

CALIFORNIA DEPARTMENT OF TOXIC SUBSTANCES CONTROL HUMAN AND ECOLOGICAL RISK OFFICE (HERO)¹



HERO ECOLOGICAL RISK ASSESSMENT (ERA) NOTE 7

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ISSUE: Update to DTSC 1996 recommendations for ecological risk assessment: sampling considerations for environmental media, including soil, sediment, pore water and soil vapor; ERAS's position on incremental sampling methodology; appropriate use of reporting and detection limits; and evaluation of bioaccessible fractions.

Abstract

The Department of Toxic Substances Control's guidance documents for conducting ecological risk assessments, *Guidance for Ecological Risk Assessment at Hazardous Waste Sites and Permitted Facilities* (DTSC, 1996a; 1996b), have not been formally revised since they were originally published. Since the publication of these guidance documents, many technical advances and risk-assessment decisions have been made regarding the conduct of ecological risk assessments, some of which have been conveyed through the HERD Ecological Risk Assessment (ERA) Notes, and some of which have been implemented less formally through site-specific decisions. HERO ERA Note 7 provides updated recommendations regarding sampling methods to supplement or replace out-of-date portions of the previous DTSC guidance and HERD ERA Notes 1–6.

The procedures and suggested approaches set forth here are intended solely to provide guidance to DTSC, other government employees, and contractors. This guidance does not constitute rule-making by DTSC and should not be interpreted as creating enforceable standards. The Human and Ecological Risk Office (HERO) staff responsible for preparation of these scientific guidelines include James M. Eichelberger, Brian C. Faulkner, Edward A. Fendick, Darrel Lauren, and James M. Polisini.

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¹ Formerly known as the Human and Ecological Risk Division (HERD)

General Sampling Considerations

Sampling and Analysis Plans which will be used for current or future scenario ecological risk evaluations should be developed in consultation with DTSC/HERO staff of the Ecological Risk Assessment Section (ERAS), with the goal of characterizing the vertical and horizontal limits of contaminated media sufficiently to allow for the development of an ecological risk assessment. ERAS recommends the use of the Data Quality Objectives (DQO) process, as described in by the U.S. Environmental Protection Agency (USEPA, 2006), for all sampling plans in order to efficiently and systematically estimate the time and resources needed for data collection, and also to maximize the likelihood that the collected data will be adequate for ecological risk assessment and other project goals

Discrete Sampling

Plans for discrete sampling should be developed with the goal to provide a sufficient number of samples to delineate the extent of contamination and calculate descriptive statistics with an acceptable level of confidence. Sampling plans should be developed in collaboration with HERO risk assessors and other members of the technical support groups on the DTSC project team. Draft sampling and analysis plans should be provided for review and concurrence **in advance** of the actual sampling efforts. Inclusion of the technical staff at all stages of the process will identify issues earlier and reduce the need for repeated sampling efforts to meet project goals. ERAS supports the use of a DQO-oriented process for the development of all sampling and analysis plans.

Incremental Sampling Methodology (ISM)

ERAS supports the application of the incremental sampling methodology (ISM) for site evaluations when site-specific circumstances are appropriate, and ISM data that are collected properly are usable in ecological risk assessments. To ensure that such data are collected properly, the decision to apply ISM and the specifics regarding how it will be applied should be developed in consultation with the DTSC project team on a site-specific basis. This should be done through development and approval of a work plan in advance of sampling. If ISM is applied improperly, it may result in data that are not usable in risk assessments. Please note that incremental sampling for ecological risk assessment may require triplicate sampling so that appropriate 95% upper confidence limit on the mean (95UCL) exposure-point concentrations (EPCs) can be calculated and to ensure that relative standard deviations of mean values may be estimated. Samples also must be appropriately homogenized prior to chemical analysis, using an appropriate standard operating procedure. See the ITRC Incremental Sampling

Methodology (ISM) guidance (online at <http://www.itrcweb.org/Guidance>) for more information regarding requirements for implementation of an ISM approach for risk assessment. Also note that ISM may require an appropriate ISM-based background or ambient study so that the appropriate background/ambient statistics may be developed for characterization and screening. ERAS recommends that ISM sampling be used at sites for which ecological risk will be evaluated only as previously approved by ERAS and other project team members. A sampling work plan, which includes the rationale for using ISM and a detailed description of the proposed study design, should be submitted for project team review and concurrence in advance of work being conducted. This recommendation includes the development of an ISM background/ambient study. Comparing **ISM site data to background/ambient values developed from discrete data is generally not appropriate, although such a comparison may be acceptable as a line of evidence in the uncertainty evaluation of an ecological risk assessment.** If a management decision is made that discrete and ISM samples will be quantitatively compared, ERAS recommends this comparison be evaluated in consultation with a statistician.

Sample Handling and Extraction

All sample collection, handling, extraction, and analytical methods should be described in a comprehensive sampling and analysis work plan submitted for approval by DTSC (including project management, HERO human-health and ecological risk assessors, and the DTSC Geological Services Branch (GSB), as warranted for a particular site) prior to field implementation. In general, ERAS expects that nearly all sample collection, handling, extraction, and analytical methods will follow procedures compiled from scientifically-accepted and publicly-available state and federal source documents.

Minimum Reporting and Detection Limits

Project method reporting limits (MRLs) should, ideally, be below ecological risk-based concentrations. This is to ensure that chemical concentrations may be accurately measured at levels which may adversely affect ecological receptors (and equally important, concentrations which would not adversely affect receptors). Achieving low reporting limits is sometimes not technically feasible nor practical. In these cases, the use of estimated concentration data (“J flagged”), which are between the MRL and the method detection limit (MDL), is acceptable for use in ecological risk assessments. The use of estimated concentration data in an ecological risk assessment should be discussed in the uncertainty section of the ecological risk assessment report. ERAS recommends that MRLs and MDLs be compared to risk-based screening levels in the work-plan preparation phase, prior to developing the ecological risk assessment. Issues with achieving appropriately low targets for ecological risk assessment should be

discussed with HERO and presented for concurrence regarding how such issues will be addressed in the ERA. Updated recommendations for identifying background threshold values and ecological screening levels, which can be used for comparison to MRLs/MDLs, will be covered in ERA Note 8.

Soil

Specific concerns for soil sampling generally center on the selection of appropriate locations and appropriate sampling depths.

Sampling locations

Soil sample locations should be selected:

- 1) Near known or suspected contamination sources such as outfalls;
- 2) In drainages or erosion pathways physically linked to known sources;
- 3) In areas of stained soils and their drainages;
- 4) Between terrestrial sources and waterways;
- 5) In low areas with or without apparent drainage connections to known or suspected sources; and
- 6) In areas known or likely to be utilized by ecological receptors (note that this may include areas which have been disturbed by human activities).

Sampling Depths

For evaluation of exposures of surface-dwelling and shallow-soil-dwelling wildlife, ERAS recommends a sampling interval from the surface (0 inches below ground surface [bgs]) to 6 inches bgs as the interval most likely to be encountered during foraging and from which chemicals of potential ecological concern (COPECs) will be available to surface-dwelling and/or shallow-soil dwelling ecological receptors. Concentrations in this surface stratum represent the horizon in which contaminants are most likely to have accumulated from surface deposition, often over an extended time, and often accounts for chemicals that were deposited during the peak of industrial activity, when most legacy sites were originally contaminated. If more recent surficial releases are the objective of the sampling, a shallower (0–2 inches bgs) sampling interval may be appropriate. Similarly, sampling intervals up to approximately 1-foot bgs may be warranted to better capture the uppermost organic-soil horizon (USEPA, 2015). Appropriate sampling depths for shallow soil should be discussed with ERAS during sampling and/or work plan development, prior to the initiation of field sampling because these may depend on site-specific conditions,

With certain receptors, such as burrowing (fossorial or subterranean) animals and plants with roots that extend to depths deeper than the surface-soil horizon, other depth ranges should be considered. Subsurface sampling depths have previously been recommended to cover the soil interval down to 6 feet bgs (HERO ERA Note 1). This is only a general recommendation; the appropriateness of this soil interval may be evaluated in a sampling and analysis plan and determined on a site-specific basis in consultation with ERAS staff if there is a rationale for a different interval. For the evaluation of toxicity to plants in an ecological risk assessment, EPCs should be developed from samples collected within the appropriate rooting zone for plants which appear to be adversely affected. Following uptake by plants, metals generally accumulate in the roots, with limited translocation to the aerial portions of the plant, although this is not true for all plant species all the time.² Site-specific uptake factors applicable to a larger geographic site may be generated from a relatively small number of discrete sampling points when root-zone soil concentrations (spanning a representative site-specific range) are evaluated in combination with collocated plant tissue concentrations.

Fossorial wildlife may be exposed to volatile organic chemicals (VOCs) in subsurface soil or from deeper groundwater sources, and subsurface soil-vapor samples may be required, generally limited to a maximum depth of 6-feet bgs (see Soil Vapor, below). ERAS **does not** recommend collection of soil-matrix samples for estimating soil-vapor concentrations, nor does it recommend estimation of soil vapor from groundwater concentrations of VOCs; direct soil vapor sampling should be utilized whenever possible for ecological risk assessment.

Bioaccessibility and Bioavailability as Additional Lines of Evidence

Parallel to measuring bioaccessible concentrations in sediment pore-water samples (see later text), ERAS suggests that Soluble Threshold Limits Concentration (STLC) data from bulk soils (derived for comparison to “California Code of Regulations [CCR] Title 22 hazardous waste criteria”) may also provide a useful supplemental line-of-evidence in the estimation of bioaccessible concentrations in soil. The STLC method uses a pH 5 digestion, in contrast to the strong-acid near-total extraction used in standard methods for bulk soil chemical analyses. This STLC may provide a less-conservative but more-realistic estimate of soil bioaccessible metal concentrations. STLC samples should be collected in the same manner as bulk soil samples. The STLC water extract should be filtered to remove particulates, and the bioaccessible

² Perchlorate and some metals are known to accumulate in aerial portions of certain plants, for example. Also certain plant species are hyper-accumulators of specific metals such as arsenic and molybdenum. Additional sampling within the root zone may be necessary if these are site-related chemicals.

fraction back-calculated to an estimated bulk soil concentration from the extracted (soluble) concentration and the dilution volume, which should then be expressed on a dry weight basis. The ratio of the analyte bulk soil concentration to the soil extracted concentration may be used in conjunction with uptake regressions as a refinement to estimate the bioaccessible doses of chemicals in soil for wildlife.

HERO has also published a method for evaluating site-specific arsenic bioavailability based on a porcine model (HERO Human Health Risk Assessment [HHRA] Note 6).³ Human-health risk-based screening concentrations are below typical naturally occurring concentrations of arsenic, so HHRA Note 6 addresses a need that is more critical to human health risk assessment than the ecological risk assessment. However, there may be ecological evaluations which could benefit from a site-specific bioavailability estimate for arsenic, and such estimates would provide an additional line of evidence for some mammalian receptors.

Sediment

Sediment sampling from beneath onsite surface-water features (and offsite features, if warranted) is required if aquatic habitats are potentially affected by site contamination. Specific sampling concerns are detailed below.

Bulk Sediment

Similar to soils, bulk sediments should be collected from the biotic zone, commonly the 0-6 inch bgs interval that benthic invertebrates, fish, and wildlife are most likely to encounter. While a deeper biotic and/or bioturbation zone may be present (see USEPA, 2015) and may be contaminated, the greater depths are typically reducing environments (i.e., oxygen deficient) and organisms in these deeper zones are generally limited. If contaminants are present in deeper strata, the need for additional evaluation should be determined in consultation with ERAS staff. If current or recent releases are the objective of a sampling program, a shallower (0–2 inches bgs) sampling may be appropriate, depending on the depositional environment. If equilibrium partitioning (EqP) is to be used to estimate the bioaccessible fraction of contaminants in sediment, then total organic carbon (TOC) and/or acid volatile sulfide and simultaneously extracted metals (AVS/SEM) must also be measured in bulk sediment samples.

³ <https://dtsc.ca.gov/wp-content/uploads/sites/31/2018/01/HHRA-Note-6-CAB-Method.pdf>

Sediment Pore Water

ERAS recommends the collection of sediment pore water over the use of mathematical predictive methods based on bulk sediment data. Sediment pore water should be collected from bulk-sediment samples or, where the sediment consists of large particles with large pore spaces, by direct methods such as push probes or piezometers. In consolidated sediments, it may be necessary to collect surface sediments from a large number of shallow cores. Depending upon the chemicals to be measured, the pore water may be separated from the bulk sediment by centrifugation or vacuum filtration when evaluating non-volatile contaminants of potential ecological Concern (COPECs). The dissolved fraction may also be collected directly at the sediment/water interface using semi-permeable membrane devices (SPMDs), or within sediments using solid-phase microextraction (SPME) fibers or other passive samplers. For more information on passive samplers and methodologies, ERAS recommends the USEPA (2012) *Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites*, which is available at https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NHEERL&dirEntryId=238596) or other more-recent literature as appropriate/available. Consultation with ERAS staff and submission of a sampling and analysis plan prior to initiation of these types of sampling procedures is highly recommended.

Surface Water (and Ground Water, if appropriate)

In shallow waterbodies, surface water samples should be collected within 0-6 inches of the sediment surface, but without disturbing the sediment surface and increasing the sample's turbidity. Mid-water-column depths may be proposed for deeper waterbodies to assess exposure for pelagic ecological receptors.

Filtration

Water samples, regardless of originating source, should be filtered through a 0.45- μm filter to conform to the California Toxics Rule (CTR). An unfiltered sample may also provide useful information for the ecological risk assessment, and may be required for other uses.

Soil Vapor

Sites with concentrations of VOCs in subsurface soil or ground water may pose an inhalation hazard to burrowing animals. Soil-vapor samples should be collected to characterize the in-burrow subsurface environment from depths of approximately 5–6 feet bgs (but generally not shallower due to potential influences of ambient air on soil-vapor extraction). ERAS also suggests that direct measurements of burrow air would be the most appropriate measurements to conduct to address this issue if circumstances

permit. Note that any soil-vapor sampling program should be coordinated with other disciplines working on the contaminated site (e.g., human-health risk assessors).

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