APPENDIX 21-E

EVALUATING BIOACCUMULATIVE CHEMICALS

Evaluation of Risks of Bioaccumulative Chemicals

A bioaccumulative chemical is one that is taken up and retained for some duration by a living organism; the chemical may or may not have a measurable adverse effect on the organism in which it is measured. Once an organism incorporates a chemical into its tissues, the organism becomes a secondary source of contamination to other organisms that feed on it.

The terms bioconcentration, bioaccumulation, and biomagnification are sometimes used interchangeably in the literature; however, each describes a specific process, as described below (based on USEPA 2000i).

- **Bioconcentration** – the process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g., by gill or epithelial tissue) and elimination.

- **Bioaccumulation** – the accumulation of a chemical in the tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, or sediment pore water.

- **Biomagnification** – the net result of the process of bioconcentration and bioaccumulation by which tissue concentrations of bioaccumulated chemicals increase as the chemical passes up through two or more trophic levels. The term implies an efficient transfer of chemicals from food to consumer, so that residue concentrations increase systematically from one trophic level to the next. (The movement of contaminants from prey to predator is called trophic transfer.)

Chemicals known to bioaccumulate may also cause direct toxicity to organisms exposed through simple ingestion or direct contact with sediment or water. For example, some invertebrates are adversely affected by direct exposure to copper in water and sediment. Organisms that are less susceptible to direct effects may survive and grow, incorporating the copper into their tissues. At some tissue concentration, which may be well above the sediment concentration the organism was initially exposed to, the accumulated copper may begin to exert a toxic effect on the organism. Additionally, the organism (and its tissue burden of copper) has become a concentrated source of copper to its predator. Thus, copper must be evaluated for both its direct effects and as a bioaccumulating chemical. The relative importance of direct effects versus effects resulting from bioaccumula-
tion varies by species and chemical, as some species are capable of regulating, transforming, or eliminating some chemicals.

Most sources agree on the basic list of bioaccumulative chemicals derived from decades of empirical evidence (see Table 21-7). Several metals (arsenic, copper, lead, mercury, and zinc); most if not all organochlorine pesticides (DDT, chlordane, endrin, dieldrin); PCBs; dioxins/furan; and some PAHs are considered bioaccumulative under most circumstances and are included as such in this guidance.

These bioaccumulative chemicals share several traits: (1) hydrophobicity (excluding metals); (2) log K_{ow} > 3.5; (3) documented tissue concentrations under many environmental conditions; and (4) empirical evidence of toxicological effects of tissue concentrations (ODEQ 2017; USACE et al. 2016). Note that it is possible, although unlikely, to measure elevated concentrations of a bioaccumulative chemical in tissues without detecting the chemical in collocated sediment or water samples. This could occur under conditions of high bioavailability of the chemical in the sediment or water, coupled with high laboratory detection limits. Alternatively, the organism could have accumulated the chemical from a different location. The HEER Office ERA Guidance is designed to identify areas where risk is likely, and so focuses on sediment sites with measurable concentrations of target contaminants.

Predicting the bioaccumulative potential of a chemical not listed in any of the references cited below is less straightforward and subject to nuances of chemistry and physiology. The risk assessor is responsible for designating the bioaccumulation potential of each chemical detected at the site and providing rationale for the designation. Generally, all chemicals on Table 21-7 are considered bioaccumulators, and any other chemical with a log K_{ow} greater than 3.5 must be discussed with the HEER Office (note that log K_{ow} is not a reliable predictor of bioaccumulation for organotins).

Suggested references for developing a list of bioaccumulative chemicals include Beyer et al., 2011; Hoffman 2007; ODEQ 2017; Northwest Regional Sediment Evaluation Team (RSET 2016); USEPA 2000i.

Steps for Evaluating Risks of Bioaccumulative Chemicals

The SLERA (described in Section 21) evaluated direct effects of bioaccumulating chemicals. If the direct effects are nonlethal and the organism incorporates the chemical into its tissues, indirect effects may occur. This subsection describes the process of evaluating risk of bioaccumulating chemicals within the tissues of living organisms, both to the organism itself and to its predators. The evaluation of such indirect effects of bioaccumulating chemicals is more complex because the physiology of the target organisms must be taken into account.

The HEER Office encourages the risk assessor to use existing information to the extent possible, and to conduct a focused field investigation when necessary to fill gaps in essential data. Close coordination with the HEER Office will ensure that data collection efforts are appropriate to support an ERA. The eight steps below describe essential components of the ERA for bioaccumulating chemicals. However, each ERA is necessarily tailored to an individual site.

- Step 1 – Identify Potential Bioaccumulative Chemicals
Step 2 – Determine Likely Exposure Pathways

Step 3 – Compare Site-Specific Concentrations with Background/Reference/Ambient Concentrations

Step 4 – Compile Screening Level Data for Bioaccumulating Chemicals

Step 5 – Compile Toxicity Reference Values (TRV)

Step 6 – Identify Chemicals of Potential Ecological Concern (COPEC)

Step 7 – Determine the Need for Additional Information

Step 8 – Conduct a Site-Specific Bioaccumulation Investigation

Step 1 – Identify Potential Bioaccumulative Chemicals

The ERA Scoping Checklist requests information on chemicals detected or suspected at the site, and asks whether any of the chemicals are bioaccumulative. If any chemicals listed in Tables 21 B-1 or 21 B-3 are known to bioaccumulate (based on Table 21-7 or other source), then it is necessary to complete this evaluation.

If the bioaccumulative status of any chemical at the site is unknown, the risk assessor should use the published literature to determine the potential bioaccumulative properties of the chemical. For example, the Technical Support Document for Revision of the Dredged Material Management Program Bioaccumulative Chemicals of Concern List (Hoffman 2007) provides four groups of chemicals with shared bioaccumulative properties:

- List 1 – Primary Bioaccumulative Chemicals of Concern (Table 9 in Hoffman 2007)
- List 2 – Candidate Bioaccumulative Contaminants (Table 10 in Hoffman 2007)
- List 3 – Potentially Bioaccumulative Contaminants (Table 11 in Hoffman 2007)
- List 4 – Not Currently Considered Bioaccumulative Contaminants (Table 12 in Hoffman 2007)

Although some of the discussion of chemicals in Hoffman (2007) pertains to regional ambient concentrations, most of the logic for identifying bioaccumulating chemicals is relevant to marine sediments sites in Hawai‘i.

The Northwest Regional Sediment Evaluation Team, (RSET 2016) modified the lists in Hoffman (2007) to remove some of the metals that are not known to occur in organic forms. The chemicals on Lists 1, 2, and 3 in Appendix C of Northwest Regional Sediment Evaluation Team, (RSET 2016) provide a reasonable starting point for evaluating chemicals not on Table 21-7 of the HEER Office guidance. New chemicals should be considered bioaccumulative based on the following considerations:

- A site-related chemical not included on any of the lists discussed above should be considered bioaccumulative if
  - its Log $K_{ow}$ is greater than 3.5; or
it has been demonstrated to bioaccumulate in living organisms.

Step 2 – Determine Likely Exposure Pathways

The exposure pathways should have been described in the conceptual site model (CSM) during a previous phase of the ERA. The exposure pathways for bioaccumulating chemicals may be refined at this time to focus on the likely routes of uptake by target receptors. Note that some information on diet and sediment ingestion is included in the species profiles in Appendix 21A. The risk assessor should supplement the information using the published literature as needed.

Step 3 – Compare Site-Specific Concentrations with Background/Reference/Ambient Concentrations

The uncertainty associated with evaluating bioaccumulating chemicals stems in part from the complexity of trophic transfer, which includes processes that are difficult to measure or observe, including uptake, biotransformation, sequestration, depuration, and excretion. In most cases, measuring in-situ trophic transfer is beyond the scope of an ERA. Modeling necessarily relies on conservative assumptions, which drives the protective screening level toward zero. It is not uncommon for a calculated screening level to be lower than background/ambient/reference concentrations, calling into question the legitimacy of the ERA. Rather than allow conservative exposure assumptions of BCFs, BSASFs, and toxicity thresholds to drive the ERA, the HEER Office recommends first refining the list of bioaccumulative chemicals by comparing site concentrations with background/ambient/reference concentrations.

The HEER Office is currently compiling background/ambient/reference concentrations of sediment and tissue from published reports across Hawai‘i. Ideally, the risk assessor will be able to search the database by habitat, chemical, species, and other variable to locate sediment and tissue concentrations considered representative of background/ambient/reference concentrations. Until that database is available, the risk assessor should discuss the need for collecting background/ambient/reference samples as part of the ERA.

In general, a minimum of three background/ambient/reference samples should be collected during the site-specific investigation. The samples should be collected from an area with similar sediment and wave energy that is believed not to be impacted by the chemicals under investigation at the site or any direct chemical release. The proposed reference locations should be discussed with the HEER Office early in the process to ensure that the samples are acceptable and representative.

Step 4 – Compile Screening Level Data for Bioaccumulating Chemicals

Evaluation of bioaccumulating chemicals may include comparing site-specific concentrations in tissue, sediment, and water with regional reference areas and/or toxicity-based screening levels, as described below. The risk assessor should compile information relevant to the site based on habitat, species, and chemicals. Include bioaccumulation factors, laboratory bioaccumulation tests, and other available information to provide regional context for the site.

Tissue Screening Level: Critical Body Residues
A critical body residue is a chemical concentration in a tissue (or whole body) that is considered protective of the receptor that accumulates the chemicals through exposure to sediment, water, and/or prey. As described below for sediment screening levels for bioaccumulating chemicals, CBRs taken from the published literature may or may not be appropriate for use at coastal marine sites in Hawai‘i. The use of CBRs in ERAs is relatively undeveloped and heavily reliant on temperate North American species and locations. The process of deriving CBRs described in Appendix E of Northwest Regional Sediment Evaluation Team, *(RSET 2016)* is technically sound, but the resulting values are not necessarily appropriate for sites in Hawai‘i. Moreover, in many cases back-calculating protective sediment concentrations from CBRs yields sediment screening levels that are lower than ambient concentrations. The HEER Office does not support any method that results in suggesting remediation of sediments that are already within background concentrations.

In lieu of adopting CBRs from temperate sites, the HEER Office recommends that site-specific tissue concentrations be compared with concentrations from either a pre-approved local reference location or from published studies in Hawai‘i. The species profiles presented in Appendix 21A provide some data on tissue concentrations reported in other studies. The HEER Office continues to collect and compile relevant data from across the state to support this element of the ERA Program.

**Sediment Screening Levels for Bioaccumulating Chemicals**

The sediment screening level for a bioaccumulating chemical is a concentration in sediment considered to pose little to no risk to ecological receptors exposed to the sediment. At concentrations less than the screening level, bioaccumulation is expected to be low enough to allow the receptor to live in the sediment without experiencing adverse effects caused by bioaccumulation of the chemical. In principle, the screening level concentrations in sediment should ensure that the receptor would not bioaccumulate the chemical to concentrations greater than the CBR of any target receptor.

Development of a sediment screening level for a bioaccumulating chemical requires that a biota-sediment accumulation factor (BSAF) be used to model the accumulation of the chemical in an organism based on the sediment concentration. Although theoretically possible, development of BSAFs is a complicated process that is influenced by numerous factors such as the developmental stage, age, sex, reproductive state, and condition of the receptor; physico-chemical features of the sediment such as organic carbon content, pH, salinity, redox, and temperature; and the form of the chemical present in the sediment. BSAFs reported in the literature can vary widely and are not reliably transferred from one site to another, especially from temperate fluvial habitats to tropical marine habitats. Few BSAFs are available for species and habitats in Hawai‘i. For these reasons, the HEER Office does not recommend the use of literature-based BSAFs to estimate tissue concentrations unless the BSAF was derived from a regionally-appropriate study. Therefore, the HEER Office is not providing sediment screening levels for bioaccumulating chemicals at this time. The risk assessor may conduct studies as needed to develop site-specific BSAFs or measure tissue concentrations directly at the site.

**Surface Water Screening Levels**
Surface water screening levels for bioaccumulating chemicals are similar to the sediment screening levels described above. Development of a surface water screening level for a bioaccumulating chemical requires that a bioconcentration factor (BCF) be used to model the accumulation of the chemical in an organism based on the concentration in surrounding water. However, species and site-specific water quality conditions (pH, temperature, conductivity, and other water quality parameters) influence the value of the BCF. Moreover, most bioaccumulative chemicals are hydrophobic (not water soluble) and are not often detected in surface water. The dynamic movement of water, especially in coastal Hawai‘i, further complicates the link between water concentrations and tissue concentrations. Finally, chemical concentrations in surface water are spatially and temporally more variable than in sediment, as water is influenced by rainfall, suspended and dissolved solids, and other factors. The HEER Office does not provide surface water screening levels for bioaccumulating chemicals. The risk assessor may provide literature supporting the use of existing BCFs at the site or propose site-specific studies in support of BCF derivation.

**Step 5 – Compile Toxicity Reference Values**

A TRV is a chemical dose, given in mg of chemical per kg body weight per day; it is used to evaluate risk to a receptor ingesting bioaccumulative chemicals in sediment, water, and prey. Most TRVs are derived from laboratory studies of a few standard test species measuring effects on growth, reproduction, and mortality. Although the ideal TRV is specific to a chemical-receptor pair that occurs at the site, data limitations generally require the risk assessor to apply a general TRV to an entire class of receptors, such as birds or mammals. The HEER Office has compiled TRVs for some receptors and chemicals (see Appendix 21-A). The risk assessor is responsible for reviewing the available information and supplementing it as needed with current toxicological data from the published literature. The risk assessor should prepare a list of proposed TRVs, with rationale, for review by the HEER Office.

**Step 6 – Identify Chemicals of Potential Ecological Concern (COPEC)**

The decision process below should be applied to each chemical separately to identify which bioaccumulating chemicals will be retained as chemicals of potential ecological concern (COPEC) for further evaluation in the ERA.

- Are site sediment concentrations greater than background/ambient/reference concentrations?
  - If no, the chemical is not retained as a COPEC.
  - If yes, the chemical is retained as a COPEC.
  - If no background/ambient/reference concentrations are available, the chemical is retained as a COPEC and additional investigation may be required. Consult with the HEER Office.

- Are site tissue concentrations greater than background/ambient/reference concentrations?
  - If no, the chemical is not retained as a COPEC.
  - If yes, the chemical is retained as a COPEC.
If no background/ambient/reference concentrations are available, the chemical is retained as a COPEC and additional investigation may be required. Consult with the HEER Office.

- Are site tissue concentrations greater than all CBRs?
  - If no, the chemical is not retained as a COPEC.
  - If yes, the chemical is retained as a COPEC.
  - If no CBRs are available, the chemical is retained as a COPEC and additional investigation may be required. Consult with the HEER Office.

Note that this decision process will be modified if and when screening levels for bioaccumulating chemicals in sediment and surface water become available.

**Step 7 – Determine the Need for Additional Information**

To proceed with the ERA for bioaccumulating chemicals, the following information is required:

- List of COPECs (specific to each receptor or group of receptors)
- Exposure point concentration for each COPEC in each medium (sediment, prey items)
- CBRs for target receptors
- TRVs for target species-chemical pairs (for example marine mammal – PCBs)
- Values for key exposure parameters for target receptors, such as body weight, ingestion rates for food and sediment, diet, site use factors, and others (see Subsection 21.3.4.3)

If any of the information above is unavailable and cannot be estimated using literature values relevant to Hawai‘i, additional site-specific work may be required before the ERA can be completed.

**Step 8 – Conduct a Site-Specific Bioaccumulation Investigation**

When a bioaccumulating chemical is present at a site at concentrations greater than regional background/ambient/reference concentrations, the most efficient way to evaluate risk of the chemical is to measure its bioaccumulation in target receptors at the site that have small home ranges (if the receptors are not legally protected). If site-specific tissue cannot be obtained, tissue concentrations may be estimated using concentrations in sediment and BSAFs, when available. Alternatively, laboratory bioaccumulation tests of site sediment samples can provide tissue concentrations and BSAFs for benthic invertebrates. A detailed sampling and analysis plan should be submitted to the HEER Office for review to ensure that any field sampling effort addresses the necessary requirements for an ERA. At a minimum, the following components of field sampling should be addressed in the sampling and analysis plan:

**Sediment Sampling**

- Depth of samples (should reflect exposure of target receptors)
- Number of sediment samples (minimum = 5)
Multi Increment sampling (MIS) and decision unit (DU) design (see Appendix 21-C and TGM Sections 3, 4, and 5).

**Biota Sampling**

- Target receptors (should be relevant to CSM and linked to existing reference data, if possible)
- Rationale for selection of species (e.g. small home range, known to accumulate the chemical, availability of background/ambient/reference tissue concentrations, etc.)
- Number of samples (minimum = 5 site; 3 reference)
- Sample composition: composite vs individuals; age; sex; size/length; reproductive condition
- Sample processing methods (e.g. whole body, specific organs, muscle only, etc.)
- Seasonal considerations
- MIS and DU considerations
- Chemical/physical analyses; percent moisture; percent lipid

**Laboratory Bioaccumulation Study**

- Number of samples (minimum = 7 site)
- Method for selecting samples (ensure a concentration gradient)
- Test species relevant to Hawaiʻi (e.g. *Neanthes arenaceodentata* polychaete)
- Method for calculating the BSAF
- Duration of test
- Sample processing methods (depuration)
- MIS and DU considerations
- Chemical/physical analyses of sediment and tissue; percent moisture and percent lipid in tissue