total measurement error variance, including variance due to sample collection, preparation, analysis, and data processing. They do not discriminate between-batch error variance. If the duplicate is collocated, contaminant sample variation caused by a heterogeneous medium is also included in the measure. The precision of the measurement error estimate is subject to the number of duplicates on which the estimate is based. Exhibit 49 gives the estimated precision of the measurement error based on the number of duplicate pairs. With three duplicates, the true measurement error variance could be as much as 13.89 times the observed variance, if a 95% level of confidence is required. The resources needed for the collection and analysis of duplicates depend on the magnitude and variability of the concentration of concern for the chemicals of potential concern.

- Little room for measurement error exists if the level of concentration of concern is near the method detection limit, and the precision of the estimate of measurement error is critical.
- If the natural variability of the chemicals of potential concern is relatively large, the major planning effort will be to collect more samples from the exposure areas, rather than collecting more QC samples. More detailed discussions of the use of QC measures and selection of the appropriate number of QC samples may be found in *A Rationale for the Assessment of Errors in the Sampling of Soils* (EPA 1990c).

Planning for 100% completeness for critical samples. Certain samples in a sampling plan may be designated by the RPM or risk assessor as critical in determining the potential risk for an exposure area. For example, if only one background sample is taken for a given medium and exposure area, then that sample would be considered

EXHIBIT 49. CONFIDENCE LEVELS FOR THE ASSESSMENT OF MEASUREMENT VARIABILITY

Number of Duplicate Pair Samples	Interval for 95% Confidence that Measurement Error is Within Limits				
	Observed Variance (s^2)		True Variance		Observed Variance (s^2)
2	.27	≤	σ^2	≤	39.21
3	.32	≤	σ^2	≤	13.89
4	.36	≤	σ^2	≤	8.26
5	.39	≤	σ^2	≤	6.02
6	.42	≤	σ^2	≤	4.84
7	.44	≤	σ^2	≤	4.14
8	.46	≤	σ^2	≤	3.67
9	.47	≤	σ^2	≤	3.33
10	.49	≤	σ^2	≤	3.08
15	.54	≤	σ^2	≤	2.40
20	.58	≤	σ^2	≤	2.08
25	.62	≤	σ^2	≤	1.91
50	.70	≤	σ^2	≤	1.61
100	.77	≤	σ^2	≤	1.35

s^2 = Observed variance (precision of an estimate).

σ^2 = True variance (population variance).

Note: Assumes data are or have been transformed to normal distribution.
Source: EPA 1990c.

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"critical." All data associated with such a sample must be complete. The only acceptable level of completeness for critical samples is 100%.

> ☛ *Focus planning efforts on maximizing the collection of useable data from critical samples.*

Hot spots and the probability of missing a hot spot. Hot spots are primarily an issue in soil sampling. The RPM and risk assessor must determine whether hot spots exist in the exposure area and the probable size of the hot spot. This information can often be deduced from historical data and assisted by judgmental sampling, although judgmental sampling alone cannot produce estimates of the probability that a hot spot has been missed. Procedures for determining the probability of missing a hot spot are not as effective in random designs as in systematic and geostatistical designs. However, a search strategy which stratifies the area based on grids and then randomly samples within each grid can be used within the classical technique. Systematic and geostatistical design approaches provide the best approach to unknown hot spot identification.

Appendix IV describes numerical procedures and assumptions to determine the probability that a given systematic design will detect a hot spot and provides a calculation formula based on a geometrical approach. To employ this formula, the distance between grid points and the estimated size of the hot spot as a radius must be specified.

Historical data comparability. The RPM may wish to assess historical data along with current results or may anticipate that the current data will need to be compared with results from future sampling activities. Consult a statistician in either of these cases to determine if the current sampling design will allow the production of data of known comparability. Factors other than statistics may need to be considered when attempting to combine data from different sampling episodes. Physical properties of the site such as weather patterns, rainfall and geologic characteristics of different exposure areas may need to be considered. Temporal effects, such as the seasonality or time period of sampling, or seasonal height of a water table, may also be important. Analytical methods have been modified over time and many required detection limits have been revised.

> ☛ *The ability to combine data from different sampling episodes or different sampling procedures is a very important consideration in selecting a sampling design but should be done with caution.*

4.1.4 Soil Depth Issues

The appropriate depth or depths to take soil samples can be a major issue in determining a sampling design. Exhibit 50 is a worksheet designed to help the RPM and risk assessor to determine an appropriate soil sampling depth. The conceptual site model (Exhibit 6) provides the basis for completing this worksheet. The nature and depth of soil horizons at the site should be established wherever possible. Features such as porosity, humic content, clay content, pH, and aerobic status often affect the movement or fate of chemicals of potential concern through a soil. As with other worksheets provided in this guidance, this worksheet is intended as a guide or basis for development. RPMs, in consultation with the risk assessor and other staff, can revise or modify this worksheet as appropriate to the site. Consider both current and future land use scenarios in soil exposure areas because of the sorptive and retentive properties of soils.

Completing the Soil Depth Sampling Worksheet

1. **Land Use Alternatives**

   A. Identify current or future land use.

   B. Identify exposure scenario.

   The exposure scenario should be identified for current or future land use. Identify the scenario according to *Role of Baseline Risk Assessment in Superfund Remedy Selection Decision* (EPA 1991c) and *Human Health Evaluation Manual Supplemental Guidance: Standard Default Exposure Factors* (EPA 1991d). A residential exposure scenario should be used whenever there are, or may be, occupied residences on or adjacent to the site. Unoccupied sites should be assumed to be residential in the future unless residential land use is unreasonable. Sites that are surrounded by operating industrial facilities can be assumed to remain as industrial areas unless there is an indication that this assumption is not appropriate. Other potential land uses, such as recreation and agricultural, may be used if appropriate.

2. **Chemicals of Potential Concern**

   A. Specify class of chemical.

   Circle the classes of chemicals of potential concern (e.g., volatile organics (VOAs), semivolatile organics (semi-VOAs), inorganics or metals, or special class) that apply.

EXHIBIT 50. SOIL DEPTH SAMPLING WORKSHEET

Step 1 - Land Use Specifications*

1A (check one)	1B (check one)
_ Current _ Future _ Current & Future, Same	_ Residential _ Commercial/Industrial _ Other (Specify) _ Recreational _ Agricultural

Sampling Depth Considerations	Step 6. Expected Depth of Contamination by Chemicals of Potential Concern		Step 7. Exposure Pathways			Step 8. Representative Sample Depths (units _____)
	Surface Units	Subsurface	Ingestion	Dermal	Inhalation	
Step 2: Chemicals of Concern **A** Class: VOAs, Metals, semi-VOAs, Special (e.g., PCBs, dioxin) **B** Physical Properties: Mobile, Soluble, or Leachable **Step 3:** Soil Characteristics **A** Taxonomy _____ **B** Organic Content _____ **C** Particle Size _____ **D** Concern for Migration to Other Media, (Air, SW, sediments, GW)_____ _____ **Step 4:** Vegetative Cover Heavy/Sparse/Intermittent **Step 5:** Other Factors _____ _____						

* The complexity of a site determines if multiple worksheets are necessary to distinguish between current and future land use scenarios (e.g., mix of residential and commercial use for different areas of a site, possible future residential use, etc.).

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B. Record physical properties.

Circle the physical properties of the chemicals of potential concern that apply. These properties can be estimated from factors such as the octanol/water partition coefficient, Henry's law constant, and water solubility appropriate to each chemical.

3. **Soil Characteristics**

A. Record the taxonomic designation of the soil, if known.

B. Record the organic matter content of the soil.

C. Record the most common particle size of the soil.

D. Identify any concern for migration of the chemicals of potential concern to other media (e.g., air, sediment, surface water, and groundwater).

4. **Vegetative Cover**

Circle whether the vegetative cover of the site is heavy, sparse or intermittent.

5. **Other Factors**

List other factors or considerations that influence the desired depth of soil sampling. For example, geological factors (e.g., depth to groundwater or bedrock) could influence soil sampling.

6. **Expected Depth of Contamination by Chemicals of Potential Concern**

Enter expected depth (and units) of contamination by chemicals of potential concern, given the chemicals, soil characteristics and vegetative cover. Depth can be influenced by disposal practices or deposition patterns, soil characteristics, vegetative cover, and physical and chemical properties of the chemicals of potential concern.

7. **Exposure Pathways**

Enter exposure pathways by chemicals of potential concern, soil characteristics and vegetative cover. Physical and chemical properties of the chemicals of potential concern will influence their activity in the exposure pathway (e.g., VOAs and the inhalation pathway). Soil characteristics and vegetative cover will also influence the exposure pathway (e.g., groundwater and water ingestion pathway).

8. **Representative Sample Depths**

Record representative sample depths (including units) indicated by the data completed in Steps 2 through 7.

Basic Soil Depth Definitions

Surface dust is the top 0 to 2 inches of soil that can be carried by the wind and tracked into houses.

Surface soil is the top 0 to 6 inches of soil. If the surface is grass covered, surface soil is considered the 2 inches below the grass layer.

Subsurface soil can typically range from 6 inches to 6 or more feet in soil depth. For example, at sites with potential soil moving activity, soil depths greater than 6 feet could be of concern in risk assessment.

Other Performance Measures. Other performance measures may be designated to facilitate the monitoring and assessment of sampling. For example, field spikes and field evaluation or audit samples can be used to assess the accuracy and comparability of results. Field matrix spikes are routine samples spiked with the contaminant of interest in the field and do not increase the number of field samples. Field evaluation samples are of known concentration, which are introduced in the field at the earliest stage possible and subject to the same manipulation as routine samples. Field evaluation samples will increase the total number of samples collected. Performance measures for field spikes and evaluation samples are expressed in terms of percent recovery. Difficulties associated with field spiking, especially in soil, have resulted in limited use of this practice (EPA 1989f).

4.1.5 Balancing Issues for Decision-Making

Completing a number of Sampling Design Selection Worksheets (Exhibit 45) for different exposure areas, media, and sampling design alternatives will enable the RPM and risk assessor to compare and evaluate sampling design options and consequences and select the appropriate sampling design for each medium and exposure pathway. Practical tradeoffs between response time, analytical costs, number of samples, sampling costs, and level of uncertainty can then be weighed. For example, perhaps more samples can be collected if less expensive analyses are used. Or, if the risk assessment is based on a point source, collection of additional samples to estimate chemical concentrations and distribution can be avoided.

Computer programs are useful tools in developing and evaluating sampling strategies, especially in trading off costs against uncertainty, and identifying situations when additional samples will not significantly affect the useability of the data (i.e., the point of diminishing returns). Each automated system has specific data requirements and is based on specific site assumptions. The major systems that support environmental sampling decisions are listed, contacts for information given, and brief descriptions provided in Exhibit 51.

4.1.6 Documenting Sampling Design Decisions

It is important to document the primary issues considered in balancing tradeoff to accommodate resource concerns and their impact on data useability. Fully document all final sampling design decisions, including the rationale for each decision. During the course of the RI, continue to document pertinent issues that arise and any sampling plan modifications which are implemented.

4.2 STRATEGY FOR SELECTING ANALYTICAL METHODS

This section describes how to use the Method Selection Worksheet shown in Exhibit 52 as a data collection and decision-making tool to guide the selection of analytical methods that meet the needs of the risk assessment and to select the most appropriate method for each analyte. The RPM and risk assessor should consult the project chemist and use this worksheet in method selection. Alternatively, it can be a model to create a worksheet specifically suited to their needs. Methods selected in this process may be routine or non-routine.

EXHIBIT 51. AUTOMATED SYSTEMS* TO SUPPORT ENVIRONMENTAL SAMPLING

System	EPA Contact	Description
Data Quality Objective (Training) - Expert System	Dean Neptune USEPA Quality Assurance Management Staff (202) 260-9464	Training system designed to assist in planning of environmental investigations based on DQO process.
ESES Environmental Sampling (Plan Design) - Expert System	Jeff Van Ee Exposure Assessment Div. USEPA, EMSL-LV (702) 798-2367	Expert system designed to assist in planning sample collection. Includes models that address statistical design, QC, sampling procedures, sample handling, budget, and documentation. Current system addresses metal contaminants in a soil matrix. (Expanded application under development, contact EMSL-LV.)
GEOEAS Geostatistical Environmental Assessment Software	Evan Englund Exposure Assessment Div. USEPA, EMSL-LV (702) 798-2248	Collection of software tools for two-dimensional geostatistical analysis of spatially distributed data points. Programs include file management, contour mapping, kriging, and variogram analysis.
SCOUT Multivariate Statistical Analysis Package	Jeff Van Ee Exposure Assessment Div. USEPA, EMSL-LV (702) 798-2367	A collection of statistical programs that accept GEOEAS files for multivariate analysis.
ASSESS	Jeff Van Ee Exposure Assessment Div. USEPA, EMSL-LV (702) 798-2367	System designed to assist in assessment of error in sampling of soils. Estimates measurement error variance components. Presents scatter plots of QC data and error plots to assist in determining the appropriate amount of QC samples.

* All systems will run on any IBM-compatible PC AT with a minimum of 640K RAM. A fixed disk is recommended.

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EXHIBIT 52. METHOD SELECTION WORKSHEET

I. Analytes		II. Medium	III. Critical Parameters				IV. Routine Available Methods[4]
A. Chemical or Class of Chemicals of Potential Concern	B. Reporting Requirement[1] (Y or N)		A. Turnaround Time (enter hours or days)	B. ID Only or ID Plus Quant (ID or ID+Q)	C. Concen-tration of Concern[2] (or PRG)	D. Required Method Detection Limit[3]	

[1] Y= Total reported for compound class.
[2] N = Each analyte reported separately.
[3] Preliminary remediation goal.
[4] Method detection limit should be no greater than 20% of concentration of concern.
Refer to Appendix III for specific methods. Recommend consultation with chemist and/or automated methods search to determine all methods available. (Exhibit 53 lists computer systems that support method selection.)

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☛ *Ensure that critical requirements and priorities are specified on the Method Selection Worksheet so that the most appropriate methods can be considered.*

- Routine methods are issued by an organization with appropriate responsibility (e.g., state or federal agency with regulatory responsibility, professional organization), are validated, documented, and published, and contain information on minimum performance characteristics such as detection limit, precision and accuracy, and useful range.
- Non-routine methods address situations with unusual or problematic matrices, low detection limits or new parameters, procedures or techniques; they often contain adjustments to routine methods.

☛ *Use routine methods wherever possible since method development is time-consuming and may result in problems with laboratory implementation.*

4.2.1 Completing the Method Selection Worksheet

1. **Identify analytes.**

   List the chemicals of potential concern to risk assessment for the site on the Method Selection Worksheet. Use the same list of chemicals that appears on the Sampling Design Selection Worksheets. Under Column 1B, indicate whether the concentration for each analyte should be reported separately, or the total for the compound class reported.

2. **Identify medium for analysis.**

   Specify the analysis medium (e.g., soil, sediment, groundwater, surface water, air, biota).

3. **Decide on critical parameters.**

   Specify the required data turnaround time (IIIA) as the number of hours or days from the time of sample collection. Indicate whether chemical identification alone is desired or identification plus quantitation (IIIB). Specify the concentration of concern (IIIC) and required detection or quantitation limit (IIID).

4. **Identify routine available methods.**

   Use the final worksheet column, in consultation with the project chemist, to list the methods available that satisfy the requirements in the preceding steps. Reference sources and software are available to assist in identifying routine analytical methods applicable for environmental samples (Exhibit 53). The most common routine methods for organics and inorganics analyses for risk assessment are listed in Appendix III. The methods in the appendix are from the following sources:

   - Contract Laboratory Program (CLP) Statements of Work for Routine Analytical Services (EPA 1990d, EPA 1990e),
   - *Test Methods for Evaluating Solid Waste (SW846): Physical/Chemical Methods* (EPA 1986b),
   - *Standard Methods for the Examination of Water and Wastewater* (Clesceri, *et. al.*, eds. 1989), and
   - EPA Series 200, 300, 500, 600 and 1600 Methods (EPA 1983, EPA 1984, EPA 1988d, and EPA 1989g).

   Other sources of methods are:

   - Field Analytical Support Project (FASP) (EPA 1989h),
   - *Field Screening Methods Catalog* (EPA 1987b),
   - *Field Analytical Methods Catalog*,
   - *ERT Standard Operating Guidelines*,
   - *Close Support Analytical Methods*,
   - *A Compendium of Superfund Field Operations Methods* (EPA 1987c),
   - Association of Official Analytical Chemists (AOAC), and
   - American Society for Testing and Materials (ASTM).

   Several computer-assisted search and artificial intelligence-based tools are available, including the Environmental Monitoring Methods Index (EMMI), the Smart Methods Index, and a computerized reference book on analytical methods. Some of these systems are designed as teaching tools, as well as informational compendia. All offer the ability to rapidly search and compare lists of chemicals and method characteristics from accepted reference sources. Exhibit 53 lists software products that aid method selection, identifies contacts for information, and gives a short description of the product.

EXHIBIT 53. AUTOMATED SYSTEMS* TO SUPPORT METHOD SELECTION

System	Contact	Description
Environmental Monitoring Methods Index (EMMI)	W. A. Telliard USEPA Office of Water (202) 260-7120	An automated sorting and selection software package that currently contains over 900 methods and over 2600 analytes from more than 80 regulating and non-regulating lists. These are cross-referenced to facilitate selection based on required needs (e.g., analyte detection limit, instrument).
Smart Methods Index	John Nocerino Quality Assurance Div. USEPA, EMSL-LV (702) 798-2110	Natural language expert system prototype that provides interactive queries of databases cross-referenced by method, analyte, and performance features.
Geophysical Techniques Expert System	Aldo Maggella Advanced Monitoring Div. USEPA, EMSL-LV (702) 798-2254	An expert system that suggests and ranks geophysical techniques, including soil-gas, for applicability of use based on site-specific characteristics.
EPA Sampling and Analysis Data Base	Lewis Publishers 1-800-272-7737	A three-volume set of diskettes and a printed manual provides a search of sampling and analytical method summaries from a menu-driven program of 150 EPA-approved methods. The database can be searched by method, analyte, matrix, and various QA considerations.

*All systems will run on any IBM-compatible PC AT with a minimum of 640K RAM. A fixed disk is recommended.

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4.2.2 Evaluating the Appropriateness of Routine Methods

☛ *Analyte-specific methods that provide better quantitation can be considered for use once chemicals of potential concern have been identified by a broad spectrum analysis.*

Choice of the proper method is critical to the acquisition of useable data. See Section 3.2 for a more detailed discussion. Routine methods provide data of known quality for the analysis of chemicals and sample types described in the method. Data quality issues (precision, accuracy, and interferences) are usually described in the method. Consult the project chemist and examine available methods with respect to the criteria defined on the Method Selection Worksheet. It may be helpful to divide the analyte list into categories based on the types of analysis. For example, a requirement for chromium, cadmium, and arsenic data could not be generated by the same analysis as data for chlorinated hydrocarbons because of sample extraction and treatment procedures. It may be possible to use several methods independently and combine the data sets for risk assessment purposes. This is done routinely by the CLP, where inorganics (elemental analysis), volatiles, extractable organics, and pesticides are analyzed by different methods. In some cases, no routine method or series of methods will be able to satisfy all criteria and compromises must be considered. The RPM, with the advice of the risk assessor, must then determine which criteria are of highest priority and which can be modified. For example, if a low detection limit is of high priority, turnaround time and cost of analysis will likely increase. Alternatively, low detection limit and precision requirements may need to be modified if an initial broad spectrum analysis is of high priority to quickly determine the largest number of chemicals present at the site.

Turnaround time. Turnaround time is determined by the available instrumentation, sample capacity, and methods requirements. Turnaround times for field analyses can be as short as a few hours, while those for fixed laboratory analyses include transport time and range from several days to several weeks. Field instruments can provide the quickest results, especially if the data do not go through a formal review process. However, the confidence in chemical identification, and particularly quantitation, may not be as high. In general, methods with quick turnaround times may be less precise and have higher detection limits. If data are needed quickly, a field method can be used for initial results and a fixed laboratory method used to produce more detailed results (or confirm the earlier results), thereby increasing the confidence in field analyses.

Sample quantitation limits. Risk assessment often requires a sample quantitation limit at or below the detection limit for routine methods for many chemicals of toxicological concern (see Section 3.2.4). The sample quantitation limits vary according to the size, treatment, and analysis of each individual sample. The quantitation limits for chemicals in water samples are often far lower than for the same chemicals in soils because of co-extractable components in the soil. Interferences known for the method may hinder acquisition of data of acceptable quality and are more pronounced near the method detection limit. Compare documented method interferences with site conditions to identify potential method problems. Some common sources of interference in organic and inorganic analyses are summarized in Exhibits 54 and 55. If needed sample quantitation limits cannot be met by available methods, consult the project chemist for the feasibility of detection at the desired level in the required sample type. The chemist can help determine if method adaptation can resolve the problem, or if a non-routine method of analysis can be used.

Useful range. The useful range of a method is the range of concentration of chemicals for which precise and accurate results can be generated. This range is analyte-specific. The lower end of the useful range is the method detection limit, often generically referred to as

EXHIBIT 54. COMMON LABORATORY CONTAMINANTS AND INTERFERENCES BY ORGANIC ANALYTE

Contamination or Interference	Fraction	Matrix	Effects on Analysis	Removal*/ Action
Fat/Oil	Extractable organics, pesticides, and PCBs	Tissue, waste, soils	Increased detection limit, decreased precision/ accuracy	GPC (all groups), florisil (pesticides), acid digestion (PCBs only)
Sulfur	Extractable organics, chlorinated and phosphorus-containing pesticides	Sediment, waste, soils	Presence/ absence, detection limits, precision/ accuracy	GPC, copper, mercury, tetrabutyl ammonium sulfate
Phthalate Esters	Chlorinated pesticides, PCBs, and extractable organics	All	False positive identification (pesticides and extractable organics) or positive bias (pesticides and extractable organics)	Florisil, GC-MS confirmation of identity (pesticides, PCBs), evaluation of reagents and method blanks for contamination
Laboratory Solvents	Volatile organics (methylene chloride, acetone, and 2-butanone)	All	False positive identification or positive bias	Confidence in data use based on interpretation of blank data

*Source: EPA 1986a.

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the "detection limit." If a lower detection limit is required, use of a larger sample or smaller final extract volume can sometimes compensate. However, any interfering chemicals are also concentrated, thereby producing greater interference effects. Above the useful range, the response may not be linear and may affect quantitation. This causes inaccurate and/or imprecise measurements. Reducing the sample size for analysis or diluting the extracted material may bring the concentration within the useful range. With individual environmental samples, some chemicals are sometimes present at the low end of the useful range of the method, while others are above the useful range. In this situation, two analyses, at different effective dilutions, are necessary to produce accurate and precise data on all chemicals. If detailed criteria for performing and reporting such actions are not already part of the analytical Statement of Work, then the laboratory should be instructed to notify the RPM if this situation occurs, to allow for sufficient time for reanalysis within the specified holding time. All relevant analyses should be reported to maximize the useability of both detected and non-detected analytes.

☛ *All results should be reported for samples analyzed at more than one dilution.*

Precision and accuracy. Routine methods often specify precision and accuracy with respect to specific analytes (chemicals) and matrices (sample media). However, be aware that environmental samples are often difficult to analyze because of the complexity of the matrix or the

EXHIBIT 55. COMMON LABORATORY CONTAMINANTS AND INTERFERENCES BY INORGANIC ANALYTE

Analyte	Technique	Interference	Removal/ Action
Arsenic	GFAA	Iron, Aluminum	Background correction (not deuterium) (Zeeman).
	ICP	Aluminum	If above 100 ppm, correction factor utilized.
Beryllium	ICP	Titanium, Vanadium	If above 100 ppm, correction factor utilized.
Cadmium	GFAA	None except possible sample matrix effects	Background correction for matrix effects.
	ICP	Iron	If above 100 ppm, correction factor utilized.
Chromium	GFAA	Calcium	Add calcium, standardize suppression, background correction.
	ICP	Iron, Manganese	If above 100 ppm, correction factor utilized.
Lead	GFAA	Sulfate	Lanthanum nitrate addition as matrix modifier, background correction.
	ICP	Aluminum	If above 100 ppm, correction factor utilized.
Mercury	CVAA	Sulfide, High Chloride	Remove interferences with cadmium carbonate (removes sulfide), potassium permanganate (removes chloride), excess hydroxylamine sulfate (removes free chlorine).
Selenium	GFAA	Iron, Aluminum	Alternate wavelength for analysis, background correction (not deuterium) (Zeeman).
	ICP	Aluminum	Above 100 ppm, correction factor utilized.
Cyanide	Colorimetric/ spectrophotometric	Acids, Sulfide, Chlorine oxidizing agents	Increase pH to > 12 in field to remove acids, cadmium carbonate (removes sulfide), ascorbic acid (removes free chlorine).

Key: ICP = Inductively coupled plasma.
GFAA = Graphite furnace atomic absorption.
CVAA = Cold vapor atomic absorption.

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presence of a large number of contaminants; this usually results in lower levels of precision and accuracy than those cited in the method.

4.2.3 Developing Alternatives When Routine Methods are not Available

If routine methods are not available to suit the parameters of interest, it is often due to one or more of the following factors:

- The detection limit of commonly available instrumentation has been reached, and a lower detection limit is required for the risk assessment,
- An unusual combination of chemicals are of potential concern,
- The sample matrix is complex, and
- The chemicals of potential concern or other analytical parameters are unique to a particular site.

Consult an analytical chemist for specific guidance on the potential limitations of alternative approaches. These may include adaptation of a routine method or use of a non-routine method. Be aware that certain conditions, such as extremely low detection limits for some chemicals, may be beyond the capability of current analytical technology. Turnaround times and costs may also be increased.

Adaptation of routine methods. Adapting routine methods may be a solution when routine methods will not provide the desired data even after compromises have been made with respect to parameters such as turnaround time and cost. Using the completed Method Selection Worksheet as the starting point, work closely with an analytical chemist to formulate suitable modifications to the routine method. Evaluate and document any effects on data quality that will result from the modifications.

Within the CLP, such analyses can be obtained by special analytical requests. Before analysis of site samples, it is advisable to confirm a laboratory's ability to perform the adapted method with preliminary data.

Use of non-routine methods. Existing non-routine methods that meet criteria can be used if a routine method cannot be adapted to provide the necessary data. Such analyses can be found in the research literature, usually catalogued by analyte or instrument. On-line computerized search services can be of considerable help in identifying such methods. Work interactively with an analytical chemist in reviewing selected methods. Recognize that non-routine analyses require a greater level of capability and experience from the analytical laboratory, and that turnaround time can be longer because the method may need alteration during analysis if problems develop.

Development of new methods. Developing new methods should be the option of last resort. The RPM, risk assessor, and project chemist should consider recommending the development of new methods only for chemicals of substantial potential concern that cannot currently be analyzed at appropriate limits of detection.

Although designing a method based on data available for a given instrument and analytes may seem straightforward, the process is time-consuming and expensive. Unforeseen problems can often arise when the method is implemented in the laboratory. Problems can occur even when laboratory personnel have superior training and experience. Consider the following points when requesting the development of a new method:

- If possible, select a laboratory with a recognized reputation for performance and flexibility in a related area. Treat laboratory personnel as partners in the development process. This is true whether a commercial or a government laboratory is used.
- Identify sources for authentic standards of the chemicals in question to support method development. Computerized databases such as the EPA EMMI (see Exhibit 53) may be useful for such a determination.
- Be aware that turnaround time for useable data may be long (potentially several months) because of the likelihood of trying different approaches before discovering an acceptable procedure.

4.2.4 Selecting Analytical Laboratories

In selecting a laboratory to produce analytical data for risk assessment purposes, identify and evaluate the following laboratory qualifications:

- Possession of appropriate instrumentation and trained personnel to perform the required analyses, as defined in the analytical specifications,
- Experience in performing the same or similar analyses,
- Performance evaluation results from formal monitoring or accreditation programs,
- Adequate laboratory capacity to perform all analyses in the desired timeframe,

- Intra-laboratory QC review of all generated data, independent of the data generators, and
- Adequate laboratory protocols for method performance documentation and sample security.

For non-routine analyses, the laboratory should have highly trained personnel and instrumentation not dedicated to production work, especially if new methods or untested modifications are requested.

Accreditation programs monitor the level of quality of laboratory performance within the scope of their charters. Many of these programs periodically provide performance evaluation samples that the laboratories must analyze within certain limits in order to maintain their status. Prior to laboratory selection, request that laboratories provide information about their performance in accreditation programs. This information can be used for evaluation of laboratory quality, in the case of similar matrices and analytes. Laboratory adherence to standards of performance such as the Good Laboratory Practices Standards (*Annual Book of ASTM Standards*) also provides a measure of laboratory quality.

4.2.5 Writing the Analysis Request

Include the following items in the analysis request:

- A clear, complete description of the sample preparation, extraction, and analysis procedures including detailed performance specifications. For adaptation of routine methods, specify the routine method and explicitly state alterations with applicable references.
- Documented reporting requirements.
- Laboratory access to required authentic chemical standards.
- A mechanism for the laboratory to obtain EPA technical assistance in implementing method modifications or performing non-routine methods.

If the analysis request is for a non-routine method, reference the published material with a detailed specification of procedures and requirements prepared by the analytical chemist who has been working with the RPM and risk assessor. The specification must include the frequency, acceptance criteria, and corrective action requirements for each of the following:

- Instrument standardization, including tuning and initial and continuing calibration,
- QC check samples such as surrogate compound and internal standard recoveries,
- Method blank performance (permissible level of contamination),
- Spike sample recovery requirements,
- Duplicate analysis requirements, and
- Performance evaluation or QC sample results.

Allow time for the laboratory to review the analysis request and question any part of the description that seems unclear or unworkable according to its experience with the analytes or sample matrix. Preliminary data, such as precision and accuracy data on a subset of the analytes, can be requested to determine if the laboratory can implement the proposed method. Should the criteria not be met in the preliminary analyses, the analytical chemist should advise the laboratory on additional method modifications to produce the required data. In some cases, even qualitative data can be used to note the presence of chemicals of potential concern.

In all cases, require the laboratory performing the analyses to contact the project chemist at the first sign of a problem that may affect data quality. The RPM and the site technical team can then judge the magnitude of the problem and determine appropriate corrective action.

4.3 BALANCING ISSUES FOR DECISION-MAKING

Resource issues. Resource limitations are a major reason for sampling design modification. The number of samples required to achieve desired performance measures may exceed resource availability. Modifying the sampling design and the efficiency of statistical estimators can reduce sample size and costs, and improve overall timeliness for the risk assessment. Analytical methods such as field analyses may also reduce cost. Systematic and geostatistical sampling designs can often achieve the required performance measures with fewer samples than classical random sampling (Gilbert 1987). Pilot sampling can be used to verify initial assumptions of the SAP, increase knowledge of contaminant distribution, and support SAP modifications to reduce the number of samples. Explain resource issues and record potential design modifications in documentation developed during planning.

Completing a number of Sampling Design Selection Worksheets (Exhibit 45) for different exposure areas,

media, and sampling design alternatives will enable the RPM and risk assessor to compare and evaluate sampling design options and consequences and select the appropriate sampling design for each medium and exposure pathway.

Computer programs are useful tools in developing and evaluating sampling strategies, especially in trading off costs against uncertainty, and identifying situations when additional samples will not significantly affect the useability of the data (i.e., the point of diminishing returns). Each automated system has specific data requirements and is based on specific site assumptions. The major systems that support environmental sampling decisions are listed, contacts for information given, and brief descriptions provided in Exhibit 51.

Documenting design decisions. It is important to document the primary issues considered in balancing tradeoffs to accommodate resource concerns and their impact on data useability. Several compromises among options are discussed in this section. Features of analytical options available for organic and inorganic analytes are summarized in Exhibits 56 through 59. Fully document all final sampling and analytical design decisions, including the rationale for each decision. During the course of the RI, continue to document pertinent issues that arise and any plan modifications which are implemented.

The goal of balancing issues in the selection of analytical methods is to obtain the best analytical performance without sacrificing risk assessment requirements. The selection of analytical methods often involves tradeoffs among the required detection limit, number of analytes involved, precision and accuracy, turnaround time, and cost. Some choices may conflict with others.

Cost should be considered only after the most appropriate methods have been determined. Methods requiring specialized instrumentation, such as high resolution mass spectrometry, will be more expensive. Methods for use on matrices such as soil, can be more expensive than similar methods for a simpler matrix such as water. Less expensive methods often have higher detection limits and less specific confirmation of identification. However, the turnaround times are often quicker and a larger number of samples can be analyzed. This often significantly increases sampling precision and reduces the probability of missing hot spots. Less expensive methods are often chosen if the site has already been characterized by broad spectrum analyses. In evaluating routine methods, consider whether analysis of more samples through use of less expensive methods can provide a similar level of data quality to that achieved through the use of more expensive methods on fewer samples. By remaining aware of the effect of individual issues on the data quality, the RPM can determine the optimum choices.

> ☛ *Field analysis can be used to decrease cost and turnaround time, providing data from a broad spectrum analysis are available.*

In addition to turnaround time for analysis, time must also be scheduled for data review. This will not hinder the availability of laboratory and field data for preliminary use if a tiered data review sequence is incorporated.

When using the tiered approach, consider the use of split samples (i.e., sending sample splits for analysis by field and fixed laboratories). Quantitative comparison can then be made between the precision and accuracy of the field analyses and those of the fixed laboratory. Confirmation of identification by both field and fixed laboratories also increases data confidence and useability. It is recommended that field methods should be used with at least a 10% rate of confirmation or comparison by fixed laboratory analyses.

EXHIBIT 56. COMPARISON OF ANALYTICAL OPTIONS FOR ORGANIC ANALYTES IN WATER

Method	MDL	Quantitative Confidence	Timeliness	Precision & Accuracy	Comparability
FIELD SCREEN/FIELD ANALYSIS (Assumes preparation step)					
GC(PCB)	√	√	√		√
GC (Pesticides)	√		√		√
GC (VOA)	√		√		√
G C (Soil Gas)	√		√		
GC (BNA)	√		√		√
PHOTO VAC Detector			√		
FIXED LABORATORY					
CLP RAS					
VOA		√			√
BNA		√			√
Pesticides					√
Dioxin		√		√	√
CLP LOW CONC					
GC	√			√	√
VOA	√	√		√	√
BNA	√	√		√	√
500 SERIES					
GC	√				√
VOA	√	√			√
BNA	√	√			√
600 SERIES					
GC	√				√
VOA	√	√			√
BNA	√	√			√
SW846					
GC	√				√
VOA		√			√
BNA		√			√
1600 SERIES					
GC	√			√	√
VOA		√		√	√
BNA		√		√	√
Dioxin		√		√	√
PCDDs, PCDFs		√		√	√

Key: √ = Method strength

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EXHIBIT 57. COMPARISON OF ANALYTICAL OPTIONS FOR ORGANIC ANALYTES IN SOIL

Method	MDL	Quantitative Confidence	Timeliness	Precision & Accuracy	Comparability
FIXED LABORATORY					
CLP RAS					
VOA		√			√
BNA		√			√
Pesticides					√
Dioxin (2,3,7,8 TCDD)		√		√	√
SW846					
GC	√				√
VOA		√			√
BNA		√			√
1600 SERIES					
GC	√			√	√
VOA		√		√	√
BNA		√		√	√
Dioxin		√		√	√
FIELD SCREEN					
GC(PCB)	√	√	√		√
GC(Pesticides)			√		√
GC(VOA)	√		√		√
GC(Soil Gas)	√		√		
GC(BNA)	√		√		√
PHOTO VAC Detector			√		

Key: √ = Method strength

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EXHIBIT 58. COMPARISON OF ANALYTICAL OPTIONS FOR INORGANIC ANALYTES IN WATER AND SOIL

Method	MDL	Quantitative Confidence	Timeliness	Precision & Accuracy [1]	Comparability [2]
FIXED LABORATORY					
CLP RAS					
ICP		√		√	√
GFAA	√	√		√	√
Flame AA					
200 Series					
GFAA	√	√		√	√
AA					
ICP-MS[3]	√	√			√
ICP-Hydride[3]	√				
FIELD SCREEN					
XRF			√		
AA			√		

Key: √ = Method strength

[1] CLP inorganic water assays are more accurate and precise than soil assays.

[2] ICP and GFAA are comparable at medium to high ppb levels. For As, Pb, Se, Tl and Sb at less than 20 ppb, GFAA is the method of choice.

[3] ICP-MS and ICP-Hydride methods are relatively new; therefore, precision, accuracy, and comparability estimates based on large statistical sampling are not available.

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EXHIBIT 59. COMPARISON OF ANALYTICAL OPTIONS* FOR ORGANIC AND INORGANIC ANALYTES IN AIR

Method	MDL	Quantitative Confidence	Timeliness	Precision & Accuracy	Comparability
FIXED LABORATORY					
CLP VOA					
Cannister	2-5 ppb	√		√	
Tenax	2-30 ppb (for most)	√		√	
CLP BNA	0.00001-0.001 ug/m3	√		√	
CLP Metals	3-10 ng/m3	√		√	

Key: √ = Method strength

* The methods described are new Statements of Work.

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