

The Use of Field Screening or Rapid Sediment Characterization (RSC) Tools for Sediment Assessments

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INTRODUCTION

The primary goals of a sampling and analysis plan for an Ecological Risk Assessment (ERA) or a sediment site assessment are to identify potential contaminant sources and to delineate areas of concern. However, traditional sampling and analysis approaches do not always provide the information necessary to support the decision-making process in a cost- and time-effective manner. Site assessments performed in the marine environment are often hindered due to the complexity and heterogeneity of marine ecosystems. Because of the complex nature of marine ecosystems, U.S. Navy policy [1] specifically requires that sampling programs focus primarily on the identification of potential contaminant sources and on the delineation of areas of contaminated media. Navy policy further dictates that sampling programs should make use of advanced chemical and biological screening technologies, data quality objectives, and statistical procedures to minimize overall sampling requirements. Implementation of advanced chemical, physical, and/or biological screening technologies (i.e., rapid sediment characterization tools) at different stages of the ERA process can aid in focusing sampling requirements and can ultimately facilitate reaching final decisions.

WHAT IS RAPID SEDIMENT CHARACTERIZATION?

Rapid sediment characterization (RSC) tools are field-transportable analytical tools that provide measurements of chemical, physical, or biological parameters on a near real-time basis. A variety of tools exist that are capable of making these types of measurements. Many technologies have been used to characterize different types of environmental media (e.g., soil, sediment, water, and air). These technologies are described in several Environmental Protection Agency (EPA) documents [2 and 3], including the online Field Analytical Technologies Encyclopedia (FATE) [4]. This encyclopedia provides information about technologies that can be used in the field to characterize contaminated soil and ground water, to monitor the progress of remedial efforts, and in some cases, to confirm sampling and analysis for site closeout. Although not all of the technologies currently available are applicable to sediment sites, several have been tested and demonstrated at Navy marine sediment sites (Table 1). Examples can also be found in standard environmental textbooks such as Gilbert's 1987 *Statistical Methods for Environmental Pollution Monitoring*, which provides specific examples of the use of screening and laboratory data together to optimize for reduction in cost and data variability [5].

ABSTRACT

This paper discusses several rapid site characterization (RSC) technologies that can be used at marine sediment sites, including X-ray fluorescence (XRF) for metals, ultraviolet fluorescence (UVF) for polycyclic aromatic hydrocarbons, QwikSed bioassay for assessing toxicity, and other techniques. Examples are provided to illustrate the efficacy of applying RSC tools to different stages of the Ecological Risk Assessment (ERA) process. Finally, recommendations are given for the evaluation, selection, and application of RSC tools for the ERA process.

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WHY IS RCS IMPORTANT?

An ERA evaluates the likelihood that exposure to one or more stressors (e.g., contaminants) will result in adverse ecological effects [6]. The purpose of the assessment is to provide information relevant to the management decision-making process. Ideally, ERAs should be scientifically based, defensible, cost-effective, and protective of human health and the environment (see, for example, [1]). Collection of data necessary to support decisions at sediment sites in a cost-effective manner is often hindered by the complexity and heterogeneity of marine ecosystems. Detailed site investigations require extensive sampling and subsequent laboratory analyses for both metal and organic contaminants. Samples are often collected without any *a priori* knowledge of the nature and extent of contamination. Because of the high cost of laboratory analyses, the number of samples taken is often cost-limited. Thus, zones of contamination can be missed or, if located, overestimated or underestimated. To obtain more detailed spatial information on the extent of contamination, researchers must often sample and analyze sites of interest in an iterative manner. Chemical assays are often combined with additional laboratory analyses, including one or several bioassays to determine whether there are adverse biological effects of these contaminants in various media (e.g., sediment, elutriate, water column). This approach can be prohibitively costly, slow, and labor-intensive. When used appropriately, RSC tools can streamline many aspects of the ERA process, delineating areas of concern, filling information gaps, and ensuring that expensive, certified analyses have the highest possible impact.

To determine if RSC tools are appropriate to assess contamination at a given site, several questions should be asked. For example: What are the goals of the investigation? What are the contaminants of concern? Are the contaminants known? What are the action limits? What are the strengths and weaknesses of the analytical methods being considered? Do instrument detection limits meet action limit requirements? By asking these questions before sampling begins and by considering the advantages and disadvantages of different techniques, appropriate decisions can be made on how best to implement a technology or suite of technologies to facilitate the ERA process. Table 2 lists the relative advantages and limitations of RSC methods and standard methods. A brief description of some RSC technologies that have been tested in sediments is provided below. All of these technologies described are commercially available.

TABLE 1. Examples of rapid sediment characterization tools tested in marine sediments.

Analytical Technique	Parameter(s)
X-ray Fluorescence (XRF) Spectrometry	Metals (e.g., Cu, Zn, Pb)
UV Fluorescence (UVF) Spectroscopy	Polycyclic Aromatic Hydrocarbons (PAHs)
Immunoassays	Polychlorinated biphenyls (PCBs), PAHs and Pesticides
QwikSed Bioassay Microtox	Acute and Chronic Toxicity Acute Toxicity
Laser Particle Scattering	Grain Size (% fines)

TABLE 2. Advantages and limitations of screening and standard laboratory methods.

RCS Analysis	Standard Laboratory Analysis
Benefits · rapid results can guide sampling locations · potential for high data density for mapping · reduced cost per sample	Benefits · standard methods that are very quantitative · can often remove interferences
Limitations · often non-specific · semi-quantitative · matrix sensitive	Limitations · often blind-sampling · long delays to results · expensive (\$K/sample)

EXAMPLES OF RSC TECHNOLOGIES: GENERAL PRINCIPLES

X-ray Fluorescence Spectrometry Metals

Commercially available, portable X-ray fluorescence (XRF) spectrometry analytical instruments can provide rapid, multi-element analysis of metals in sediment. Samples are exposed to X-ray energy, which liberates electrons in the inner shell of metal atoms. As the outer electrons cascade toward the inner shells to fill the vacancies, energy is released, or fluoresced. The fluorescing energy spectrum identifies the metals and each peak's intensity is proportional to concentration. Generally, XRF can detect and quantify elements from sulfur to uranium. For common metals, such as lead, zinc and copper, this method yields a detection limit range from 50 to 150 parts per million (ppm) and requires 2 to 5 minutes per analysis in soils and sediments. Commercial XRF instruments are readily available for purchase (~ \$11,000 to \$56,000) or lease (~ \$150/day to \$6000/month) depending on options and equipment size required. To accommodate field application, many instruments weigh less than 30 pounds and can be operated with batteries for 8 to 10 hours [4 and 7].

Ultraviolet Fluorescence Spectroscopy: PAHs

Fluorescence is a standard analytical technique that can be used to measure the concentration of various analytes in different matrices. Ultraviolet fluorescence spectrometry (UVF) can be used for the determination of polycyclic aromatic hydrocarbons (PAHs) in sediments. This technique is based on the measurement of fluorescence observed following UV excitation of either bulk samples or organic solvent extracts of sediments. However, detection limits are greatly enhanced by extraction. When UV light is passed through a sample, the sample emits light (fluorescence) proportional to the concentration of the fluorescent molecules (e.g., PAHs) in the sample [8]. An analysis, with extraction, can be done in 10 to 30 minutes, and for PAHs, the range for detection limits when using UVF is from 1 to 5 ppm total solid phase. UVF instruments are commercially available from various vendors for purchase (~ \$10,000 to \$12,000) or for weekly rental.

Immunoassays: PCBs, PAHs, Pesticides

This technique can be used for the identification and quantification of many organic compounds (e.g., polychlorinated biphenyls [PCBs], PAHs, and pesticides). Immunoassays use antibodies that have been developed to bind with a target compound or class of compounds. Concentrations of analytes are identified through the use of a sensitive colorimetric reaction. The determination of the target analyte's presence is made by comparing the color developed by a sample of unknown concentration with the color developed by a standard containing the analyte at a known concentration. The concentration of the analyte is determined by the intensity of color in the sample and is measured through use of a spectrophotometer. Immunoassay kits are relatively quick and simple to use. Several test kits are commercially available and range in cost from \$10 to \$40 per sample test kit. Detection limits can vary, depending on the dilution series used. For example, the detection limit for PCBs in sediments ranges from 50 to 500 parts per billion (ppb) [4 and 9].

Screening Bioassay Tests

The Microtox bioassay is a commercial test that measures the inhibition of light emitted by a bioluminescent microorganism. Any decrease in

light output relative to controls suggests bioavailable contaminants or other stressors. Several studies have compared Microtox response to other bioassays (e.g., [10]).

The QwikSed rapid bioassay system is proving to be a valuable asset for conducting bioassays on marine sediments. The basis of detection is to measure a reduction in light from a bioluminescent dinoflagellate such as *Gonyaulux polyedra* or *Ceratocorys horrida* following exposure to a toxicant. The toxic response is usually measured within 24 hours from the start of the test and can be conducted for a 4-day acute test or a 7- to 11-day chronic test. A measurable reduction or inhibition in bioluminescence indicates an adverse effect. The cost of the QwikSed analyzer (Sealite Instruments, Inc., Ft. Lauderdale, FL) and supporting software is approximately \$15,000. The data from the QwikSed bioassay can be correlated with more conventional toxicity tests such as amphipods and sea-urchin development.

RAPID CHARACTERIZATION TOOLS IN THE ERA PROCESS

The Chief of Naval Operations (CNO) Policy for conducting ERAs identifies a three-tiered approach that incorporates different levels of assessment complexity.

- Tier 1 - Screening Risk Assessment (SRA) (Steps 1 and 2)
- Tier 2 - Baseline Ecological Risk Assessment (BERA) (Steps 3 to 7); and
- Tier 3 - Evaluation of Remedial Alternatives (Step 8)

This approach, which is consistent with the EPA Superfund Interim Final Ecological Risk Assessment Guidance for Superfund [6] consists of eight steps (Figure 1). RSC tools can be used to assist several step of this process.

Screening Risk Assessment

The goal of a Screening Risk Assessment (SRA) is to determine whether an exposure pathway is present between each chemical of interest and selected ecological receptors and to estimate risks for those chemicals for which pathways are identified. Such an assessment should employ existing data, and should not require additional data collection. Site data, however, do not always exist. If data are lacking, rapid characterization can map the extent of contamination in order to guide sampling for full contaminant of potential ecological concern (COPEC) analysis. By using

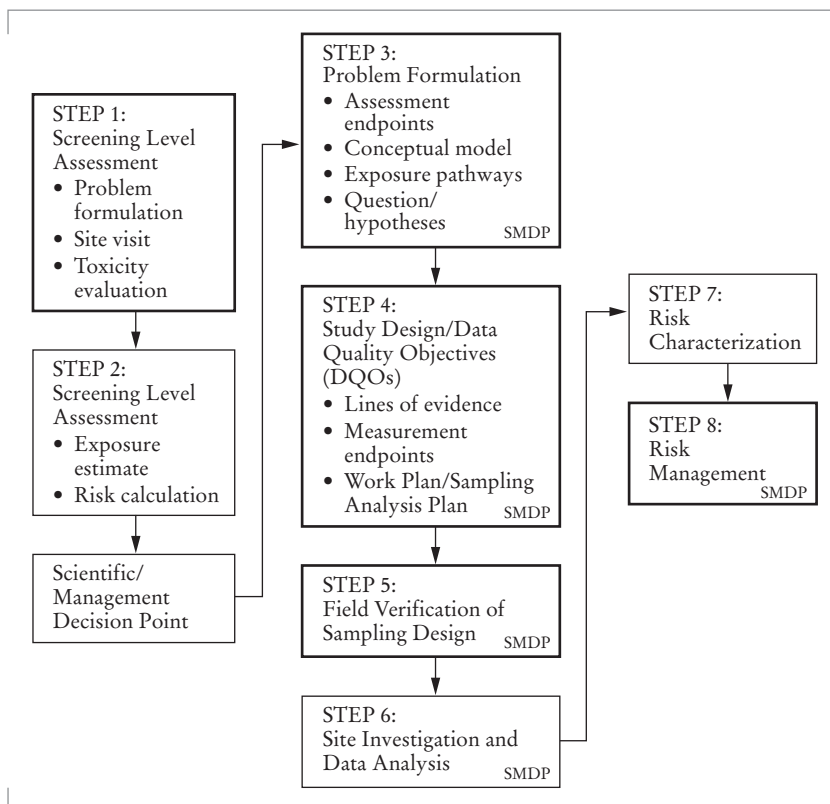


FIGURE 1. Navy Ecological Risk Assessment approach. Highlighted boxes indicate steps in which RSC tools can be used to facilitate the process.

RSC data to quickly map the area under investigation, subsequent sampling for full COPEC analysis can be more focused.

Baseline Ecological Risk Assessment

A Baseline Ecological Risk Assessment (BERA) is typically the most extensive activity within the ERA process, in terms of data collection and analysis, cost, and effort. There are several steps within the BERA in which rapid characterization tools can play a critical role, including Problem Formulation, Study Design/Data Quality Objectives (DQO) Process, and Verification of Field Sampling Design.

For example, two RSC tools were used for a sediment screening study at Hunters Point Shipyard to support a BERA sampling design (Steps 4 and 5). Surface sediment samples were collected in a grid-pattern from 94 locations in the five offshore areas of concern. Samples were screened for PCBs and heavy metals using the immunoassay technique and XRF spectrometry, respectively, at the SSC San Diego laboratory. The results were used to refine the sampling design for a more detailed study of sediment chemistry, toxicity, and bioaccumulation. In particular, screening results were used to ensure that the baseline assessment study sampling stations spanned the entire range of contaminant concentrations and, therefore, represented the full range of potential exposure. Ten percent of the screening samples were submitted to a standard analytical laboratory in order to obtain a quantitative analysis of all contaminants of concern, verify screening results, and provide additional surface sediment data supporting the assessment study.

Plots of PCB and copper (Cu) results are shown from one of the five offshore areas of concern (Figure 2). These results indicate two potential source areas for elevated PCBs in these offshore sediments, one on the northeast side and one on the west side of the embayment. Although the northeast area may be impacted by Navy operations, the source area to the west is at a creek mouth with potential non-Navy contributions of the target analytes from upstream locations onto Navy property. In the case of Cu, one potential source is indicated on the northeast side of the embayment, again potentially related to Navy operations. The screening

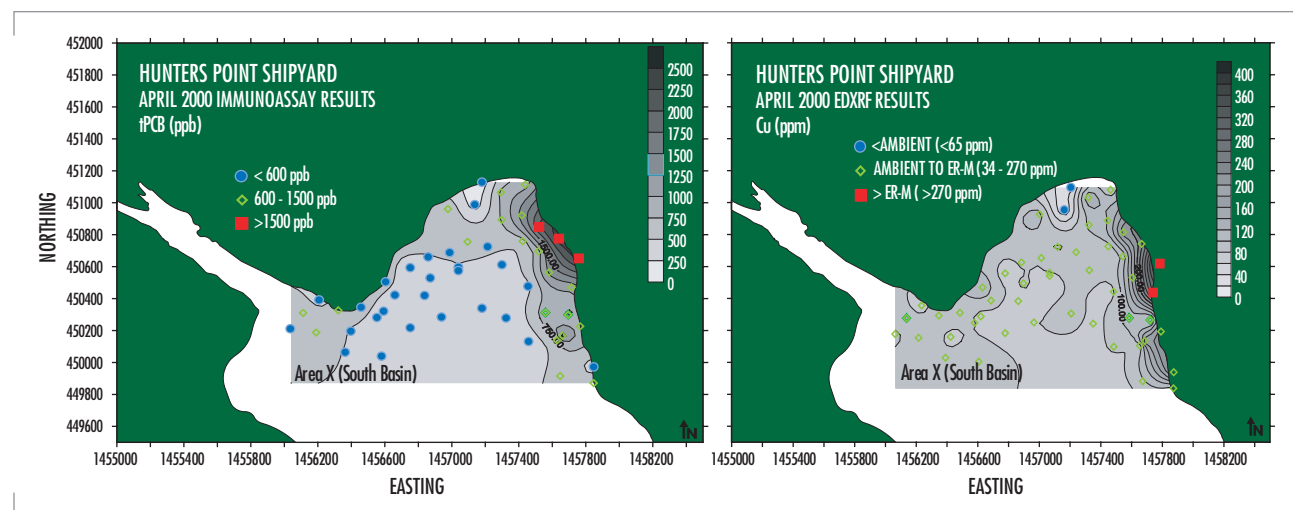


FIGURE 2. RSC tools implemented during BERA Steps 4 and 5 at Hunters Point Shipyard, CA. Immunoassay results for PCBs (left) and XRF results for Cu (right) are shown.

results can be used to delineate boundaries of impacted areas to ensure each potential source is sampled and laboratory data will be available to estimate relative source contributions to Navy sediments. As is often the case in sediment assessments, multiple potential sources are present. These sources need to be considered in the design of a sampling plan for the baseline assessment.

Evaluation of Remedial Alternatives

The purpose of this step is to ensure that remedial alternatives are adequately evaluated from an ecological perspective, so that the outcome of the remediation is not more detrimental to the environment than if the site had not been remediated [6]. Rapid characterization tools can play a role in this tier as well. If a remedial option is selected, costs are critically dependent on volumes or areas to be managed. Rapid characterization can be used to map out areas or volumes at higher density than were used for the assessment. Rapid characterization can also be used to verify the efficacy or completeness of a remedial option such as containment, cap or remove impacted sediments, and monitor the long-term efficacy and impact of management strategies.

CONCLUSIONS

A few important points must be considered in the selection and application of RSC tools to the ERA process. First, it is important that site-specific project goals and parameters as defined by the DQO Process must be considered. It is critical to ensure that the contaminants or criteria that are deemed to be decision drivers are detectable with the RSC tools that are available. Also, as with any method or technology, certain limitations exist. The primary limitations to RSC technologies are that they are often (1) non-specific, (2) semi-quantitative, and (3) matrix-sensitive. Because of these limitations, the data produced by RSC tools/methods are not necessarily equivalent to those generated by standard methods. Depending on the data quality requirements established during the DQO Process, a well-designed RSC protocol, paired with laboratory validation, will be able to provide data that can be of sufficient quality and great value to the risk assessment. It is important to note that results can be misleading if non-equivalent data are combined without careful intercalibration. A few different approaches to the documentation and reporting of data can be used to avoid such problems when reporting results, particularly those from RSC methods. The first reporting approach is to always flag numbers generated by a non-standard method in spreadsheets and data reports, and to include text, references, or qualifiers that address any potential offsets from standard analyses. A second approach is to carry out site-specific calibration of RSC analyses and to report only corrected, calibrated data. A third option, particularly for RSC analyses that generate only qualitative data (i.e., data that identify the presence or absence of target analytes, but may have no relationship to true concentrations of the analytes) is not to report numerical values, but instead report qualitative values (e.g., non-detect, etc). Samples are either ranked or ranges are reported. Finally, a concern voiced by many potential users of RSC tools is that, since they are not subject to the same quality assurance/quality control (QA/QC) protocols and rigors as are standard procedures, they will make the user vulnerable by not standing up to regulatory or legal scrutiny. While these concerns are not trivial, it is clear

that there are a growing number of case studies in which remedial project managers, regulators, and the user community have accepted RSC data as a critical, though not stand-alone, part of the analytical and decision-making process. In any case, the intent to use RSC tools, and how the resulting data will be interpreted and managed, should be addressed up front with regulators and other stakeholders.

Implementation of rapid characterization tools in ecological risk assessments will improve sampling and reduce uncertainty at several steps of the remedial investigation/feasibility study process without the enormous cost of traditional resampling efforts. Use of these tools moves the ERA process forward in the most time- and cost-effective manner with minimum uncertainty.

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