.gov/superfund/soil-bioavailability-superfund-sites), as has the U.S. Department of Agriculture (search http://www.ars.usda.gov/research), the National Institute of Environmental Health and Science (https://tools.niehs.nih.gov/srp/researchbriefs/index.cfm), and by industry coalitions such as the Electric Power Research Institute (http://www.epri.com). Internationally, there have been several important research and regulatory initiatives, notably in Canada (http://www.bioavailabilityresearch.ca), Australia, and the European Economic Community. This white paper cannot cover all of the research available, even on the contaminants of most interest to DoD, but several key references from other efforts are included for context.

This document first describes the process for making investment decisions through the relevant Expert Panel Workshops, and the recommendations resulting from those workshops. It then summarizes the research conducted to date, how and where those investments have been applied to contaminated site restoration, and briefly describes the successful work products that have developed from the Programs. This document is also intended to serve as a future investment guide, and therefore summaries of a series of conversations regarding research and technology transfer needs with several experts in soil and sediment bioavailability are included. Finally, this document can serve as an introduction to the resources available on the SERDP and ESTCP website, and an overview of the current state of the science.

2. SERDP AND ESTCP WORKSHOPS

SERDP and ESTCP have long recognized the need to hold strategic planning workshops to identify and prioritize research needs that could have the greatest impact on site restoration. The Programs have convened these workshops drawing on the expertise from academia, industry, and the Military Services to examine the current state of the science and engineering on specific environmental problems (workshop reports are available at https://www.serdp-estcp.org/News-and-Events/Conferences-Workshops/Past-ER-Workshops). Beginning in 2004, experts at the workshops consistently identified bioavailability as a critical research need. Through the workshop process, technology and information gaps were identified and prioritized in terms of their importance to DoD. These workshops form the fundamental investment guide for the Programs, highlighting where investments in research, technology development, field demonstration, and technology transfer could have the greatest impact on DoD's ability to address its environmental requirements. Brief summaries of the workshop relating to bioavailability in soils and sediments are provided below.

2.1 2004 *IN SITU* SEDIMENT MANAGEMENT WORKSHOP

The importance and utility of research into the bioavailability of contaminants in sediments was first identified to the Programs in the August 2004 workshop on sediment management. This workshop, held in Charlottesville, VA, brought together roughly 70 experts from DoD, Federal agencies, academia, and the private sector to identify the research needed to improve sediment management. The report, *SERDP and ESTCP Expert Panel Workshop on Research and Development Needs for the In Situ Management of Contaminated Sediments* (SERDP and ESTCP, 2004) identified roughly 80 research needs, 7 of which directly addressed bioavailability. Two critical research and development (R&D) needs were identified: (1) development and demonstration of tools to measure the truly bioavailable contaminant fractions in sediments, and (2) development and application of *in situ* remedies using materials that would sequester and make contaminants biologically unavailable.

As will be discussed more in Section 3 of this white paper, in both of these cases, the subsequent research efforts have been highly successful. Several widely used tools have been developed to provide *in situ* measures of hydrophobic organic compounds (HOCs) in sediments, and passive remediation through additions of active carbon to sediments has been demonstrated as a method to render PCBs and PAHs biologically unavailable. A third promising area of research that incorporates bioavailability assessments as part of the remedy has been the development of a methodology that would allow the use of monitored natural recovery (MNR) as a viable and environmentally protective remedial alternative for contaminated site management.

2.2 2008 SOIL AND SEDIMENT BIOAVAILABILITY WORKSHOP

The initial success of bioavailability tools developed as a result of the 2004 workshop recommendations, along with the need to update the investment portfolio strategy for both soils and sediments, led to the 2008 workshop in Annapolis, MD. This second workshop brought together over 80 experts and practitioners, with an increased participation of Federal and state site managers to share insight on how to increase the use of bioavailability for risk-based remedial decision-making. The 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 (SERDP and ESTCP, 2008), includes background papers and presentations on DoD risk pathways and drivers, the state of the science in bioavailability, and the status of bioavailability use in the decision-making process. This workshop was structured into breakout groups that were carefully constructed to include DoD site managers, USEPA and state Remedial Project Managers (RPMs), university scientists, and consultants to identify key issues, barriers to regulatory acceptance, and research, development, and technology transfer needs. The workshop format was highly successful, resulting in the identification and prioritization of research and demonstration opportunities that, if addressed, could facilitate regulatory acceptance and field implementation of bioavailability concepts to support risk assessments at DoD sites. The Workshop Report guided the SERDP and ESTCP solicitation calls from 2008 to 2012.

2.3 2011 STRATEGIES FOR MEETING DOD RESTORATION GOALS WORKSHOP

The DoD has many sites in various stages of restoration. Some sites have achieved full closure with no further actions required, some with active remediation systems in place, but often those sites require long-term management before final closure is possible. For many other sites, the remaining cost to complete (CTC) for contaminated sites is still very high. A workshop was convened on 16 June 2011, in Salt Lake City, UT, to determine future research and demonstration needs to support DoD-evolving restoration goals, and the resulting report on *Investment Strategies to Optimize Research and Demonstration Impacts in Support of DoD Restoration Goals* is available on the SERDP and ESTCP website (SERDP and ESTCP, 2011). The specific objectives of the workshop were to (1) review the current cleanup goals and management processes of the different Services; (2) evaluate current and potential future issues associated with site closure, particularly under performance-based contracts; and (3) identify research and demonstration strategies that can improve remediation approaches, reduce risk, and ultimately reduce the CTC. One relevant need was for better characterization of the risks of metals in soils at Military Munitions Response sites, which represent a large fraction of the total CTC estimates for DoD sites. Bioavailability assessments were also identified as a promising opportunity to reduce the uncertainty in risk assessments, along with a better understanding of vapor intrusion and ecological risks. Other key needs included technologies to delineate and treat contaminants in low-permeability zones, remediation technologies for complex sites (e.g., fractured bedrock and large, dilute plumes), and improved long-term monitoring techniques.

2.4 2012 LONG-TERM MANAGEMENT OF CONTAMINATED SEDIMENTS WORKSHOP

To update the sediment investment strategies, the Programs convened a workshop on *Research and Development Needs for Long-Term Management of Contaminated Sediments* (SERDP and ESTCP, 2012) in July 2012, in Seattle, WA. This workshop summarized the state of work conducted by the Programs to date, reviewed the status of DoD facilities in their long-term management implementation of contaminated sediments, and engaged the Federal and state RPMs on specific tools, demonstration, or information-transfer needs that would facilitate both long-term management decision-making and long-term monitoring of these sites. The critical needs identified included greater understanding of added carbon amendments to reduce bioavailability, as well as improvements to passive samplers (including samplers able to measure bioavailable contaminants). Other key needs included development of amended caps to both contain and treat contaminants, monitored natural recovery guidance, tools to evaluate the placement of

amendments, better understanding of sediment migration and recontamination potential, and the use of food web models to assess the risk of contaminants in sediments.

2.5 FUTURE WORKSHOPS

While there are no workshops planned for the immediate future, SERDP and ESTCP have held smaller, regional meetings annually with the Program-funded principal investigators (PIs), DoD site managers, and local USEPA and state regulators. For example, in March 2014, a meeting was held in San Diego, CA, at the Navy's Space and Naval Warfare Systems Command (SPAWAR) Point Loma research facility that included the Program's PIs, as well as representatives from USEPA Regions 9 and 10, the U.S. Army Corps of Engineers, and state and local regulators from California, Oregon, and Washington. These meetings allow investigators working in similar areas to discuss their recent progress, and to introduce DoD and regulators to the current research efforts and to learn first-hand how these may be incorporated into the regional remedial programs.

3. SOIL BIOAVAILABILITY

For soils, bioavailability is explicitly recognized when establishing risk-based criteria by allowing the use of relative bioavailability adjustments. The original critical studies used to determine cancer slope factors or reference doses incorporate an *absolute bioavailability* value, which represents the bioavailability of the contaminant in the form used to administer the dose in those studies. Site-specific (or matrix-specific) testing is designed to establish the *relative bioavailability* (RBA, defined as the bioavailability from the environmental media of concern relative to the availability based on the original testing). The relative bioavailability of contaminants in soil is often considerably less than the default values used (often 100%, although USEPA has recommended a 60% RBA factor for both arsenic [As] and lead [Pb]).

The importance of contaminant bioavailability in soils was recognized over 30 years ago (Weissenfels et al., 1992), but the use of site-specific bioavailability adjustments in state and Federal cleanups remains limited. The NRC (2003) attributed the "hesitancy to explicitly consider bioavailability processes during site-specific risk assessments" to costs (for *in vivo* testing), anxiety about public acceptance, the lack of supporting data, concerns over the specific tools used (especially *in vitro* tests), and the absence of formal national guidance. Over ten years later, these limitations remain, although progress has been made in the last decade, both in guidance and in generating the high-quality data needed for regulatory acceptance of *in vitro* tools.

SERDP and ESTCP have funded research on contaminant bioavailability in soils for over a decade (Appendix A). The early work indicated that the bioavailability of contaminants important to DoD (notably Pb, As, and PAHs) was often low and potentially could be predicted with some confidence by soil properties and *in vitro* tests. This work led to the 2008 SERDP and ESTCP workshop to define the future research needs. The workshop concluded that:

1. Explicitly assessing contaminant bioavailability can result in setting more technically defensible cleanup goals and establishing more realistic cleanup priorities.
2. The science supports incorporating site-specific bioavailability measurements into risk assessments and site management decisions.
3. Methods for assessing and reducing contaminant bioavailability should continue to be refined and validated.

Recent SERDP and ESTCP soil bioavailability projects, as well as related work funded by others (particularly USEPA) have been completed or are nearing completion (described in the following sections). In several cases (notably As and PAHs), relatively low-cost *in vitro* tests have been developed that appear to correlate well with approved *in vivo* test results (which are much more expensive and time-consuming). Key SERDP and ESTCP soil bioavailability projects are provided in Appendix A.

3.1 STATUS OF RESEARCH AND DEVELOPMENT IN SOILS BIOAVAILABILITY

The key specific R&D needs identified from the 2008 workshop are identified below, with a summary of recent progress:

1. **Extend *In Vitro* Lead (Pb) Approach to Arsenic (As).** Dr. Nicholas Basta of the Ohio State University (SERDP Project ER-1742) has tested several *in vitro* assays for Pb and As on the same soils, and validated their performance by performing *in vivo* assays on the same soils. Dr. Susan Griffin of the USEPA (ESTCP Project ER-200916) validated an *in vitro* As assay that proved useful, with the exception of high-iron (Fe) soils (such as those found in many As-containing mining wastes). Along with the USEPA-funded work on high-Fe soils in California, this work has laid a foundation for credible guidance on the use of *in vitro* tests for Pb and As. Regulatory acceptance seems likely at some point.

2. **Develop Cost-Effective Methods for Measuring the Relatively Bioavailability of DoD-Relevant Organics**. Ms. Yvette Lowney of Exponent (SERDP Project ER-1743) is evaluating *in vitro* methods for measuring the relative bioavailability of PAHs, and validating these tests by comparison to *in vivo* testing of the same samples. Following several years of discussion and methods development, the work is on track to develop credible guidance on site-specific testing of human oral bioavailability of carcinogenic PAHs.

3. **Develop Soil Repository for Bioavailability R&D.** Dr. Basta (SERDP Project ER-1742) has collected and analyzed several soils, and used these soils to validate *in vitro* assays.

4. **Develop/Adapt *In Vitro* Methods for Evaluating Treated Soils.** *Additional work is needed in this area.* This is often mentioned as an outstanding research need.

5. **Develop Technically Valid Soil Limits for Equilibrated Contaminants.** Dr. Roman Lanno of Ohio State University (SERDP Project ER-1210) developed methods to measure bioavailability in soil systems for PAHs, trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and metals (Cd, Pb, As, and Zn) and use the results to establish Ecological Soil Screening Levels (Eco-SSLs). Dr. Thomas Trainor of University of Alaska Fairbanks (SERDP Project ER-1770) has completed comprehensive fundamental research on the speciation and bioavailability of Pb and Sb at shooting range soils. Dr. Geoffrey Sunahara of NRC Canada (SERDP Project ER-1416) developed toxicity benchmarks and bioaccumulation information for the most important N-based organic explosives. To date, there is little evidence of regulatory acceptance of these efforts.

6. **Cost-Effective Methods for Determining Dermal Absorption of Organics.** *Additional work is needed in this area.* This topic may become critical for PAHs if the proposed benzo(a)pyrene (BaP) dermal cancer slope factor is adopted.

3.1.1 Lead (Pb) and Arsenic (As) Bioavailability in Soils

Protocols for testing the bioavailability of Pb and As were adopted by USEPA, but the early protocols relied on costly juvenile swine testing, extraction testing, and geochemical speciation methods (USEPA, 2007). These protocols have been used to adjust bioavailability factors for Pb- and As-contaminated soils. *In vitro* test methods designed to make site-specific testing easier and less costly have also been developed, and future bioavailability adjustments for soil criteria are likely to be developed and adopted (Naidu et al., 2013).

Lead bioavailability guidance is the most widely adopted. Based on several years of research, national guidance has been developed for using bioavailability for Pb. For Pb, an *in vitro* assay has been accepted, allowing relatively rapid and inexpensive site-specific tests

(http://www.epa.gov/superfund/lead-superfund-sites). The *in vitro* assays can be considered validated, at least for soils prior to treatment (Juhasz et al., 2009; 2013a, b).

Arsenic, however, remains more problematic. The USEPA (2012) issued guidance in December 2012, establishing a 60% bioavailability default value, and site-specific *in vitro* testing protocols are in development. An ongoing USEPA Brownfields project in California (fact sheet available at http://www.epa.gov/brownfields) is modifying the USEPA Region 8 protocol for high-Fe soils, and the resulting guidance and methods should soon be available. Recent work suggests *in vitro* tests can be useful for assessing As bioavailability (Basta and Juhasz, 2014; Bradham et al., 2011).

Antimony is of particular concern to DoD, especially at firing ranges where Sb has been used as an alloy to harden bullets. Fundamental studies of the bioavailability of Sb and Pb in firing range soils in ER-1770 have provided a detailed understanding of the factors controlling the release, fate, and ultimate bioavailability of these metals under differing soil and environmental conditions. The work has also tested passive sensors capable of measuring the rate and extent of metal release.

On the regional or state level, individual risk assessors may adjust the bioavailability factor for other contaminants based on *in vitro* results, geochemical speciation, or the scientific literature. Hawaii, which has natural and anthropogenic As in relatively unique soils, has developed guidance based on *in vitro* measures of bioaccessibility (Hawaii Department of Health, 2013). However, there are few examples to date of the use of bioavailability adjustments for contaminants other than Pb and As, and anecdotal evidence suggests that such adjustments are rarely used.

3.1.2 Bioavailability of Organic Contaminants in Soils

Despite over 20 years of research, bioavailability adjustments for organic contaminants in soil are not yet accepted. Although it is clear from research that the bioavailability of hydrophobic contaminants in soil is often far less than the default values used in risk assessments, accepted methods are not yet available. Ongoing SERDP-funded work is close to development of a validated *in vitro* method (SERDP Project ER-1743), and this approach is being tested at the Naval Petroleum Reserve near Bakersfield, CA (U.S. Department of Energy-funded).

This ongoing work may be less valuable if proposed dermal cancer slope factors for BaP are enacted. Recent draft guidance would make dermal exposure far more important than oral exposure; so much of the work currently being done on *in vitro* tests to measure oral bioavailability could have relatively little impact. Research on dermal bioavailability of PAHs and other organics has been done, including work under ER-1743; however, there are still concerns about *in vitro* dermal testing (Andersen et al., 2014).

4. SEDIMENT BIOAVAILABILITY

The importance of bioavailability in contaminated sediment management has been recognized for over 20 years. The difficulties involved in sampling and managing sediments, and the volumes impacted at concentrations above typical default criteria, have made it economically important to evaluate bioavailability. Further, scientists have long realized that site-specific factors, notably the quantity and quality of organic carbon, have an enormous impact on bioavailability, and these characteristics can vary tremendously in sediment materials. Finally, the contaminants impacting sediments are often relatively insoluble and often subject to bioaccumulation, so bioavailability has long been recognized as an important site-specific parameter (Ehlers and Luthy, 2003; NRC, 2003). The increasing use of bioavailability for sediment sites was highlighted in the recent guidance developed by the Interstate Technology & Regulatory Council (ITRC, 2011) that described 35 case studies of its use at sediment sites, including a wide range of inorganic and organic contaminants. Further evidence of the increasing incorporation of bioavailability into restoration and monitoring is the Battelle 2015 International Conference on Remediation and Management of Contaminated Sediments, where there were 60 presentations and two short courses that were a direct outgrowth of work either directly funded, or followed on from, work developed through the Programs.

The Programs have made a considerable investment into research on bioavailability in sediments over the last decade, because contaminated sediments represent a large potential liability for DoD. This sediment bioavailability research has been driven by two main objectives: (1) to develop tools to measure the bioavailable fraction, and (2) to develop *in situ* remedies based on reducing the bioavailability of contaminants of concern (COCs). This section highlights the investments in research (SERDP), bench and field scale demonstrations (ESTCP), and the technical transfer efforts undertaken to date by the Programs in both of these areas. Where applicable, other sites where these bioavailability tools are being used are also discussed. Section 6 of this white paper will discuss other areas where additional work in both research and technical transfer can be made.

4.1 TOOLS TO MEASURE BIOAVAILABILITY

4.1.1 General Tools to Measure Contaminants in Sediments and Porewater

SERDP and ESTCP have invested in tools that are capable of monitoring water and contaminant migration at the groundwater-surface water interface (ESTCP Project ER-200422), as well as an integrated sampling device that is can be deployed on the sediment surface to conduct *in situ* bioassays (ESTCP Project ER-201130). Direct sampling of groundwater discharge through sediments can be accomplished using the Trident probe and the Ultraseep. The Trident is a multi-sensor sediment probe device that is designed to rapidly identify groundwater-surface water discharge zones, and to sample porewater from these areas. Used in conjunction with the Ultraseep, which was developed to make continuous, direct measurements of the groundwater seepage rate, the systems allow the determination of the flux of contaminated water and allow for the measurement of bioavailable contaminants in that water (Chadwick et al., 2003; Chadwick and Hawkins, 2008; Smith et al., 2003).

More recently, the Sediment Ecotoxicity Assessment (SEA) Ring system was developed as an *in situ* measure for sediment toxicity and bioaccumulation testing. The SEA-Ring consists of a circular carousel capable of housing an array of *in situ* bioassay chambers and passive sampling

devices, and works with the Trident and UltraSeep systems. These systems have been commercialized and have been employed at a number of DoD- and Superfund-contaminated sediment sites.

4.1.2 *In Situ* Samplers for Hydrophobic Organic Compounds (HOCs)

Among the most successful tools developed with Program support are three techniques that have allowed reliable and repeatable measures of the bioavailability of HOCs. HOCs of importance to the DoD include PCBs, PAHs, dioxins, and chlorinated pesticides. The tools developed with Program funding include solid phase microextraction (SPME), polyoxymethylene (POM), and polyethylene (PE). These studies are listed in Appendix A, and include ER-200709, ER-1207, ER-1496, ER-200915, ER-200624, and ER-201216. These tools have found far-reaching application both within the United States and abroad (Ghosh et al., 2014). ESTCP also funded the only comparative evaluation to date between these methods for PCBs, and compared those measures to bioaccumulation in *Lumbriculus* (Gschwend et al., 2013).

4.1.3 *In Situ* Samplers for Metals

Tools to measure *in situ* concentrations of metals are still in the R&D stage within SERDP. Most of the work to date has been on bioavailability of As, copper (Cu), Pb, mercury (Hg), and zinc (Zn). Excellent basic research has been conducted with SERDP funding (e.g., ER-1744, ER-1746, ER-1748, and ER-1771). While these metals are a persistent problem at DoD sediment sites, to date the research conducted has not resulted in a measurement tool that has the demonstrated precision, accuracy, and reproducibility needed to be employed in the field. One project to demonstrate an *in situ* probe (ESTCP Project ER-201128) produced limited results since the probe was unable to accurately measure metal concentrations.

4.1.4 *In Situ* Munitions Constituents (MCs)

The Programs have made considerable investment in documentation of the toxicity and bioavailability of underwater military munition constituents (MC). This work has been principally done through SERDP and includes research ranging from fate and transport processes, to uptake, bioavailability, and risk assessment. A separate workshop was held by the Programs in 2007, on the technologies for characterization, management, and remediation for MCs in aquatic environments. A summary of ongoing efforts as well as an appraisal of needs and accomplishments within SERDP and ESTCP are highlighted in the Munitions in Underwater Environment Initiative (SERDP and ESTCP, 2007). Completed and on-going projects include ER-2122, ER-2123, ER-2124, ER-2125, ER-1453, ER-1431, and ER-1129 (Appendix A). SERDP has also funded a project that will compile and review all work conducted to date on the ecological risks associated with MCs (ER-2341).

Recently, *in situ* samplers have been developed by Navy researchers to the point where field demonstrations are possible. A demonstration of these so-called Polar Organic Chemical Integrative Samplers (POCIS) has recently been funded (ESTCP Project ER-201433). The use of POCIS is intended to demonstrate the practical application on sampling for environmentally relevant concentrations of MCs and compare those measured concentrations comparison with predicted MC behaviors based on laboratory studies.

4.2 *IN SITU* REMEDIES TO REDUCE BIOAVAILABILITY

4.2.1 Activated Carbon

The use of activated carbon (AC) for contaminated sediment site management is making the jump from research and demonstration/validation to full-scale remedial application. AC can be applied to manage contaminated sediments in-place by tightly sequestering HOCs such as PCBs and PAHs. The technology has the potential to replace or augment other intensive management practices such as dredging or capping. Built upon SERDP research and ESTCP demonstration, AC has moved into the mainstream "tool box" for contaminated sediment management.

The initial bench-scale work sponsored by SERDP was so successful that the work was extended into field demonstration and validation in ESTCP. The laboratory scale demonstrations were relatively easy; developing engineering solutions for applying the AC into sediments in the field required work on multiple levels. One of the early ESTCP developments, because AC floats, was to formulate the carbon into a pelletized form that would sink, could be applied using conventional equipment, achieve an even distribution on the sea floor, and then dissolve to release the AC into the contaminated sediments (SERDP Project ER-1491). Completed or on-going demonstrations at DoD sites have included the Army's Aberdeen Proving Ground (ESTCP Projects ER-200835 and ER-200825), Hunters Point Naval Shipyard (SERDP Project ER-1207), Naval Air Station Dallas (SERDP Project ER-1493), and the Puget Sound Naval Shipyard (ESTCP Project ER-201131). Additional contaminated sediment sites, outside of the Programs, where AC has been applied or is being considered as a remedy are discussed further below.

4.2.1 Metal Sequestration

SERDP has sponsored similar research evaluating amendments to sequester metals in sediments (as well as in soils). The research has included the addition of minerals such as apatite, zeolites, bauxite, and alumina for metals or metalloids; ion exchange resins for metals or other inorganic contaminants; or lime for pH control or nitroaromatics degradation (see list in Appendix A for ER-1350, ER-1351, ER-1352). On-going research also suggests that Hg bioavailability may be controlled by the application of AC; demonstration of the efficacy of this work is on-going at the Army's Aberdeen Proving Ground (ESTCP Project ER-200835) and the Puget Sound Naval Shipyard (ESTCP Project ER-201131). Other related work includes mixtures of permeable concrete and chemically active amendments to produce caps that prevent the migration of sediment contaminants while being stable on sloping shorelines and environments subject to dynamic forces (SERDP Project ER-2134)

4.3 ACTIVE REMEDIATION SITES USING BIOAVAILABILITY TOOLS

Example projects of bioavailability tools developed or demonstrated with SERDP and ESTCP funding that are being used in site management or monitoring are given below. A review on the state of global application of passive samplers to measure HOCs may be found in Lydy et al. (2014). The Programs are funding the development of additional guidance, with case studies, as further discussed in Section 5.2.

4.3.1 Passive Samplers

Eagle Harbor Superfund Site, WA. Passive SPME samplers have been used to evaluate the efficacy of a placed cap over PAH-contaminated sediments at the Eagle Harbor Superfund Site at Bainbridge, WA. The samplers, demonstrated under ER-200624, were used to evaluate whether PAHs from the capped non-aqueous phase liquid (NAPL)-containing sediments were leaching up and through the cap surface. Using an innovative testing design, researchers from the University of Texas at Austin (Reible and Lotufo, 2012; Thomas et al., 2012) were able to demonstrate that the cap is effectively isolating the sediment contaminants, and that PAHs observed in the cap surface sediments were from off-site source.

Pacific Sound Resources (PSR) Superfund Site, WA. SPME samplers were also similarly used for the cap at the PSR Superfund site in Seattle, WA (USEPA/USACE, 2010; Reible and Lu, 2011). Monitoring of cap bulk surface sediments had not detected PAHs. A data gap was identified relating to the potential for dissolved PAH NAPLs to be released at water depths that would be logistically difficult to sample by conventional means (e.g., to 80 feet below Mean Lower Low Water). USEPA Region 10 elected to deploy vertical-profiling SPME passive sampling methods (PSMs) to determine whether dissolved-phase contaminants currently impact surface water quality at the site. Those results demonstrated that the cap was effectively isolating the contaminated sediments.

Palos Verde Shelf, CA. The USEPA is employing passive sampling to measure bioavailable DDT congeners and their breakdown products, and 43 PCB congeners in the vicinity of the marine Superfund site on the Palos Verdes Shelf, CA (Fernandez et al., 2012a, b). Both SPME and PE samplers have been deployed at the site for baseline monitoring. Capping of the most contaminated sediments near the outfall has been selected as the preferred remedial alternative. Passive samplers will be used for post-remedial monitoring of both PCBs and DDx.

United Heckathorn Superfund Site, CA. PE samplers were used to monitor water column concentrations of DDT and dieldrin in the water column before, during, and after remediation at this Superfund site (Ells et al., 2010; Kohn and Kropp, 2002).

Lower Duwamish River Superfund Site, WA. PE samplers were recently used at the Lower Duwamish Superfund Site near Seattle, WA. The objective of this work was to develop a basis of comparison between the conservative estimates of PCB in porewater used for a Food Web Model, and actual measures of PCB congeners in porewater. The model is being used to develop sediment-based remedial goals for the site; the actual porewater measures are being considered for use in validating or changing the model (Gschwend et al., 2013).

4.3.2 Amended Caps

As discussed in Section 4.2, Program-sponsored field applications of AC at contaminated DoD sites has led the way for a broader acceptance of this technology both in the United States and in Europe (Ghosh et al., 2011). The number of pilot-scale sites where AC has been placed and tested since 2006 has increased, and while acceptance of amendments as a means for controlling HOC bioavailability increasingly is being considered in feasibility studies, broader acceptance and implementation is still lagging. The status of these sites is shown in Table 4-1.

Table 4-1. Pilot, Planned, and Implemented Sediment Remedial Sites Using Activated Carbon (adapted from ER-200825)

Site	Contaminant	Year Initiated	Pilot Project	FS or Remedial Design Stage	Full-Scale Implemented	Project Comments
Anacostia River, Washington, DC	PAHs	2004	X			Placed coke breeze in geotextile to control long-term mobility. Full scale project not implemented
Hunters Point, San Francisco Bay, CA	PCBs & PAHs	2005	X	X		Pilot project under SERDP-1207 and ESTCP ER-200510. Full-scale remedial project under consideration
Grasse River, Massena, NY	PCBs	2006	X			Pilot project with AC mixed into PCB-contaminated sediment. Full scale project not implemented.
Trondheim Harbor, Norway	Dioxins/furans	2006	X			Placed AC and capped with sand for erosion protection
Spokane River, WA	PCBs	2006			X	Placed full-scale coal-amended cap to control long-term mobility
St. Louis River Superfund Site, Duluth, MN	NAPL/PAHs	2007			X	Reactive core mat with activated carbon. Mat thickness was typically 11 mm over 11 acres
Chocheco River, Dover, NH	PAHs	2008	X			Pilot scale project testing mats of geotextile with AC, organoclay, and apatite.
Naval Air Station, Cottonwood Bay, Dallas, TX	Metals, PAHs	2009	X			Small-scale pilot project under SERDP ER-1493. Geotextile mats with AC, apatite, and organoclay
De Veenkampen, Netherlands	Clean sediment	2009	X			Pilot project that evaluated benthic community effects at different AC doses
Grenlandsfjords, Norway	Dioxins/furans	2009	X			Pilots project to demonstrate efficacy of a hydraulic application of AC/clay mixture at depth
Bailey Creek, VA	PCBs	2009	X			Pilot project under SERDP ER-1491. Full scale project under consideration
Canal Creek, MD	PCBs & mercury	2010	X			Pilot project under ESTCP ER-200825 and ER-200835. Still under field evaluation
Onondaga Lake, NY	Chlorinated benzenes & PAHs	2011	X		X	Successful pilot, followed by full-scale implementation of cap with AC.
South River, VA	Mercury	2011	X			Evaluate placement of biochar and bioavailability control in pond
Sandefjord Harbor, Norway	PCBs, TBT & PAHs	2011	X			Evaluate placement of AC pellets and bioavailability control in estuary
Bergen Harbor, Norway	PCBs and TBT	2011	X			Evaluate effectiveness of AC-amended versus traditional caps
Leirvik Sveis Shipyard, Norway	PCBs, TBT & metals	2012			X	Full-scale controlled placement of AC-amended cap
Naudodden, Farsund, Norway	PCBs, PAHs, TBT & metals	2012			X	Full-scale placement of layered isolation cap with AC amendment
Berry's Creek, NJ	Mercury & PCBs	2012			X	Evaluate bioavailability control in vegetated wetland
Puget Sound Naval Shipyard, WA	PCBs & mercury	2012	X			Evaluate placement of AC pellets in under-pier areas
Custom Plywood, Fidalgo Bay, WA	Dioxins/furans	2012	X			Evaluate AC and cap effects in sensitive eelgrass environment
Duwamish Slip 4, WA	PCBs	2012			X	Full-scale AC-amended cap to control long-term mobility
McCormick and Baxter, Portland, OR	NAPL, PAHs	2012			X	Organo-clay and organo-clay mats incorporated into full scale cap. Long-term monitoring on-going
Lower Duwamish Waterway, WA	PCBs	2013		X		AC alternative written into the FS. Pilot project under consideration.
Lower Willamette Waterway, OR	PCBs, Dioxin/furans	2013		X		AC alternative written into the FS. Pilot project under consideration.
Lauritzen Canal, Richmond, CA	DDx	2013		X		AC alternative being evaluated in a feasibility study for residual management after dredging

5. BIOAVAILABILITY WORK PRODUCTS

In addition to the individual project reports and the associated articles published in the scientific literature, the Programs have directly and indirectly supported development of guidance documents that are being used by state and Federal regulators. Guidance on using bioavailability has been adopted more rapidly for sediments than soils. There are several reasons for the faster development for sediments, including the greater range of environmental conditions in soils and the greater potential for direct human exposure to soil. Relevant work products for each of these matrices are described briefly in the following sections.

5.1 SOILS

5.1.1 Validated *In Vitro* Arsenic (As) Bioavailability Assays

The work done under ESTCP Project ER-200916 showed an excellent correlation between the RBA values measured using the validated *in vivo* swine and monkey models and those measured using an *in vitro* testing protocol. The study tested 37 different soil samples and validated the protocol for most soil types. The *in vitro* method is highly reproducible, and allows testing a wide range of concentrations and locations at a site in a reasonable cost and time. *In vitro* testing can reduce costs from up to $50,000 to as low as $100 per sample, and results can be obtained in a few days instead of several months. *In vitro* testing of As can be complicated, however, and different *in vitro* test conditions may be needed for some materials, notably those with high Fe contents. SERDP Project ER-1742, which is near completion, has tested several *in vitro* protocols and developed guidance on conducting site-specific As bioavailability tests.

5.1.2 Protocols for Predicting Metal Bioaccessibility

Mr. Philip Jardine of University of Tennessee (SERDP Project ER-1166) studied the bioaccessibility of both chromium (Cr) and As in a wide range of soils, and found that both metals are significantly less bioavailable when added to soil, and the bioaccessibility could be reasonably predicted from soil properties. For example, the bioaccessibility of As in soils depends mainly on the soil's pH and iron oxide content. Screening-level models were developed from these data, and the protocol was named the Soil BioAccessibility Tool, or SBAT (Heuscher et al., 2004). More recent work conducted by Ms. Amy Hawkins of Naval Facilities Engineering Command (NAVFAC) (ESTCP Project ER-200517) has extended these models by testing more soils and including models for Pb and Cd, as well as successfully validating the SBAT approach. In addition, extraction tests were developed and validated to predict bioaccessibility. These extraction tests and predictive models can be used to prioritize sites and screen different locations within a site as part of a site-specific bioavailability assessment.

5.1.3 Remediation Techniques Based on Reducing Bioavailability

Mr. Jardine (SERDP Project ER-1350) evaluated several potential approaches to remediating metal-contaminated soils by adding amendments that can reduce chemical lability and bioavailability. Relatively inexpensive approaches (orthophosphate additions) reduce Pb bioaccessibility but increase that of As, so work focused on combinations of amendments for metal mixtures (Pb, Cd, Cr, and As). Combinations including cerium showed promise for reducing As

bioaccessibility as well, although this approach has not been adopted commercially. Dr. Katherine Banks of Purdue University (Project ER-1351) tested amendment strategies, including phosphates for Pb immobilization and soluble Fe to reduce As bioaccessibility, both of which were promising.

5.2 SEDIMENTS

5.2.1 Guidance for Monitored Natural Recovery at Contaminated Sediment Sites

As a remedial alternative, MNR includes evaluations of chemical bioavailability, in addition to other such metrics as sediment deposition, chemical or biological transformation, erosion and dispersion of particle-bound contaminants, and general reductions in contaminant mobility to higher level trophic organisms. Developed under ESTCP Project ER-200622, the document contains practical guidance on how to assess and monitor bioavailability, as well as cases studies of sites where bioavailability was used to support an MNR decision.

5.2.2 Demonstration of Enhanced Monitored Natural Recovery at DoD Sites

Enhanced monitored natural recovery (EMNR) is a hybrid remedy that generally relies on the combined effects of a thin layer cap (enhancement) and natural recovery, and is verified over time through monitoring. Like MNR, EMNR requires, in part, demonstration of reduced bioavailability and mobility of contaminants over time. Under ESTCP Project ER-200827, a case study review was developed as a resource for site managers who are considering EMNR as a remedy, and placed online.

5.2.3 Guidance Manual for *In Situ* Wetland Restoration Demonstration

This guidance manual provides DoD, Federal, and state site managers a framework for evaluating the potential of using reactive amendments such as AC to manage HOC-contaminated wetlands. Under ESTCP Project ER-200825, a limited informal survey of Navy project managers identified approximately 7,000 acres of contaminated wetlands and a number of sites where substantial and costly wetland remediation plans are currently in place. This guidance includes recommendations for site characterization and monitoring, available technologies, and suggested considerations for pilot scale, design, and full-scale implementation.

5.2.4 Incorporating Bioavailability Considerations into the Evaluation of Contaminated Sediment Sites

SERDP and ESTCP provided major support and technical writing to the February 2011 report by the ITRC Contaminated Sediments Team. This highly-cited document provides technical and regulatory guidance to assist state regulators and practitioners in understanding and incorporating the fundamental concepts of bioavailability in contaminated freshwater or marine sediment management practices.

5.2.5 Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments

The Programs provided major funding to support a recent workshop on passive sampling that was organized by the Society of Environmental Toxicology and Chemistry (SETAC), and which was attended by nine current and former SERDP and ESTCP PIs. A summary of the workshop may

be found online (Parkerton et al., 2013). Additionally, a series of articles on the state of the science were published in the April 2014 issue of *Integrated Environmental Assessment and Management* (Volume 10, No. 2). The workshop reached a consensus that passive samplers targeting the freely-dissolved fraction were useful for assessing bioavailability and could improve sediment management (Parkerton and Maruya, 2014).

5.2.6 Processes, Assessment, and Remediation of Contaminated Sediments

SERDP and ESTCP have fostered monographs on innovative and cost-effective remediation technologies written by leading experts. The book "Processes, Assessment and Remediation of Contaminated Sediments" released in 2014 (edited by Dr. Danny Reible) includes several chapters that highlight the use of bioavailability in remedial site management, including: Assessing Biological Effects (Lotufo et al., 2014), Assessing Bioavailability of Hydrophobic Organic Compounds and Metals (Lu et al., 2014), Monitored Natural Recovery (Fuchsman et al., 2014), *In Situ* Treatment for Control of Hydrophobic Organic Compounds (Cho et al., 2014), and Monitoring Remedial Effectiveness (Gustavson and Greenberg, 2014).

5.2.7 Passive Sampling at Contaminated Sediment Sites: Background and Practices Manual

ESTCP and the USEPA are completing a guidance document on how to conduct passive sampling and analyses for application at contaminated sediments sites. The document will include Standard Operating Procedures (SOPs) for preparing, deploying, retrieving, and chemically analyzing passive samplers for both organic compounds and metals. This document, produced through ESTCP Project ER-201216, will be released in 2016.

5.2.8 Use of Amendments for *In Situ* Remediation

The Programs have been on the forefront of the development of applying amendments for *in situ* remediation of contaminated sediments since the 2004 Expert Panel Workshop (SERDP and ESTCP, 2004). SERDP and ESTCP have developed a practices manual that will be available in 2016. USEPA has published a guidance document, *Use of Amendments for In Situ Remediation at Superfund Sediment Sites* that draws in part from the Program-developed research and demonstration projects. This guidance (USEPA, 2013) recognizes that amendment caps can be effective, and should foster the adoption of this promising and cost-effective remediation technology.

6. IDENTIFIED RESEARCH AND TECHNOLOGY TRANSFER NEEDS

A series of telephone interviews were conducted to elucidate what may be the critical research or technical transfer needs to gain broader acceptance of the use of bioavailability tools for soils and sediment management. Contacts included past and current PIs in the Programs, previous Workshops attendees, and DoD, Federal, and state RPMs. Questions included the understanding of the state of the science in respective organizations, what role bioavailability had in managing contaminated sites, the barriers to using bioavailability tools and measures, and what additional research or technology transfer are needed. The key recommendations from these interviews are summarized below.

6.1 SOILS

Broad support was expressed for an ITRC team on bioavailability of contaminants in soil, to develop guidance on the appropriate methods for different situations and needs, and the issues to consider when designing and interpreting bioavailability testing results. This team focuses on both inorganics and organics, although the current status differs for the two categories of contaminants.

ITRC is particularly useful for technology transfer because it is focused on providing technical guidance for state regulators, and consists of private- and public-sector members from all 50 states. ITRC's goal is to reduce barriers to the use of innovative environmental technologies, and thereby reduce compliance costs and maximize cleanup efficacy (www.itrcweb.org). ITRC produces documents and training that broaden and deepen technical knowledge and expedite quality regulatory decision-making while protecting human health and the environment. Since 1995, ITRC has published hundreds of documents and reached tens of thousands of participants through training courses on hundreds of topics.

The need for regulatory guidance is greatest for As bioavailability, although guidance would also be useful for Pb and other metals. The As research has reached a point where bioavailability testing could make a meaningful difference for some situations, and useful guidance is possible. Many decisions are made at the state level, but few states have the expertise to evaluate proposed bioavailability adjustments. Sanctioned guidance focused on state regulators would be very useful. The key research need in this area is for testing on soils treated to reduce bioavailability, both for Pb and for As.

The work on organics—specifically PAHs—is not as developed, although the researchers are optimistic that reliable correlations of *in vitro* and *in vivo* testing will result from the ongoing work. However, the ongoing work is focused on oral bioavailability, but proposed dermal cancer slope factors may make this pathway less important. Dermal bioavailability work is not as advanced, but it is not yet clear that the proposed factors will be adopted. The team could end up producing credible guidance on the state of the science, but may not have a lot of impact on restoration costs.

6.1.1 Research Needs

6.1.1.1 Validate *In Vitro* Models for Treated Soils

There are some concerns and a lack of data regarding the validity of existing *in vitro* methods for soils treated for Pb and for those treated for As (with either Fe or phosphate).

6.1.1.2 Evaluate Dermal Exposure to PAHs

Develop dose-response relationships for dermal exposure to carcinogenic PAHs, and methods to evaluate dermal bioavailability of carcinogenic PAHs, especially BaP. The need for this work will likely depend on the outcome of the review of currently proposed dermal cancer slope factors.

6.1.2 Technology Transfer Needs

6.1.2.1 Develop Soil Bioavailability Decision Guidance

The soil bioavailability decision guidance should probably be developed through ITRC. The focus of this guidance would be primarily on Pb and As, though discussions of other relevant contaminants should be included. The guidance should include the following topics:

- When should bioavailability be considered?
- What tests are best suited for use given the site-specific conditions (soil types, contaminant forms, exposure scenarios) and objectives?
- What data are needed to make site-specific decisions?
- Summaries of Case Studies where bioavailability has been used
- Summaries of available tests: advantages, limitations, costs, precautions
- Recommended uses of data in site-specific decisions

6.1.2.2 Evaluate the Mouse Model for As and Other Metals

Using mice to measure bioavailability *in vivo* is considerably less expensive than the swine model, which has been used (about $5,000 per soil versus $50,000–$100,000). The mouse model has been validated for As (Bradham et al., 2011; 2013), and is being tested for other metals, notably Cr.

6.2 SEDIMENTS

The 2012 workshop attendees identified a number of critical and high-priority research and demonstrations needs relative to bioavailability. These needs related principally to gaining acceptance of the use of passive samplers in assessing risk and setting remedial goals, and the need to demonstrate the long-term effectiveness of *in situ* amendment additions that sequester contaminants, i.e., reducing the contaminant bioavailability. The 2012 research needs are listed in Table 6-1.

Table 6-1. Identified Research and Demonstration Needs (SERDP, 2012)

	Critical	High
Research	• Improved understanding and use of passive sampling measures in sediments • Improved understanding of off-site source assessment and potential recontamination of sites • Improved assessment of parameters that impact long-term effectiveness of *in situ* amendments and amended caps • Evaluation of confined aquatic disposal for dredged materials • Evaluation of food web models in setting remedial goals and long-term monitoring requirements	• Extension of passive samplers to other contaminants • Tools for measuring facilitated transport in sediment • New approaches for implementing *in situ* amendments or amended caps
Demonstration	• Demonstration of the utility and application of passive samplers • Demonstration of enhanced monitored natural recovery design and operation • Demonstration of long-term efficacy of *in situ* amendments or amended caps • Demonstration of tools to evaluate amendment placement • Development and demonstration of new monitoring tools	• Decision analysis support
Technology Transfer	• State of the science for using AC • MC compendium • Confined aquatic disposal guidance and training • Incorporation of vessel-created erosion into remedy evaluation	

6.2.1 Research Needs

6.2.1.1 Bioaccumulation of HOCs into Shellfish and Fish Consumed by People

RPMs indicated a need to have side-by-side comparisons with not only the standard suite of sediment bioaccumulation organisms (e.g., *Nereis/Macoma/Mya* in marine sediments and *Chironomus/Hyalella/Lumbriculus* in freshwater), but also for the "organisms we are most interested in eating" and the contaminants that regulators are most concerned about (PCB congeners, dioxin/furans, and PAHs) from a human health risk standpoint. Demonstrated correlations of these HOCs of concern with measures from exposures either in laboratory or *in situ* of edible clams and mussels to contaminated sediments was suggested as a research need.

6.2.1.2 Sediments-to-Fish-to-Human Health Risks

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. Regulators stated they are necessarily focused on fish, and it can be difficult to understand how concentrations in a piece of plastic relate to fish tissue concentrations. It is unlikely that passive sampling will displace fish tissue concentrations in the near future, because regulators and the public will remain more comfortable with direct measures of fish tissue.

In the near term, passive sampling measures should be used to demonstrate improved accuracy in bioaccumulation modeling. Sediment cleanups are being driven by remedial action levels (RALs) in bulk sediments that are derived by "back-modelling" from a fish tissue-based chemical concentration estimated to cause and increase in excess lifetime cancer risk. The research and demonstration need is then to have these RALs derived from science-based partitioning values, advective or diffusive flux from sediments to water, and representative time-averaged concentrations of HOCs.

6.2.1.3 Case Studies and Demonstration Projects

Across the interviews, while there was general acceptance that the laboratory research supporting the use of AC as a remedial alternative was promising, there remains a reluctance to make a remedial decision without longer-term monitoring data from AC pilot projects. A near-term product from the Programs could be a report compiling the information from the projects listed in Table 4-1. The information needed include how the design of the project was decided upon; the bench-scale testing done to support the design; the engineering methods used for placement; tools for monitoring; and the results to-date on reductions in uptake of contaminants into benthic infauna, reductions in flux of contaminants through the treated sediments, and whether the AC caused changes to benthic populations (toxicity testing or population surveys).

Pilot demonstration projects are still needed, particularly for contaminants other than PAHs and PCBs. Dioxin/furans and metals were specifically highlighted by several regulators.

6.2.1.4 Metals

The need to be able to assess bioavailability of metals, and possible mechanisms for *in situ* treatment, was listed as a remaining research need.

6.2.1.5 Amendment Treatability Studies

A suggested research need is to standardize *ex situ* amendment treatability studies, and to be able to develop methods for *in situ* studies. Treatability studies are required to determine the type and quantity of an amendment needed to sequester the COCs in the field. These methods often do not reflect the way the treatment will be applied. For example, if the amendment is going to be applied as a top-dressing to the sediments, the study should not mechanically mix the amendment with the sediment. Two potential ways of addressing this would be to either bring intact, multiple, surface-sediment cores from a site into the laboratory, apply the amendment, and observe whether mixing occurs and whether the advective/diffusive flux of the contaminant to the water column has been

mitigated. An alternative would be to take these same cores, preload the amendment into the core column, and place those back out onto the site. Research or demonstration of such tools could serve as a realistic first cut whether a bioavailability remedy will work or not.

6.2.1.6 Bioavailability in Tropical Systems

Despite the importance of sediments at current and former tropical DoD facilities such as Pearl Harbor or Guam, very little work has been done on bioavailability of HOCs or munitions compounds into coral reef habitats, or to the coral itself. Research topics would include not only toxicological effects, but also the uptake pathways (e.g., possible ingestion from re-suspended contaminated sediments).

6.2.1.7 Trophic Linkages/Trophic Forensics

A persistent issue associated with site management and fish bioaccumulation is what the fish are eating and whether the fish as even associated with a specific site. A suggestion was to develop deoxyribonucleic acid (DNA)-based tests that could be used to examine dietary uptake. Currently, the only method to do so would be to collect fish and do gut content analyses based on visual species identification. DNA-based methods could be developed to quickly identify what species are in the diet and the proportion of the diet those species comprise.

6.2.2 Technology Transfer Needs

Many RPMs are becoming increasingly interested in incorporating bioavailability into remedial decision-making. This includes use of passive sampler measures, as well as AC to reduce bioavailability of HOCs in sediments. A consistent theme from the telephone interviews is that good tools have been developed to measure bioavailability, and that there is a growing acceptance of the utility and validity of passive samplers as a tool for long-term monitoring in sediments and aquatic systems (see Section 4.3). What is lacking is a translation of what passive sampler data means to ecological receptors and human health. As stated by one person, there needs to be a quick, easy explanation on why using a synthetic device is more useful than interrogating a biological receptor directly.

As a tool for remedial investigations and remedial decision-making, almost all of the persons interviewed cited three critical barriers: (1) a comprehensive side-by-side comparison between measures made with passive samplers, tissue uptake into benthic organisms, and toxic response; (2) a solid connection between measures of bioavailable HOCs in sediments to concentrations in fish that are consumed by humans; and (3) lack of a standard USEPA or ASTM method with commercial laboratories accredited to conduct these analyses. These issues were also listed as critical research and demonstration needs at the 2012 workshop (see Table 6-1).

6.2.2.1 Benthic Bioaccumulation

The demonstration that the use of passive sampler measures may be used *in lieu* of standard benthic tissue/bioaccumulation studies was identified as both a technical transfer and a research need. Federal and state RPMs acknowledged that there is a large body of scientific literature of concomitant chemical measures in passive sampler measures and those in benthic organisms, but that there is a need to have a single rigorous compilation of this work that is readily accessible by

the regulatory community. To the extent possible, this document should compile all the single passive sampler (PE, POM, SPME) data against single species (e.g., *Nereis/Neanthes* or *Lumbriculus*) uptake. A recent review by Lydy et al. (2014) compiles a listing of the scientific literature to date relating passive sampling and biological update, but does not make the correlative analyses wanted by the regulators.

The Programs have supported work that examined that relationship. Figure 2 compares uptake of PCB congeners into *Neanthes* compared to concentrations in POM, polydimethylsiloxane (PDMS), and PE (Gschwend et al., 2011). While differences are noted between the different passive sampler measures, the paper concludes that in every case, uptake of individual PCB congeners accumulated by polymer sorbents correlated with uptake into this deposit-feeding organism. Figure 3 shows *Neanthes* bioaccumulation of PCBs from Hunters Point sediments (Reible and Lotufo, 2012) measured in PDMS and in lipid-normalized tissue concentrations for both untreated and AC-treated sediments. A compilation of these relationships both from the Program-sponsored studies, as well as those identified in the Lydy et al. (2014) review may serve the identified technical transfer need.

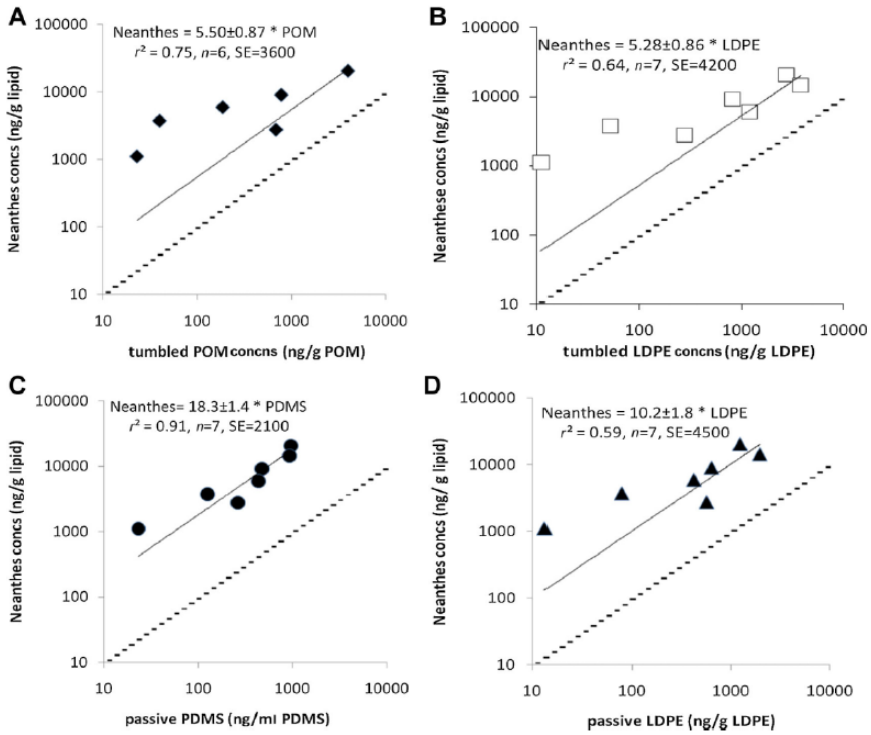

Figure 2. Comparison of concentrations of several congeners (52, 44, 101, 110, 151, 138, and 180) measured in *Neanthes* tissues (lipid normalized) after a 21-d exposure to the Hunter's Point sediment with concentrations found using polymeric samplers. (A) POM strips tumbled with the sediment for 28 d; (B) low density polyethylene (LDPE) strips tumbled with the sediment for 78 and 145 d; (C) polydimethylsiloxane (PDMS)-coated fibers inserted in a static sediment bed for 21 d with loads adjusted for disequilibria; (D) LDPE strips inserted in a static sediment bed for 32 d with loads adjusted for disequilibria (Gschwend et al., 2011).

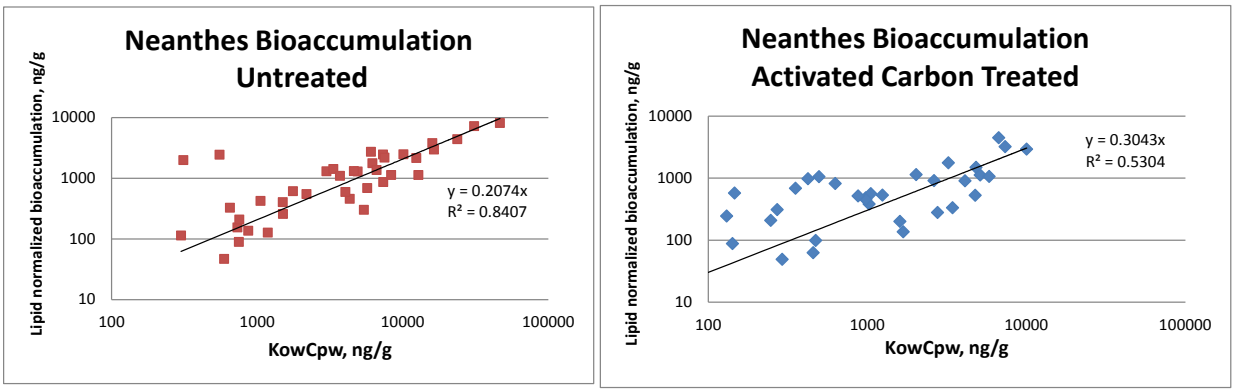

Figure 3. Bioaccumulation as a function of PDMS-measured PCB porewater concentration for both untreated (left) and AC treated (right) microcosms in Hunters Point sediment. (Reible and Lotufo, 2012; ER-200624)

6.2.2.2 Benthic Toxicity Testing

Bioassays are the first line of assessing bioavailability in sediment ecological risk assessment. While these tests do not elucidate which of the chemicals present at a contaminated site are bioavailable and causal on the endpoint being tested, Federal and state regulators view a toxic response as demonstration that the contaminants are bioavailable. However, several regulators expressed interest in evaluating whether passive sampler measures could in some way be correlated with toxic responses.

A consensus view from these discussions is that bioavailability measures of tissue levels in benthic organisms should be tied to toxicity data, and then by extension to benchmark sediment values (e.g., Apparent Effects Thresholds, Sediment Quality Guidelines [SQGs], National Oceanic and Atmospheric Administration [NOAA] Effects Ratios) that are commonly applied in risk assessment and often as remedial action levels. These again could be presented in an interim document summarizing the available data currently in the scientific literature, and also as a stand-alone demonstration project.

The Programs have supported in part these types of comparisons in past projects, and the correlations have been mixed. Figures 4 and 5 are from ESTCP project ER-200709, and compare the relationship between SPME-measured porewater concentrations of the 34 PAHs listed in *Equilibrium Partitioning Sediment Benchmarks (ESBs): PAH Mixtures* (USEPA, 2003) with the toxicity endpoints of survival and growth in the freshwater benthic organism *Hyalella azteca*. For these data collected for sediments at the Washington Navy Yard at Anacostia, MD, and supplemented with data from the industry-based Sediment Bioavailability Contaminant Alliance, there was a reasonable correlation between freely-available total PAH concentrations (expressed as “Toxic Units,” or TUs) and mortality in the freshwater amphipod (Figure 4). However, there was no correlation between growth and porewater total PAH TUs (Figure 5).

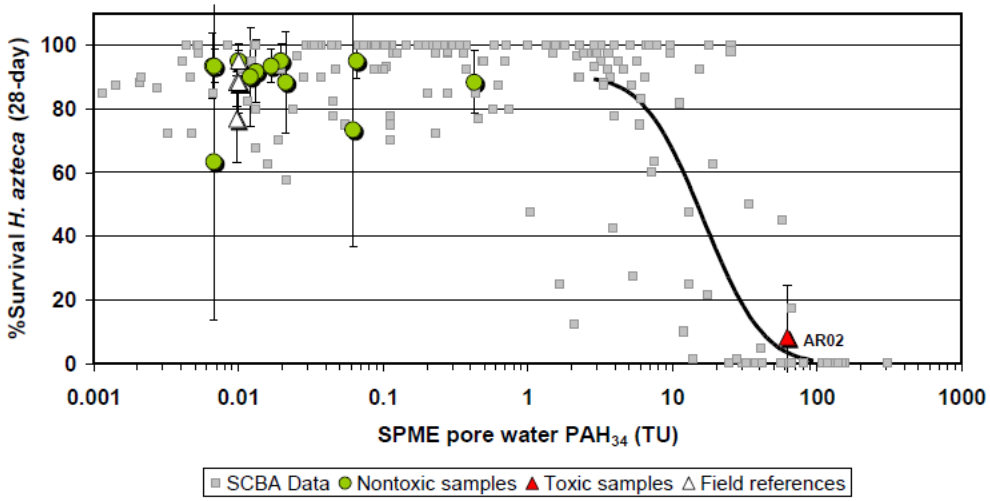

Figure 4. SPME-Measured Porewater Toxic Units (TU) for 34 PAHs Compared to Survival of *H. azteca* (Geiger, 2010; ER-200709).

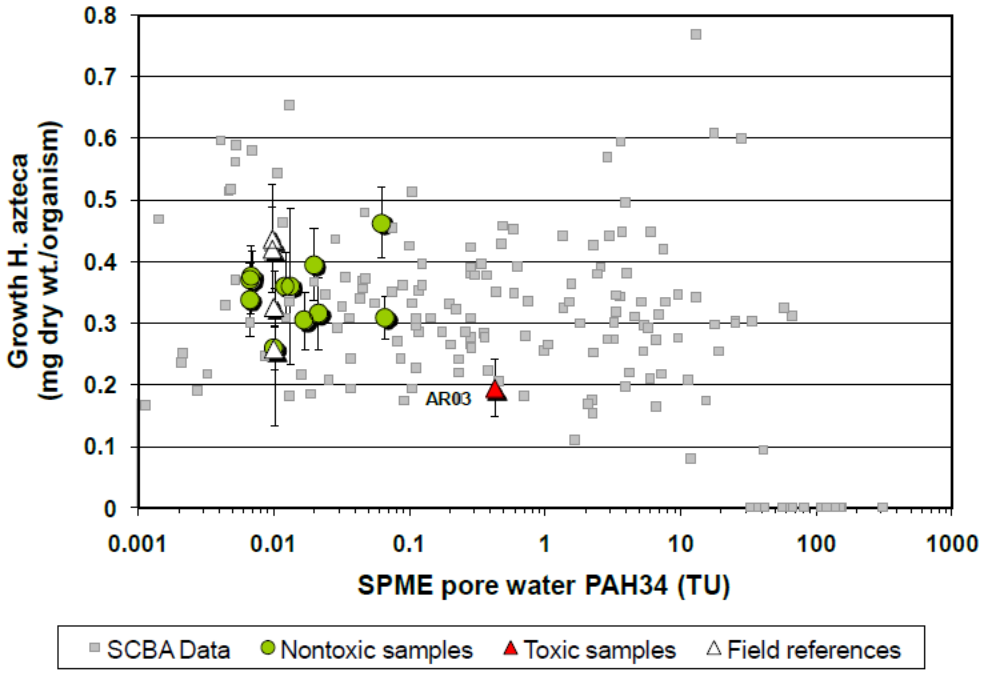

Figure 5. SPME-Measured Porewater Toxic Units (TU) for 34 PAHs Compared to Growth of *H. Azteca* (Geiger, 2010; ER-200709).

What these data do illustrate is the research need for comparing measured concentrations with toxicity testing results, especially as those relate to SQGs. SQGs, as a benthic toxicity guideline, are developed based on co-occurrence of toxicity response and the presence of a contaminant measured in bulk sediments. These mechanistic guidelines are not based on science, but have become "enshrined" in state rules and have driven cleanup at DoD sites (von Stackelberg et al.,

2008). The toxicity responses shown in Figures 4 and 5 would support a PAH cleanup value much higher than the current SQGs.

6.2.2.3 Standard Methods for Passive Sampler Deployment and Analyses

To be accepted as a measure at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), or state-lead sites, there needs to be standardized methods (USEPA or ASTM) with rigorous quality assurance/quality control (QA/QC) criteria, SOPs, demonstrated precision and reproducibility, and low detection limits that could be compared to porewater measures that have been estimated to either be protective of human health or background—typically in the pictogram range. Multiple laboratories that are accredited to conduct this work, with accreditation through an organization such as the DoD Environmental Data Quality Group, the National Environmental Laboratory Accreditation Program (NELAP), or the California Environmental Laboratory Accreditation Program, are needed. As one responder from the telephone interviews put it:

> *"A big barrier to use is that the methods are not standardized (i.e., USEPA or ASTM), and that there are not a number of accredited commercial labs doing this work. End users do not want to go to the universities to have this done; there needs to be a method that is "off-the-shelf," has appropriate QA/QC, and that can produce comparable numbers across the different laboratories. Without a "price" and a "part number," acceptance will be limited."*

7. CONCLUSIONS

Bioavailability has been an important SERDP and ESTCP initiative for over a decade. The research has had a major impact on sediment management, but so far it has had a lesser impact on contaminated soils.

For soils, SERDP's bioavailability research has focused primarily on development of *in vitro* tests to measure the bioavailability of Pb and As, and to a lesser extent, PAHs, munitions, and Sb. A validated *in vitro* assay for human oral exposure to Pb has been developed, and similar tests for As have been developed and are near validation. In addition, work is ongoing to develop site-specific tests for measuring the oral bioavailability of PAHs to humans. Finally, methods have been developed to measure bioavailability in soils for PAHs, munitions (TNT and RDX), and some metals (Cd, Pb, As, and Zn), and these results have been used to establish Eco-SSLs. Despite these advances, regulatory acceptance and use of bioavailability testing remains limited so far.

For sediments, the research has focused primarily on PCBs and other HOCs. In particular, the objectives have been to develop and demonstrate both passive samplers capable of measuring the freely-dissolved porewater concentrations cost-effectively, and to develop and validate remediation technologies based on reducing bioavailability. SERDP and ESTCP have been instrumental in the development and field testing of several passive samplers designed to measure the bioavailable fraction of the total contaminant mass. These samplers have been increasingly adopted for sediment site characterization, and there has been a scientific consensus that these passive samplers are effective. Remediation of sediments through the addition of organic carbon amendments to reduce bioavailability has proven effective. Finally, bioavailability information is an important component of MNR, and MNR guidance funded by the Programs has become an accepted strategy for managing sediment contamination.

Future research and technology transfer needs for soils include: (1) validate the current *in vitro* assays for Pb and As in untreated soils for use in soils that have been treated to reduce bioavailability; and (2) develop dose-response relationships for dermal exposure, particularly to carcinogenic PAHs. The technology transfer recommendations include: (1) develop soil bioavailability decision guidance, preferably through the ITRC team; and (2) foster use of the relatively inexpensive mouse model for *in vivo* testing for As and possibly other metals.

Future needs for sediments include: (1) better understanding of passive sampling techniques to evaluate bioavailability; (2) extension of passive samplers to a broader range of contaminants; and (3) demonstration of the long-term efficacy of amendments designed to contain or treat the bioavailable contaminants. The technology transfer recommendations include: (1) gain acceptance of the use of passive samplers in assessing risk and setting remedial goals; (2) demonstrate the long-term effectiveness of *in situ* amendments such as AC that can sequester contaminants in unavailable forms; and (3) develop a state of the science compendium on the use of AC to reduce bioavailability.

In summary, SERDP and ESTCP have made considerable progress in extending the fundamental science of bioavailability into risk assessment and site management. This work has improved assessments of Pb- and As-contaminated soils, and of sediments contaminated with hydrophobic organics, notably PCBs. However, more work is needed to extend the research to other contaminants and conditions, to foster adoption of reasonable site-specific bioavailability

adjustments, and to assist in developing credible guidance to help regulators and practitioners considering the use of bioavailability in site decision-making.

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Appendix A SERDP and ESTCP Bioavailability-Related Projects

Bioavailability of Contaminants in Soils

ER-1165, Development of Extraction Tests for Determining the Bioavailability of Metals in Soil, Yvette Lowney (Exponent) (ESTCP) (Completed 2005)

ER-1166, Quantifying the Bioavailability of Toxic Metals in Soils, Philip Jardine (University of Tennessee) (SERDP) (Completed 2003)

ER-1210, Determining the Bioavailability, Toxicity, and Bioaccumulation of Organic Chemicals and Metals for the Development of Eco-SSLs, Roman Lanno (Ohio State University) (SERDP) (Completed 2005)

ER-1416, Development of Toxicity Benchmarks and Bioaccumulation Data for N-Based Organic Explosives for Terrestrial Plants and Soil Invertebrates, Geoffrey Sunahara (NRC – Canada) (SERDP) (Completed 2013)

ER-1742, Mechanisms and Permanence of Sequestered Lead and Arsenic in Soils: Impact on Human Bioavailability, Nick Basta (Ohio State University) (ESTCP) (In progress)

ER-1743, PAH Interactions with Soil and Effects on Bioaccessibility and Bioavailability to Humans, Yvette Lowney (Exponent) (SERDP) (In progress)

ER-1770, Lead and Antimony Speciation in Shooting Range Soils: Molecular Scale Analysis, Temporal Trends, and Mobility, Thomas Trainor (University Alaska Fairbanks) (ESTCP) (In progress)

ER-200020, PIMS - Remediation of Soil and Groundwater Contaminated with Metals, Judith Wright (PIMS NW) (ESTCP) (Completed 2006)

ER-200222, Validation of a Rapid and Low-Cost Method for Prediction of the Oral Bioavailability of Lead from Small Arms Range Soils, Demond Bannon (USACHPPM) (ESTCP) (Completed 2007)

ER-200517, The Effect of Soil Properties on Decreasing Toxic Metal Bioavailability: Field Scale Validation to Support Regulatory Acceptance, Amy Hawkins (NAVFAC) (ESTCP) (Completed 2014)

ER-200916, Validation of an In Vitro*In Vitro* Bioaccessibility Test Method for Estimation of Bioavailability of Arsenic from Soil and Sediment, Susan Griffin (EPAUSEPA) (ESTCP) (Completed 2013)

Bioavailability of Contaminants in Sediments

ER-1095, Assessment & Prediction of Biostabilization of PAHs in Sediment, Jeff Talley (U.S. Army ERDC-EL) (SERDP) (Completed 2001)

ER-1494, An Integrated Field and Laboratory Study of the Bioavailability of Metal Contaminants in Sediments, Nick Fisher (Stonybrook University) (SERDP) (Completed 2012)

ER-1496, Using Passive Polyethylene Samplers to Evaluate Chemical Activities Controlling Fluxes and Bioaccumulation of Organic Contaminants in Bed Sediments, Philip Gschwend (MIT) (SERDP) (Completed 2011)

ER-1503, Biological Processes Affecting Bioaccumulation, Transfer, and Toxicity of Metal Contaminants in Estuarine Sediments, Celia Chen (Dartmouth College) (SERDP) (Completed 2011)

ER-1744, Bioavailability and Methylation Potential of Mercury Sulfides in Sediments, Heileen Hsu-Kim (Duke University) (SERDP) (Completed 2014)

ER-1745, Coupling between Pore Water Fluxes, Structural Heterogeneity & Biogeochemical Processes Controls Contaminant Mobility, Bioavailability, & Toxicity in Sediments, Aaron Packman (Northwestern University) (SERDP) (Completed 2016)

ER-1746, Predicting the Fate and Effects of Resuspended Metal Contaminated Sediments, Allen Burton (University of Michigan) (SERDP) (In Progress)

ER-1747, Robust Means for Estimating Black Carbon-Water Sorption Coefficients of Organic Contaminants in Sediments, Philip Gschwend (MIT) (SERDP) (Completed 2015)

ER-1748, Development of an Electrochemical Surrogate for Copper, Lead, and Zinc Bioaccessibility in Aquatic Sediments, Aaron Slowey (U.S. Geological Survey) (SERDP) (Completed 2011)

ER-1750, The Biology of Bioavailability: The Role of Functional Ecology in Exposure Processes, Todd Bridges (U.S. Army ERDC-EL) (SERDP) (In Progress)

ER-1771, Assessing Mercury and Methylmercury Bioavailability in Sediment Porewater Using Mercury-Specific Hydrogels, Victor Magar (Environ) (SERDP) (Completed 2015)

ER-200624, Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility, Danny Reible (University of Texas) (ESTCP) (Completed 2012)

ER-200709, The Determination of Sediment Polycyclic Aromatic Hydrocarbon (PAH) Bioavailability using Supercritical Fluid Extraction (SFE) and Ultra-Trace Porewater (UTP) Analysis, Dave Nakles (RETEC) (ESTCP) (Completed 2010)

ER-200915, Passive PE Sampling in Support of *In Situ* Remediation of Contaminated Sediments, Philip Gschwend (MIT) (ESTCP) (Completed 2015)

ER-201216, Sediment Bioavailability Initiative (SBI): Development of Standard Methods and Approaches for the Use of Passive Samplers in Assessment and Management of Contaminated Sediment, Charlie Menzie (Exponent) (ESTCP) (Completed 2016)

In Situ Treatment

Amendments

Soils

ER-1350 Decreasing Toxic Metal Bioavailability with Novel Soil Amendment Strategies, Philip Jardine (University of Tennessee) (SERDP) (Completed 2007)

ER-1351, Soil Amendments to Reduce Bioavailability of Metals in Soils: Experimental Studies and Spectroscopic Verification, Katherine Banks (Purdue University) (SERDP) (Completed 2008)

ER-1352, Facilitated Immobilization of Heavy Metals in Soil by Manipulation with Plant Byproducts, Teresa Fan (University of Louisville) (SERDP) (Completed 2004)

Sediments

ER-1207, *In Situ* Stabilization of Persistent Organic Contaminants in Marine Sediments, Dick Luthy (Stanford University) (SERDP) (Completed 2004)

ER-1208, *In-Situ* Enhancement of Anaerobic Microbial Dechlorination of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Marine and Estuarine Sediments, Max Haggblom (Rutgers University) (SERDP) (Completed 2006)

ER-1491, Rational Selection of Tailored Amendment Mixtures and Composites for *In Situ* Remediation of Contaminated Sediments, Upal Ghosh (University of Maryland, Baltimore County) (SERDP) (Completed 2009)

ER-1492, Quantifying Enhanced Microbial Dehalogenation Impacting the Fate and Transport of Organohalide Mixtures in Contaminated Sediments, Max Haggblom (Rutgers University) (SERDP) (Completed 2013)

ER-200510, Field Testing of Activated Carbon Mixing and *In Situ* Stabilization of PCBs in Sediment, Dick Luthy (Stanford University) (ESTCP) (Completed 2009)

ER-200825, *In Situ* Wetland Restoration Demonstration, Amy Hawkins (NAVFAC EXWC) (ESTCP) (Completed 2014)

ER-200835, Evaluating the Efficacy of a Low-Impact Delivery System for In-Situ Treatment of Sediments Contaminated with Methylmercury and Other Hydrophobic Chemicals, Charlie Menzie (Exponent) (ESTCP) (Completed 2015)

ER-201131, Demonstration of In-Situ Treatment with Reactive Amendments for Contaminated Sediments in Active DoD Harbors, Bart Chadwick (U.S. Navy SPAWAR Systems Center) (ESTCP) (In Progress)

ER-201215, Evaluating the Efficacy of Bioaugmentation for In-Situ Treatment of PCB Impacted Sediments, Kevin Sowers (University of Maryland, Baltimore County) (ESTCP) (In Progress)

ER-201580, Long-Term Stability and Efficacy of Historic Activated Carbon (AC) Deployments at Diverse Freshwater and Marine Remediation Sites, Todd Bridges (U.S. Army ERDC) (ESTCP) (In Progress)

ER-201639, Application of an *In Situ* PCB Removal Technique for Contaminated Sediments, Joey Trotsky (Naval Facilities Engineering Command) (ESTCP) (In Progress)

ER-2134, A Permeable Active Amendment Concrete (PAAC) for Contaminant Remediation and Erosion Control, Anna Knox (Savannah River National Laboratory) (Completed 2013)

ER-2135, Application of Biofilm Covered Activated Carbon Particles as a Microbial Inoculum Delivery System for Enhanced Bioaugmentation of PCBs in Contaminated Sediment, Birthe Kjellerup (University of Maryland, College Park) (In Progress)

ER-2136, Activated Biochars with Iron for *In Situ* Sequestration of Organics, Metals, and Carbon, Upal Ghosh (University of Maryland, Baltimore County) (Completed 2012)

Active Caps

ER-1370, Characterization of Contaminant Migration Potential through In-Place Sediment Caps, Victor Magar (Battelle) (SERDP) (Completed 2009)

ER-1371, Integrating Uncertainty Analysis in the Risk Characterization of In-Place Remedial Strategies for Contaminated Sediments, Peter Adriaens (University of Michigan) (SERDP) (Completed 2009)

ER-1493, Reactive Capping Mat Development and Evaluation for Sequestering Contaminants in Sediments, Amy Hawkins (NAVFAC ESC) (SERDP) (Completed 2010)

ER-1501, Innovative In-Situ Remediation of Contaminated Sediments for Simultaneous Control of Contamination and Erosion, Anna Knox (Savannah River National Laboratory) (SERDP) (Completed 2011)

ER-2427-14, Understanding the Relationships Among Low Level Metal Influx, Remediated Sediments, ad Biological Receptors, Anna Knox (Savannah River National Laboratory) (SERDP) (In Progress)

Ecological Risk Characterization

ER-1129, Biological Assessment for Characterizing Contaminant Risk of Military Unique Compounds at the Genetic-, Individual-, Population-Level, Todd Bridges (U.S. Army ERDC-EL) (SERDP) (Completed 2002)

ER-1158, Speciation, Sources and Bioavailability of Copper and Zinc in DoD-Impacted Harbors and Estuaries, Martin Shafer (University of Wisconsin) (SERDP) (Completed 2007)

ER-1550, Sediment Ecosystem Assessment Protocol (SEAP): An Accurate and Integrated Weight-of-Evidence Based System, Allen Burton (University of Michigan) (SERDP) (Completed 2011)

ER-1552, Measurement and Modeling of Ecosystem Risk and Recovery for *In Situ* Treatment of Contaminated Sediments, Dick Luthy (Stanford University) (SERDP) (Completed 2015)

ER-201130, Demonstration and Commercialization of the Sediment Ecosystem Assessment Protocol (SEAP), Gunther Rosen (U.S. Navy SPAWAR Systems Center) (ESTCP) (In Progress)

ER-2125, Ecological Risk Assessment of Munitions Compounds on Coral and Coral Reef Health, Cheryl Woodley (NOAA) (SERDP) (Completed 2014)

ER-2428-14, Assessment and Management of Stormwater Impacts on Sediment Recontamination, Danny Reible (Texas Tech University) (SERDP) (In Progress)

Munitions Constituents

ER-1129, Biological Assessment for Characterizing Contaminant Risk of Military Unique Compounds at the Genetic-, Individual-, Population-Level, Todd Bridges (U.S. Army ERDC-EL) (SERDP) (Completed 2002)

ER-1221, Development of Ecological Toxicity and Biomagnification Data for Explosives Contaminants in Soil, Roman Kuperman (USAECBC) (SERDP) (Completed 2003)

ER-1431, Biotic and Abiotic Attenuation of Nitrogenous Energetic Compounds (NEC) in Coastal Waters and Sediments, Mike Montgomery (U.S. Naval Research Laboratory) (SERDP) (Completed 2008)

ER-1453, Defining Munitions Constituents (MC) Source Terms in Aquatic Environments on DoD Ranges, Bill Wild (U.S. Navy SPAWAR Systems Center) (SERDP) (Completed 2013)

ER-2122, Tracking the Uptake, Translocation, Cycling, and Metabolism of Munitions Compounds in Coastal Marine Ecosystems Using Stable Isotopic Tracer, Craig Tobias (University of Connecticut) (SERDP) (In Progress)

ER-2123, Photochemical Transformation of Munitions Constituents in Marine Waters, Dianne Luning Prak (US Naval Academy) (SERDP) (Completed 2012)

ER-2124, TNT Incorporation and Mineralization by Natural Microbial Assemblages at Frontal Boundaries Between Water Masses and in Underlying Sediments in Coastal Ecosystems, Mike Montgomery (U.S. Naval Research Laboratory) (SERDP) (In Progress)

ER-2125, Ecological Risk Assessment of Munitions Compounds on Coral and Coral Reef Health, Cheryl Woodley (NOAA) (SERDP) (Completed 2014)

ER-2341 Review and Synthesis of Evidence Regarding Environmental Risks Posed by Munitions Constituents (MC) in Aquatic Systems, Todd Bridges (USACE ERDC) (SERDP) (In Progress)