

IAEA-TECDOC-1415

# *Soil sampling for environmental contaminants*



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SOIL SAMPLING FOR ENVIRONMENTAL CONTAMINANTS

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## FOREWORD

The Consultants Meeting on Sampling Strategies, Sampling and Storage of Soil for Environmental Monitoring of Contaminants was organized by the International Atomic Energy Agency to evaluate methods for soil sampling in radionuclide monitoring and heavy metal surveys for identification of punctual contamination (hot particles) in large area surveys and screening experiments. A group of experts was invited by the IAEA to discuss and recommend methods for representative soil sampling for different kinds of environmental issues.

The ultimate sinks for all kinds of contaminants dispersed within the natural environment through human activities are sediment and soil. Soil is a particularly difficult matrix for environmental pollution studies as it is generally composed of a multitude of geological and biological materials resulting from weathering and degradation, including particles of different sizes with varying surface and chemical properties. There are so many different soil types categorized according to their content of biological matter, from sandy soils to loam and peat soils, which make analytical characterization even more complicated. Soil sampling for environmental monitoring of pollutants, therefore, is still a matter of debate in the community of soil, environmental and analytical sciences.

The scope of the consultants meeting included evaluating existing techniques with regard to their practicability, reliability and applicability to different purposes, developing strategies of representative soil sampling for cases not yet considered by current techniques and recommending validated techniques applicable to laboratories in developing Member States.

This TECDOC includes a critical survey of existing approaches and their feasibility to be applied in developing countries. The report is valuable for radioanalytical laboratories in Member States. It would assist them in quality control and accreditation process.

The IAEA wishes to thank all the participants in the consultants meeting for their valuable contributions. The IAEA officers responsible for this report were B. Smoldis of the Division of Human Health and M. Rossbach of the Division of Physical and Chemical Sciences.

### *EDITORIAL NOTE*

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## 1. INTRODUCTION

In recent years, the IAEA has helped many institutions in developing Member States to set up nuclear analytical laboratories through assistance via technical co-operation and co-ordinated research projects, expert services, and fellowship awards. Some of these laboratories have now matured to approach close to self sustainability by providing service analysis for customers in many fields, including geological prospecting and environmental contamination survey.

Quality control and quality assurance concepts have been developed to assist the laboratory personnel to achieve a higher degree of transparency of procedures, minimize potential sources of error, standardize the handling of samples, instruments and data, and in the end, decrease the rate of non-conformance results.

Quality of analytical data is not only expressed by the closeness of a result to a fictive “true value” but also in a realistic estimate of the uncertainty of the results and a comprehensive documentation on how the results were obtained. It is still not common knowledge that any analytical result is associated with a specific uncertainty due to the sample matrix heterogeneity, method performance fluctuation, uncertainty of values assigned to the standards, and so on. The combined uncertainty of these factors can be estimated by repetitive analysis of independent aliquots and has to be shown together with the result.

Soil sampling and sample preparation, which have a crucial influence on the result, should be carefully documented to allow re-evaluation of results if doubts about their reliability come up. In particular, soil sampling for environmental contaminants investigation have been developed in many analytical laboratories to establish standards and quality control procedures, in order to avoid confusion relating to this very important subject.

The ultimate targets for all kinds of contaminants dispersed within the natural environment through human activities are sediment and soil. Topsoil is a particularly difficult matrix for environmental pollution studies as it is generally composed of a multitude of geological and biological materials resulting from weathering and degradation including particles of different sizes with varying surface and chemical properties. There are so many different soil types categorized according to their content of biological matter, from sandy soils to loam and peat soils, which make analytical characterization even more complicated.

External contaminants entering a soil body through wet or dry precipitation, such as radionuclides, trace elements, or organic compounds, behave differently with regard to each soil type according to the absorption properties, texture, density, humidity, and other factors. As these properties are not homogeneously developed in a certain soil bed and soil properties change largely with stratigraphy, it is extremely difficult to collect soil samples from a sampling area for chemical analysis in such a way that representativity is assured.

There are some statistical approaches trying to overcome these difficulties by either going to very large numbers compromising the analytical capabilities or by neglecting certain attributes of soils which might, however, be crucial for the problem to be solved. An example being laboratory homogenization of soils which ultimately destroys the surface properties that might have serious consequences of the binding capacity of soil for certain contaminants.

Soil sampling for environmental monitoring of pollutants is therefore still a matter of debate in the community of soil, environmental and analytical sciences. A group of experts was invited by the IAEA to discuss and recommend methods for representative topsoil sampling for different kinds of environmental issues. This document was compiled from their contributions and presents the status of soil sampling technology as applied for investigation of environmental contaminants. It will help the laboratories of developing countries Member States for improving their quality in radioanalytical techniques.

## 2. SOIL CONTAMINATION AND ITS MONITORING NEEDS

### *Soil system*

The word “soil” has a variety of different meanings depending upon its relevance to the society. Farmers consider it as the part of the earth’s surface containing decayed and organic material in sufficient quantity to grow plants and crops. Geologists take it as the residual (left over) material from underlying parent rock that supports root growth. To the engineer, soils include all earth materials overlying the rock crust and contain particles of minerals, gasses, and liquids.

According to the Soil Science Society of America (SSSA), soil is a living system that represents a finite resource vital to life on earth. It forms the thin skin of unconsolidated mineral and organic matter on the earth’s surface. It develops slowly from various parent materials and is modified by time, climate, macro- and microorganisms, vegetation, and topography.

Soils are complex mixtures of minerals, organic compounds, and living organisms that interact continuously in response to natural and imposed biological, chemical, and physical forces. Vital functions that soils perform within ecosystems include: sustaining biological activity, diversity, and productivity; regulating and partitioning water and solute flow; filtering, buffering, degrading, immobilizing, and detoxifying organic and inorganic materials, including industrial and municipal by-products and atmospheric depositions; storing and cycling nutrients and other elements within the earth’s biosphere; and providing support for socio-economic structures and protection for archaeological treasures associated with human habitation.

### *Soil quality*

There are different views about the soil quality also. For people active in production agriculture, it may mean highly productive land, sustaining or enhancing productivity, maximizing profits, or maintaining the soil resource for future generations. For consumers, it may mean plentiful, healthful, and inexpensive food for present and future generations. For naturalists, it may mean soil in harmony with the landscape and its surroundings, and for the environmentalist, it may mean soil functioning at its potential in an ecosystem with respect to maintenance or enhancement of biodiversity, water quality, nutrient cycling, and biomass production. The SSSA defines soil quality as: the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation.

Soil quality is therefore related to how well the soil does what we want it to do? This means that we need to have the complete information about the specific kind of soil or the soil characteristics which in fact are always subjected to fluctuations due to changes in management, changing rainfall patterns (including acid rain), changing water table levels and vegetation cover and other environmental factors. These changes in turn disturb the chemical equilibrium pattern in soil. In other words, soils are not material specific, many of their properties are not single valued, many are transient, and many are not randomly distributed but rather systematically time and spatially dependent.

### *Soil contamination*

The soil quality can be affected or disturbed by any of the factors described above and when a disturbance is due to the presence of substances in such concentrations which affect or tends to affect the role the soil plays in the ecosystem, it is known as contaminated soil, and the substances involved in this process are called soil contaminants. The standards or the thresholds that are fixed for the various soil contaminants through the national/international legislations provide specific definitions of soil contamination, as contamination here refers to the exceeding of the threshold limiting values prescribed in such legislations.



External contaminants entering a soil body through wet or dry precipitation, such as radionuclides, trace elements or organic compounds behave differently with regard to each soil type according to the absorption properties, texture, density, humidity, and other factors. As these properties are not homogeneously developed in a certain soil bed and soil properties change largely with stratigraphy it is extremely difficult to collect soil samples from a sampling area for chemical analysis in such a way that representativity is assured.

#### *Monitoring needs*

The development in the modern life styles especially due to the connected industrial and other developments have given rise to large risks of soil contamination and that too in a very uneven manner. The examples include erratic emissions/discharges of pollutants from industries, automobiles, indiscriminate disposal of solid/hazardous waste especially in developing countries and explosions or accidents involving hazardous substances.

While, there is an increasing pressure to control further contamination of soil, the clean up and restoration of those, which are already contaminated, or which become so due to accidents or other such reasons, require accurate assessment of the type and the level of contamination. This is very important because identification of pollutants not existing or even high estimations of those existing can result into wastage of huge amounts in the clean up or even in abandoning of a site, which is not contaminated. On the other hand, non-identification or lower estimation of contaminants may result into wastage of funds in the form of wrong uses of a site for specific purposes, as these uses may have to be dropped at a later stage. This false negative identification/estimation of contaminants can even result into adverse effects on the environment including the human beings occupying such sites. This coupled with the fact that soil contamination specially from the anthropogenic activities is mostly in an erratic manner, makes soil sampling from such areas the most important component of the whole process concerning the identification and use of sites for various purposes.

Monitoring of the soil quality to get the accurate status and distribution of the environmental contaminants is therefore not only essential but the quality of the monitoring data also becomes the basis of the objective concerning the further use of the area studied. Also, since the processing and analysis of soil samples in the laboratories are already developed that the chances of errors are relatively very small compared to errors in collecting such samples, the sampling therefore becomes the most important component in soil investigation studies specially those involving contaminated sites/areas.

### **3. EXISTING TECHNIQUES AND STRATEGIES**

#### **Status**

The developments concerning the sampling and strategies adopted in soil sampling are well described by Mason in his report prepared in 1983. The report mentioned Kriging combined with the semi-variogram, as an important tool in designing and conducting soil and waste sampling programmes.

However, the sampling of volatile organics chemicals remained a problem with this method. This limitation resulted into increasing use of soil gas sampling methods as additional aid for the identification of volatile contaminants. This steadily got further improved and use of portable gas chromatographs also came into use enabling collection of preliminary field data which could help in the preparation of appropriate sampling approaches, specially for sites involving organic spills or accidents involving such chemicals.

The U.S. EPA has also developed (U. S. EPA, 1986, 1987a, 1987b) the use of Data Quality Objectives (DQO's) as a guiding policy for all environmental sampling. The DQO process is intended to provide the decision maker with data that meet a predetermined level of precision, accuracy, representativeness, completeness, and comparability, in addition to identifying the data characteristics.

The DQO policy also enables specifications of the detection level needed, the probabilities of the acceptable false positive and false negative errors, and the minimum detectable relative difference between the data sets.

Some experts (Barth et. al 1989; Pitard 1989) have suggested the use of possible sources of variation/errors as a guide in deciding the sampling programmes. Van Ee et al (1990) has suggested, “the reallocation of resources”, approach for soil to make optimum use of the money, person, power and laboratory for deciding soil sampling programmes, as the analytical processes are not expected to contribute much to the overall data quality.

Starks (1986) has outlined the concept of support as it applies to soil sampling. The specific size, shape, orientation, and spatial arrangement of the samples constitute the support (Davis, 1986). Risk and exposure assessment data can be used to assist in defining an “action support” (Barth et. al., 1989) or the application of an action level over a particular support and location relative to the surface. The size of the support may change depending upon the purpose of the sampling effort. However, it is necessary for this concept to make sure that the supports used in the sampling programme meet the data reliability called for in the Data Quality Objectives (DQO) for the intended investigation. The amount of material required to make up the support can be determined by using the particulate sampling theory (Gy, 1982) according to which a relationship exists between a particle size and the weight of sample that must be used to provide a reliable estimate of the concentration of precious metals in a block of soil.

The particulate sampling theory links the size of particles in the material directly to the size of sample that is taken from a unit, batch, or lot of soil or ore that is being evaluated. The controlling particle size is the largest particle. Thus, samples that have been screened before analysis can be greatly biased. Fortunately, most of soils fall into a range of particle sizes wherein there is little effect upon contaminant concentrations. However, in those cases where the soil is a fine textured soil combined with cobbles, gravels, or coarse sands this may not be the case. In addition, in cases where non-liquid wastes such as rubble, construction debris, etc. are present in the soil, the concentration data may not be representative.

## **Review**

The soil sampling techniques/methods developed in the past mainly cover soil sampling for the purpose of soil characterisation in general and in fact these methods/tools got developed when the soil contamination due to release of manmade sources was not so predominant. Also, the soil within its own matrix itself is so anisotropic that it is not easy to formulate a general method which can meet the requirements of soil sampling at different locations even in the absence of soil contamination from anthropogenic sources. The monitoring of soil for environmental contaminants is even more difficult because of not only the complex soil matrices but also even the differences in soil types from site to site and a rather uncertain fate of environmental pollutants in the soil makes the situation more complicated.

Environmental contaminants entering a soil system through discharge or emissions such as radionuclides, trace elements, or organic compounds behave differently from site to site depending upon the soil absorption properties, texture, density, humidity, and other factors. In addition, the existing methods are mostly the outcomes of the studies, which were conducted in developed countries.

The situation in the developing countries with regard to soil contamination is even more complicated as the regulations for controlling of pollutants on land have got introduced only during the past one and half decade. However, it may be summarised that the sampling plan need to be designed so that even non-soil fractions concerning the analytes get accounted for either by sampling design or sample extraction and preparation. A conceptual model of how the pollutant is potentially distributed on the site can be used to design the soil component of the sampling study. The following sections provide some guidance for representative sampling, but any concrete investigation needs to address the particular circumstances being studied.

#### 4. SAMPLE REPRESENTATIVITY AND ITS ROLE/IMPORTANCE IN MONITORING OF SOIL CONTAMINATION

The first consideration for any information involving environmental analytical data is whether the samples adequately represent the site being investigated. The purpose of environmental sampling and analysis is to obtain a small but informative portion of the sampling site media being investigated. Seldom is the entire site collected for analysis. There are almost infinite soil samples that could be taken in most situations. Therefore, soil samples that are intended to be “representative” of a site are analysed and conclusions about that entire site are made based on the data obtained from them. It is now clear that most of the important and large costs involving decisions are based on the sampling data, making it essential that these data accurately characterize the conditions of the actual site. This requires that a sample or group of samples collected from a site accurately reflect the concentration of contaminants at the site. Such sample/samples are called “representative samples” for the corresponding site, and the sampling is called “representative sampling.”

Pollutants are not usually distributed evenly within a site being investigated. They are also not usually evenly distributed within the soil samples that are analysed as “representative” aliquots of an environmental site. Yet, most of the focus that defines the “quality” of data from an environmental site is centred on the analytical activities that occur at the tail end of the events that comprise the site assessment. It is very important not to make this mistake when planning where and how to obtain soil samples.

Remember that accuracy, precision, and other “data quality indicators” which characterize the “goodness” of the data do not characterize how well samples represent the site. Therefore, it does not matter how “good” the analytical data are if they do not represent the environmental site in a way that will answer questions for which analyses were being performed.

Uneven distribution (inhomogeneity) of pollutants is often the largest contributor to variability in analytical data. In addition, pollutants migrate (usually slowly over time) in all types of soils, typically from rain, and this often increases inhomogeneity. It is not uncommon for two samples of soil collected within a meter of each other to have differences of 50–100% in the concentrations of target analytes.

While, quality of the overall data on the concentration of contaminants also includes the sample transportation, preservation, processing (in the lab) and analysis, the representative sampling covers variables that are introduced in the field. These variables are related to conditions of the site, the sampling design, approach, and the techniques for collection and preparation of the samples in the field. The field variables that affect the representatives of the samples are the geological variability and the variation in the contaminant concentrations at the site, and the variations that are introduced during sample collection preparation and transportation.

It should be noted that, although variability in results that affects the manner samples are processed and analysed cannot be controlled through representative sampling, it can lead to doubts on the sampling representativity itself. It is because identifying the sources or stages is not easy, which could be actually responsible for those variations in the data.

It is important to understand that samples representative of a site are not necessarily “representative samples” in the statistical sense of the word “representative.” Many times a sample representative of the statistical distribution of the target analytes is desired, but not always. For example, soil samples may be collected at selected spots because there is evidence of pollution present (e.g. discoloured soil, or oily looking patches, or the presence of drums or other containers in certain areas of the site). These are examples of “judgmental” sample collection where specific spots or areas at a site are selected because of some reason. The reason may be visual, as in the above examples, or it may be based on historical site use, or any other information that causes the sampler to select a specific area from within the sampling site. However, although judgmental samples are not necessarily representative samples, in the sense that they represent the presence and concentration levels of the

target analytes of the whole site, they are still intended to be representative of that sub-portion of the site being investigated.

## **5. SOIL SAMPLING FOR ENVIRONMENTAL CONTAMINANTS (PURPOSE AND USEFULNESS)**

### **Basic purpose of representative soil sampling**

The primary aim of representative soil sampling is to get accurate data about the soil quality of a specific site but the ultimate objective is the purpose for which this exercise is done. These purposes, which are better known as representative sampling objectives for soil, include:

- Establishment of threat to public health or welfare or to the environment.
- Location and identification of the potential sources of contamination.
- Defining of the extent of contamination, and
- Formulation of the treatment and disposal options.

### **Usefulness/advantages of representative soil sampling**

It helps to safeguard the environment, and the data generated serve as a reliable database to substantiate compliance to local, regional and National laws and regulations;

It helps in deciding compensation and liability specially in case of spills/accidents;

It helps in deciding boundaries for clean areas and deciding priorities in regard to contaminant or clean up of contaminated sites.

It helps in overall funding priorities for use/development of different land areas.

It helps in deciding the type of treatment/disposal required for cleaning contaminated sites.

It helps in potential cost savings including those resulting from the false positive or false negative results, and

It helps in ensuring effective response arrangements in case of emergencies.

## **6. OBJECTIVES AND SCOPE OF THE REPORT**

### **Objectives**

- To provide a framework and guidance for the design and implementation of investigations of soil contamination and interpretation of resulting measurements.
- To supply a basis for effective communication between site investigators, laboratories and end users.

### **Scope**

The report provides practical advice to people involved in investigation and monitoring of soil contamination in the IAEA's Member States.

Considerations of measurement uncertainty (including contributions from sampling) and quality control are used to optimise the sampling and investigation strategy.

The report focuses on sampling strategies but not on the in-depth discussion of analytical techniques.

## 7. BASIC PRINCIPLES OF SOIL SAMPLING (WHY AND HOW)

### General steps involved in soil sampling

The basic principles of soil sampling in the context of the monitoring of environmental contaminants are expected to cover a wide range of aspects depending upon the cause of the contamination, which can vary from a gradual deposition of contaminants over a large span of time to release of shock loads from accidents/explosions leading to soil contamination. This may require designing of separate sampling plans for the monitoring of environmental contaminants for different sites. However, this in-turn requires a thorough understanding of the general steps/principles involved in soil sampling, which can be summarised as follows:

#### *Steps before the visit*

- Site selection
- Selection of the sampling team
- Development of investigation plan
- Collection of background information
- Review of background information
- Selection of area and parameters for sampling
- Selection of sampling approach
- Selection of sampling points
- Selection of monitoring equipment
- Analytical sampling equipment
- Geophysical equipment
- Soil sampling equipment
- Choice of sampling equipment
- Finalisation of investigation plan

#### *Steps at site/during the visit*

- Physical characterization and climatic conditions
- Sample collection
- Sample number
- Sample volume
- Removal of extraneous material

- Sample sieving
- Sample homogenization
- Sample splitting
- Sample composition
- Sample preparation

### **Steps before the visit**

#### *Site selection*

The identification or selection of sites for soil sampling is not required in most of the cases, as the need for investigation of a specific site for environmental contaminants gets covered in the problems such as accidents, chemical spills, explosions etc. or the intended use such as housing, park etc. of specific sites. However, identification of sites for investigation and development of a regional/national information base on soil quality or other general purposes can be done on the basis of anthropogenic and other activities of different areas which are expected to result into some or other kind of soil contamination.

#### *Selection of investigation team*

The number and the type of the persons to be involved in the team will depend upon the requirements of the problems associated with the site specific experts from the areas concerning the problem (e.g. forensic experts in case of accidents involving explosives) are required to be included in the team. Involvement of one experienced soil chemist in the team is also highly desirable irrespective of the type of the problem associated with the site to sampled.

In addition to this one scientific/technical person who is familiar with the activities at and in the proximity of site is also desirable.

The investigation team is therefore recommended to be formed by selecting experts from the subject areas relevant to the problems associated with the site. The areas relevant to soil sampling for environmental contaminants can be summarised as follows:

- Environmental sciences/engineering.
- Geo chemistry.
- Soil chemistry.
- Civil engineering.
- Specific fields related to the problems associated with the site.

### **Development of investigation plan**

#### *Collection of background information*

All possible information that is directly or indirectly related to the site to be sampled and the parameters to be measured in the samples should be collected either through correspondence and/or a reconnaissance survey of the area. The background information generally required includes the following:

- Site history — Location, soil type, climate in the vicinity, etc.

- Site use — Present and past land use pattern, details of the products manufactured and raw materials used in case of industrial activities, and details of the fertilisers, pesticides etc. used in the case of agricultural activities existing in the area.
- Site contamination — Details of (i) quality and quantity of the waste water generated from the various activities and its disposal practices, (ii) emissions generated in the area, (iii) solid and/or hazardous wastes generated and their disposal practices.
- Past Studies — Details of any studies conducted in the past for monitoring of the environmental contaminants or related purpose including the map and the sampling points covered in the studies.
- Site environment management responsibilities — The local/regional/national monitoring/regulatory agencies concerned with the environmental management of the site and the standards fixed in respect to the parameters which are to be analysed in the soil samples.
- Site documents — Location map of the area covering the site, and other available relevant documents.

#### *Review of background information*

The background information collected is reviewed by the investigation team to obtain the existing status of the site vis-à-vis the specific aim of the intended soil sampling programme.

The status should provide the following information:

- Exact location and easiest approach to the site.
- Climate, activities and other factors, which can affect the concentration of the environmental contaminants to be monitored.
- Possible contamination sources which pose threat to human health and environment.
- Existing data (if any) available on the environmental contaminants.
- Any other details which can help in the preparation of an appropriate sampling plan.

#### *Selection of area and parameters for sampling*

The selection of sampling area refers to the broad area within a site, which is to be covered in the sampling. This is done with the help of analytical and geophysical screening technique such as photo-ionization detector (PID), portable X ray fluorescence (XRF), and hazard categorization kits.

Geophysical techniques can be used to help in finding locations of any potential buried drums or tanks, buried waste, and disturbed areas. Geophysical techniques include ground penetrating radar (GPR), magnetometry, electromagnetic conductivity (EM) and resistivity surveys.

The parameters to be analysed in samples normally get identified with the problem itself e.g. a chemical spill or an explosion. In other general cases the parameters identification is done on the basis of the review of the background information for possible present and future release of environmental contaminants and their priority needs of their monitoring with respect to the future use of the site.

## Selection of sampling approach

### *Sampling approaches*

The approaches existing for collection of representative soil samples include judgmental, random, stratified random, systematic grid, systematic random, search, and transect sampling. A brief description of these is given in following paragraphs.

*Judgmental sampling* is the subjective selection of sampling locations at a site, based on historical information, visual inspection, and on best professional judgement of the sampling team. Judgmental sampling is used to identify contaminants present at areas having highest concentrations (i.e. worst-case conditions). This approach usually has no cost associated with the sampling strategy, precluding any statistical interpretation of the sampling results, but this can be included (CLR4, DEFRA, 1994)

*Random sampling* is the arbitrary collection of samples within the defined boundaries of the area of concern. Sample locations are chosen using a random selection procedure (e.g. using a random number table). The arbitrary selection of sampling points requires each sampling point to be selected independent of the location of all other points, and results in all locations within the area of concern having an equal chance of being selected. Randomization is necessary in order to make probability or confidence statements about the sampling results. Random sampling approach is suitable for the areas where the site is suspected to be homogeneous with respect to the parameters to be monitored. Figure 1.a illustrates a random sampling approach.

*Stratified random sampling* covers division of the sampling area into smaller areas called strata. This is done on the basis of historical information and prior analytical results or screening data. Each stratum is more homogeneous than the site as a whole. Strata can be defined based on various factors, including sampling depth, contaminant concentration levels, and contaminant source areas. Sample locations are fixed within each of these strata using the random selection procedures.

Stratified random sampling imparts some control upon the sampling scheme but still allows for random sampling within each stratum. Different sampling approaches may also be selected to address the different strata at the site. Stratified random sampling is a useful and flexible design for estimating the pollutant concentration within each depth interval or area of concern. Figure 1.b illustrates a stratified random sampling approach where strata are defined based on depth. In this example, soil-coring devices are used to collect samples from given depths at randomly selected locations within the strata.

*Systematic grid sampling* involves subdividing the area of concern by using a square, triangular or herringbone grid and collecting samples from the nodes (intersections of the grid lines). The origin and direction for placement of the grid is done using an initial random point. From that point, a coordinate axis and grid is constructed over the whole site. The distance between sampling locations in the systematic grid is determined by the size of the area to be sampled and the number of samples to be collected. Systematic grid sampling is often used to delineate the extent of contamination and to define contaminant concentration gradients. Figure 2.a illustrates a systematic grid sampling approach.

*Systematic random sampling* is a useful and flexible design for estimating the average pollutant concentration within grid cells, and is sometimes also referred to as stratified random sampling. The area of concern is subdivided using a square or triangular grid (as described in systematic grid sampling) then samples are collected from within each cell using the random selection procedures. Systematic random sampling allows for the isolation of cells that may require additional sampling and analysis. Figure 2.b illustrates a systematic random sampling approach.

*Search sampling* utilizes either a systematic grid or systematic random sampling approach to search for areas where contaminants exceed applicable clean-up standards (hot spots). The number of samples and the grid spacing are determined on the basis of the acceptable level of error (i.e. the chance of missing a hot spot). Search sampling requires that assumptions be made about the size, shape, and depth of the hot spots.



As illustrated in Figure 3.a, the smaller and/or narrower the hot spots are, the smaller the grid spacing must be in order to locate them. Also, the smaller the acceptable error of missing hot spots is, the smaller the grid spacing must be. This, in effect, means collecting more samples. Simple equations have been described to calculate the number of samples required to hit hot spots of known size and dimensions (CLR4, DEFRA, 1994).

*Transect sampling* involves establishing one or more transect lines across the surface of a site. Samples are collected at regular intervals along the transect lines at the surface and/or at one or more given depths. The length of the transect line and the number of samples to be collected determine the spacing between sampling points along the transect. Multiple transect lines may be parallel or non-parallel to one another. If the lines are parallel, the sampling objective is similar to systematic grid sampling. A primary benefit of transect sampling over systematic grid sampling is the ease of establishing and relocating individual transect lines versus an entire grid. Transect sampling is often used to delineate the extent of contamination and define contaminant concentration gradients. It is also used, to a lesser extent, in composting sampling schemes. For example, a transect sampling approach might be used to characterize a linear feature such as a drainage ditch. A transect line is run down the centre of the ditch, along its full length. Sample aliquots are collected at regular intervals along the transect line and are then composited. Figure 3.b illustrates transect sampling.

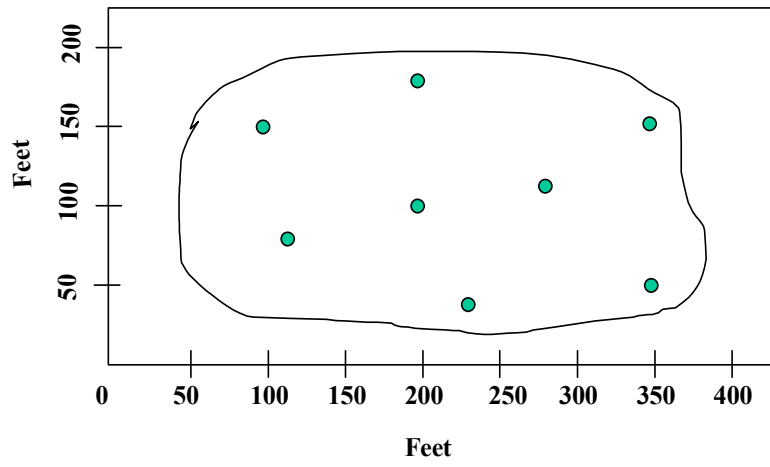
### **Choice of selection approach**

A representative sampling plan may combine two or more of the above described sampling approaches depending upon the type and distribution of the contaminants.

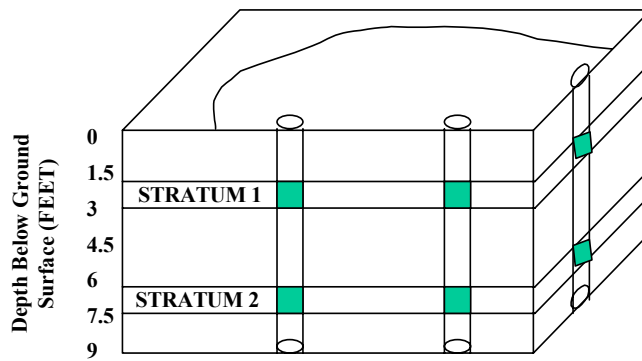
The various representative sampling approaches are summarised in Table I.

#### *Selection of sampling locations*

Sampling points may be located with a variety of methods. A relatively simple method for locating random points consists of using either a compass and a measuring tape, or a pacing, to locate sampling points with respect to a permanent landmark, such as a survey marker. Then plot sampling coordinates on a map and mark the actual sampling points for future reference. Where the sampling design demands a greater degree of precision, locate each sample points by means of a survey. After sample collection, mark each sample point with a permanent stake so that the survey team can identify all the locations.



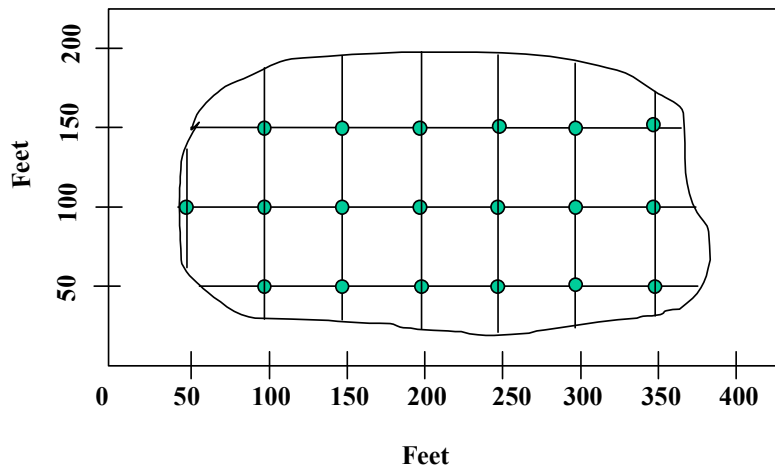
**a) Random Sampling**



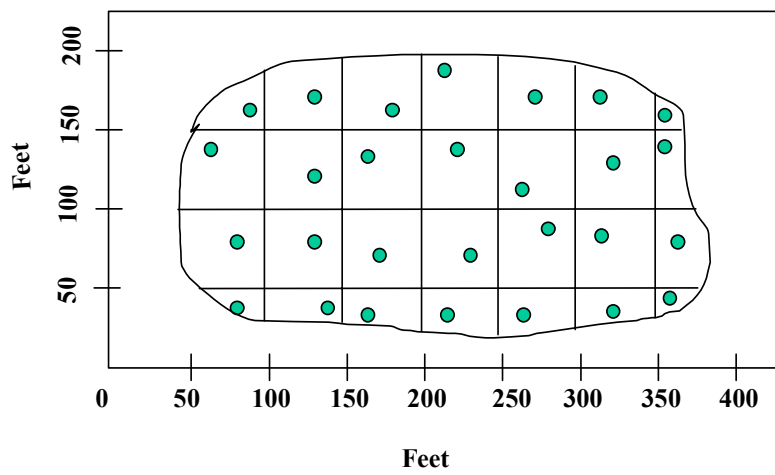
**b) Stratified Random Sampling**

● Selected Sample Location

*FIG. 1. Random (a) and stratified random (b) samplings.*



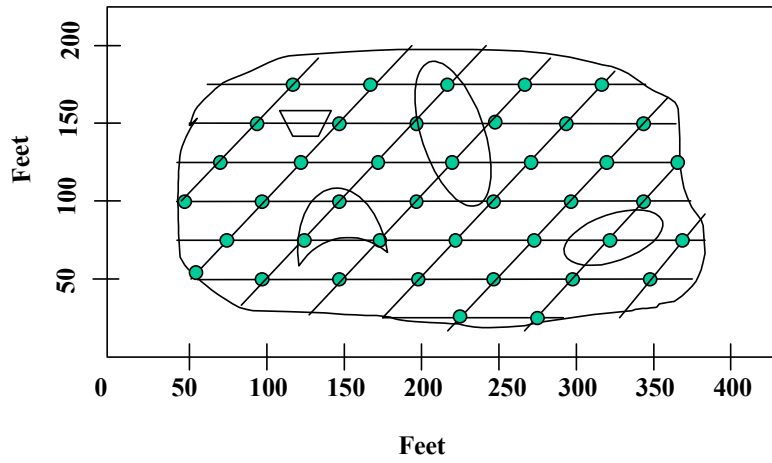
**a. Systematic Grid Sampling**



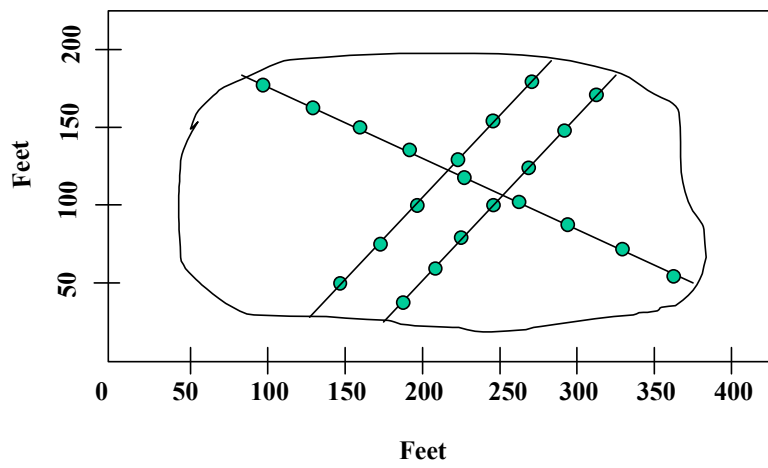
**b. Systematic Random Sampling**

● Selected Sample Location

*FIG. 2. Systematic grill (a) and systematic random (b) samplings.*



**a. Search Sampling**



**b. Transect Sampling**

 Selected Sample Location  
 Hot Spot

*FIG. 3. Search(a) and transect(b) samplings.*

TABLE I. REPRESENTATIVE SAMPLING APPROACH COMPARISON

Sampling objective	Sampling Approach						
	Judgmental	Random	Stratified random	Systematic grid	Systematic random	Search	Transect
Establish threat	1 <sup>b</sup>	4 <sup>a</sup>	3 <sup>a</sup>	2 <sup>a</sup>	3 <sup>a</sup>	3 <sup>a</sup>	2
Identify sources	1 <sup>b</sup>	4 <sup>a</sup>	2 <sup>a</sup>	2 <sup>a</sup>	3 <sup>a</sup>	2 <sup>a</sup>	3
Delineate extent of contamination	4	3 <sup>a,c</sup>	3 <sup>a,c</sup>	1 <sup>a,b</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1
Evaluate treatment and disposal option	3	3	1	2	2	4	2
Confirm clean-up	4	1 <sup>a,c</sup>	3 <sup>a</sup>	1 <sup>a,b</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>d</sup>

where:

1. Preferred approach.
2. Acceptable approach.
3. Moderately acceptable approach.
4. Least acceptable approach.
5. Should be used with field analytical screening.
6. Preferred only where known trends are present.
7. Allows for statistical support of clean-up verification if sampling over entire site.
8. May be effective with composting technique if site is presumed to be clean.

## Selection of monitoring equipment

### *Analytical screening equipment*

Analytical screening methods provide on-site measurements of contaminants of concern, limiting the number of samples, which need to be sent to an off-site laboratory for time-consuming and often costly analysis. Screening techniques can also evaluate soil samples for indications that soil contamination exists for target metals or soil gas survey for identification of buried wastes or other subsurface contamination. The commonly used screening equipment and their advantages and disadvantages are summarised in Table II.

### *Geophysical equipment*

Geophysical techniques can be used in conjunction with analytical screening to help delineate areas of subsurface contamination, including buried drums and tanks. Geophysical data can be obtained relatively rapidly, often without disturbing the site. Geophysical techniques suitable for emergency or removal activities include: ground penetrating radar (GPR), magnetometry, electromagnetic conductivity (EM) and resistivity. Specific advantages and disadvantages associated with geophysical equipment are summarized in Table III.

### *Soil sampling equipment*

The commonly used soil sampling equipment and their advantages and disadvantages are summarised in Table IV.

### *Choice of sampling equipment*

The mechanical method by which a sampling tool collects the sample may impact representativeness. For example, if the sampling objective is to determine the concentrations of contaminants at each soil horizon interface, using a hand auger would be inappropriate: the augering technique would disrupt and mix soil horizons, making the precise horizon interface difficult to determine. Depth of sampling is another factor to consider in the proper selection of sampling equipment. A trowel, for example, is suitable for unconsolidated surface soils, but may be a poor choice for sampling at 12 inches, due to changes in soil consistency with depth.

All sampling devices should be of sufficient quality not to contribute contamination to samples (e.g. painted surfaces which could chip off into the sample). In addition, the sampling equipment should be either easily decontaminated, or cost effective if considered to be expendable. Consider ease of use when selecting sampling equipment.

### **Finalisation of investigation plan**

Finalisation of the investigation plan after the selection of area, sampling locations, parameters, sampling approaches etc. is only means of finalisation of the schedule of the visit and assignment of tasks. This however needs the team to consider the following important aspects:

- Decision(s) to be made or question(s) to be answered;
- Why environmental data are needed and how the results will be used;
- Time and resource constraints on data collection;
- Descriptions of the environmental data to be collected;
- Applicable model or data interpretation method used to arrive at a conclusion;
- Detection limits for analytes of concern; and
- Sampling and analytical error.

These aspects are necessary to define the quality of the data in making the final decisions about the site and are commonly known as Data Quality Objectives (DQO). In other words the DQOs are to be established to state the level of uncertainty that is acceptable from the data collection activities and the final plan made accordingly.

TABLE II. PORTABLE FIELD ANALYTICAL SCREENING EQUIPMENT

Equipment	Application to Sampling Design	Advantages and Disadvantages
X ray fluorescence (portable)	Detects heavy metals in soils	Rapid sample analysis; may be used in situ; requires trained operator; Potential matrix interferences; may be used with a generic or site specific calibration model; detection limit may exceed action level; detects to ppm level; detection limit should be calculated on a site-specific basis.
Flame ionization detector (FID)	Semi-quantitatively detects VOCs in soils	Immediate results; can be used in GC mode to identify specific organic compounds; detects VOCs only; detects to ppm level.
Photoionization detector (PID)	Detects total concentration of VOCs and some non-volatile organics and inorganics	Immediate results; easy to use; non-compound specific; results affected by high ambient humidity and electrical sources such as radios; in soils does not respond to methane; detects to ppm level
Field test kits	Detects specific elements, compounds, or compound classes in soils	Rapid results; easy to use; low cost; limited number of kit types available; kits may be customized to user needs; semi-quantitative; interferences by other analytes is common; colorimetric interpretation is needed; detection level dependent upon type of kit used; can be prone to error.
Radiation detector	Detects the presence of selected forms of radiation in soils or other waste materials	Easy to use; low cost; probes for one or a combination of alpha, beta or gamma forms of radiation; unit and detection limits vary greatly; detailed site surveys are time intensive and require experienced personnel to interpret results.

Sources: U.S. EPA, September 1988a; U.S. EPA, December 1987; U.S. EPA 1987.

TABLE III. GEOPHYSICAL EQUIPMENT

Equipment	Application to Sampling Design	Advantages and Disadvantages
Ground penetrating radar (GPR)	Detects reflection anomalies caused by lithology changes buried objects; varying depths of investigation, 15 to 30 feet, are possible.	Capable of high resolution; generates continuous measurement profile; can survey large area quickly; site specific; best results are achieved in dry, sandy soils; clay-rich and water saturated soils produce poor reflections and limit depth of penetration; data interpretation requires a trained geophysicist.
Magnetometer	Detects presence and areal extent of ferromagnetic material in subsurface soils, including buried metal containers. Single 55-gallon drums can be identified at depths up to 10 feet and large massed of drums up to 30 feet or more.	Quick and easy to operate; good initial survey instrument; readings are often affected by nearby man-made steel structures (including above-ground fences, buildings, and vehicles); data interpretation may require geophysicist.
Electromagnetic conductivity meter (EM)	Detects electrical conductivity changes in subsurface geologic lithology, pore fluids, and buried objects. Depth of investigation from 9 feet to 180 feet depending on instrument used, coil spacing, and coil configuration.	Rapid data collection; can delineate inorganic and large-scale organic contamination in subsurface fluids; sensitive to man-made structures (including buried cables, above-ground steel structures and electrical power lines); survey planning and data interpretation may require geophysicist.
Wadi	Detects electrical conductivity changes in surface and sub-surface materials utilizing existing very low frequency (VLF) radio waves.	Utilizes existing long-distance communication VLF radio waves (10-30 Khz range); no need to induce electrical field; directional problems can be overcome with portable transmitters.
Resistivity meter	Detects electrical resistivity variations in subsurface materials (e.g. lithology, pore fluids, buried pipelines and drums). Vertical resolution to depths of 100 feet is possible.	Detects lateral and vertical variations; instrument requires direct ground contact, making it relatively labor intensive; sensitive to outside interference; data interpretation requires a trained geophysicist.

Sources : Benson, et. al. 1988 ; NJDEP, 1988.



TABLE IV. SOIL SAMPLING EQUIPMENT

Equipment	Applicability	Advantages and Disadvantages
Trier	Soft surface soil	Inexpensive; easy to use and decontaminate; difficult to use in stony, dry, or sandy soil.
Scoop or trowel	Soft surface soil	Inexpensive, easy to use and decontaminate; trowels with painted surfaces should be avoided.
Tulip bulb planter	Soft soil, 0-6 in.	Easy to use and decontaminate; uniform diameter and sample volume; preserves soil core (suitable for VOA and undisturbed sample collection); limited depth capability; not useful for hard soils.
Soil coring device	Soft soil, 0-24 in.	Relatively easy to use; preserves soil core (suitable for VOA and undisturbed sample collection); limited depth capability; can be difficult to decontaminate
Thin-wall tube sampler	Soft soil, 0-10 ft.	Easy to use; preserves soil core (suitable for VOA and undisturbed sample collection); may be used in conjunction with bucket auger; acetate sleeve may be used to help maintain integrity of VOA samples, easy to decontaminate; can be difficult to remove cores from sampler.
Split spoon sampler	Soil, 0 in.-bedrock	Excellent depth range; preserves soil core (suitable for VOA and undisturbed sample collection); acetate sleeve may be used to help maintain integrity of VOA samples; useful for hard soils; often used in conjunction with drill rig for obtaining deep cores.
Shelby tube sampler	Soft soil, 0 in.-bedrock	Excellent depth range; preserves soil core (suitable for VOA and undisturbed sample collection); tube may be used to ship sample to lab undisturbed; may be used in conjunction with drill rig for obtaining deep cores and for permeability testing; not durable in rocky soils.
Bucket auger	Soft soil, 3 in.-10 ft.	Easy to use; good depth range; uniform diameter and sample volume; acetate sleeve may be used to help maintain integrity of VOA samples; may disrupt and mix soil horizons greater than 6 inches in thickness.
Hand-operated power auger	Soil, 6 in.-15 ft.	Good depth range; generally used in conjunction with bucket auger for sample collection; destroys soil core (unsuitable for VOA and undisturbed sample collection); requires 2 or more equipment operators; can be difficult to decontaminate; requires gasoline-powered engine (potential for cross-contamination).

Sources: NJDEP, 1988; U.S. EPA, January 1991.

## **Steps at site/during the visit**

### *Physical characterization and climatic conditions*

All possible data concerning the physical characterization of soil including its type and the climatic conditions of the sites are recorded with the help of simple tests. Some of the basic soil tests are described in following paragraphs.

#### *Soil colour*

The test is aimed to identify the broad colour groups of the soil and the variations in colour within the specific soil structures. The test is based on comparison of the soil colour with the spectrum of the colour standard charts.

#### *Grain size*

There is no internationally agreed system for classification of the soil based on the grain size, it is however very useful to perform a simple test to identify the range of particles covered in the soil matrix, that are visible to the naked eye. The corresponding soil type from clay to gravel/grit etc. can be obtained directly from the conversion tables given in the soil survey field handbooks for e.g. British Soil Survey Field Handbook, Hodgson, J.M. (ed.) (1997).

#### *Compaction — Penetration test*

The penetration test, which is also known as the finger test should be also performed to find the overall compaction grade of the soil. This is a simple test for the identification of four soil compaction grades from loose to compact. A soil is loose if the index finger can be pushed into it up to the second knuckle. Soft, if it can be pushed in to the first knuckle. Firm, if only a small impression is made by the fingertip and compact if no impression is made at all. The finger should be pushed into the soil to the maximum force possible without causing pain or injury.

The test is moisture dependent and will provide different results during different climatic conditions. All the layers/fills/deposits of a structure should be tested at the same time and under the same climatic conditions. Comparisons of the compaction test results between different structures should be made with caution.

#### *Sorting*

It is a valuable test for sorting the original deposition process of a soil. This is based on the number of different grades of particles contained within the soil. A soil containing four or more grades is called poorly sorted, the one containing 2–3 particle grades is called mixed soil, and a well-sorted soil contains a homogeneous layer of a single particle grade.

#### *Sample collection*

How a sample is collected can affect its representativeness. The greater the number of samples collected from a site and the larger the volume of each sample, the more representative the analytical results can be. However, sampling activities are often limited by sampling budgets and project schedules. The following sections therefore provide guidelines on appropriate sample numbers and volumes.

### *Sample number*

The number of samples needed vary according to the particular sampling approach that is being used. For example, in grid sampling, one sample is generally collected at each grid node, regardless of grid size, and once contaminated grid node samples are located, adjoining grid cells can be sampled more thoroughly to define areas of contamination. Four aliquots (or increments) from each grid cell, situated equidistant from the sides of each cell and each other are recommended for grid cells measuring up to 100 × 100 feet. One additional aliquot may be collected from the centre of each cell, making a total of five aliquots per cell. For grid sizes greater than 100 feet × 100 feet, nine aliquots, situated equidistant from the sides of each cell and each other are recommended. Depending on budget and other considerations, grid cell aliquots can be analysed as separate samples or composited into one or more samples per cell. [Simple equations have been described to calculate the number of samples required to hit hot spots of known size and dimensions (CLR4, DEFRA, 1994)].

### *Sample volume*

Both sample depth and area are considerations in determining appropriate sample volume. Depending on the analytes being investigated, samples are collected at the surface (0–3 in.), extended surface (0-6 in.0-15cm) and/or at one-foot depth intervals. Non-water soluble contaminants such as dioxin and PCBs are often encountered within the first six inches of soil. Water-soluble contaminants such as metals, acids, ketones, and alcohols will be encountered at deeper depths in most soils except clays. Contaminants in solution, such as PCPs in diesel fuel and pesticides in solvents, can penetrate to great depths (e.g. down to bedrock), depending on soil type.

For surface samples, collect soil over a surface area of one square foot per sample. A square cardboard template measuring 12 in. × 12 in., or a round template with a 12-inch diameter can be used to mark sampling areas.

### *Removal of extraneous material*

The materials in a sample which are not relevant or vital for characterizing the sample or the site, since their presence may introduce an error in the sampling or analytical procedures are first of all identified and discarded. Examples of extraneous material in soil samples include pieces glass, twigs or leaves. However, not all non-soil material is extraneous. For example, when sampling at a junkyard, lead-contaminated battery casing pieces should not be removed from a sample if the casing composes more than 10% of the sample composition. For a sample to be representative, it must also incorporate the lead from the casing. Collect samples of any material thought to be a potential source of contamination for a laboratory extraction procedure.

### *Sample sieving*

Sieving is the process of physically sorting a sample to obtain uniform particle sizes, using sieve screens of predetermined size. For example, the sampler may wish to sieve a certain number of samples to determine if particle size is related to contaminant distribution. Sieving is generally usually conducted when preparing soil samples for XRF screening, but is also used prior to grinding and dissolution for solution techniques such as AAS and ICP. For this purpose for XRF, a 20-mesh screen size is recommended.

The aim of the sampling programme is to be kept in mind when deciding whether to sieve a sample prior to analysis. Prior to sieving, samples may need to be oven-dried. Discarding non-soil or non-sieved materials, as well as the sieving process itself, can result in physical and chemical losses. Sieving is not recommended where volatile compounds are of concern. Analyze the discarded materials, or a fraction thereof, to determine their contribution to the contamination of the site being investigated.

### *Sample homogenization*

Homogenization is the mixing or blending of a soil sample in an attempt to provide uniform distribution of contaminants. (Do not homogenize samples for volatile compound analysis). Ideally, proper homogenization ensures that portions of the bottled samples are equal or identical in composition and are representative of the total soil sample collected. Incomplete homogenization will increase sampling error. All samples to be composited or split should be homogenized after all aliquots have been combined. Manually homogenize samples using a stainless steel spoon or scoop and a stainless steel bucket, or use a disposable scoop and pan. Quarter and split the sample repeating each step a minimum of 5 times until the sample is visually homogenized. Samples can also be homogenized using a mechanically operated stirring device as depicted in ASTM standard D422-63.

### *Sample splitting*

Splitting samples after collection and field preparation into two or more equivalent parts is performed when two or more portions of the same sample need to be analysed separately. Split samples also provide a measure of the sample variability, and a measure of the analytical and extraction errors. Before splitting, follow homogenization techniques outlined above. Fill two sample collection jars simultaneously with alternate spoonfuls (or scoopfuls) of homogenized sample. To simultaneously homogenize and split a sample, quarter or mechanically split the sample using a riffle sample splitter. The latter two techniques are described in detail in ASTM Standard C702-87.

### *Sample compositing*

Compositing is the process of physically combining and homogenizing several individual soil aliquots. Compositing samples provide an average concentration of contaminants over a certain number of sampling points, which reduces both the number of required lab analyses and the sample variability. Compositing can be a useful technique, but must always be implemented with caution. Compositing is not recommended where volatile compounds are of concern.

Specify the method of selecting the aliquots that are composited and the compositing factor in the sampling plan. The compositing factor is the number of aliquots (or increments) to be composited into one sample (e.g. 3 to 1; 10 to 1). It is not allowed in some regulatory authorities. Determine this factor by evaluating detection limits or uncertainty required for parameters of interest and comparing them with the selected action level for that parameter. Compositing also requires that each discrete aliquot be the same in terms of volume or weight, and that the aliquots be thoroughly homogenized. Since compositing dilutes high concentration aliquots, the applicable detection limits should be reduced accordingly. If the composite value is to be compared to a selected action level, then the action level must (in some regulatory authorities) be divided by the number of aliquots that make up the composite in order to determine the appropriate detection limit (e.g. if the action level for a particular substance is 50 ppb, an analysis level of 10 ppb should be used when analysing a 5-aliquot composite). The detection level need not be reduced if the composite area is assumed to be homogeneous in concentration (for example, stack emission plume deposits of particulate contamination across an area, or roadside spraying of waste oils).

### *Sample preparation*

Select sample containers on the basis of compatibility with the material being sampled, resistance to breakage, and volume. For soil sampling, use wide-mouth glass containers with Teflon-lined lids. Appropriate sample volumes and containers will vary according to the parameter being analysed. Keep low and medium concentration soil samples to be analysed for organic constituents at 4°C. Package all samples in compliance with the relevant National or International Air Transport Association requirements.

It is sometimes possible to ship samples to the laboratory directly in the sampling equipment. For example, the ends of a Shelby tube can be sealed with caps, taped, and sent to the laboratory for analysis. To help maintain the integrity of VOA samples, collect soil cores using acetate sleeves and send the sleeves to the laboratory. To ensure the integrity of the sample after delivery to the laboratory, make laboratory sample preparation procedures part of all laboratory bid contracts.

### **Sources of errors**

Identification and quantification the errors or variation in sampling and laboratory analysis can be difficult. However, it is important to limit their effect(s) on the data. Four potential sources of errors are:

- sampling design;
- sampling methodology;
- sample heterogeneity; and
- analytical procedures.

These errors in the sampling and analytical procedures cause uncertainty in the measurements that needs to be quantified to enable reliable interpretation of the site.

#### *Sampling design*

Site variation includes the variation both in the types and in the concentration levels of contaminants throughout a site. Representative sampling should accurately identify and define this variation. However, error can be introduced by the selection of a sampling design, which “misses” site variation. For example, a sampling grid with relatively large distances between sampling points or a biased sampling approach (i.e. judgmental sampling) may allow significant contaminant trends to go unidentified.

#### *Sampling methodology*

Errors can be introduced by the sampling methodology and sample handling procedures, as in cross-contamination from inappropriate use of sample collection equipment, unclean sample containers, improper sampling equipment decontamination and shipment procedures, and other factors. Standardized procedures for collecting, handling, and shipping samples allow for easier identification of the source(s) of error, and can limit error associated with sampling methodology. The use of standard operating procedures aims to ensure that all sampling tasks for a given matrix and analyte will be performed in the same manner, regardless of the individual sampling team, date, or location of sampling activity. Trip blanks, field blanks, replicate samples, and rinsate blanks are used to identify error due to sampling methodology and sample handling procedures.

#### *Sample heterogeneity*

Sample heterogeneity is a potential source of error. Unlike water, soil is rarely a homogeneous medium and it exhibits variable properties with lateral distance and with depth. This heterogeneity may also be present in the sample container unless the sample was homogenized in the field or in the laboratory. The laboratory uses only a small aliquot of the sample for analysis; if the sample is not properly homogenized, the analysis may not be truly representative of the sample and of the corresponding site. Thoroughly homogenizing samples, therefore, can limit error associated with sample heterogeneity.

## *Analytical procedures*

Errors, which may originate in analytical procedures includes cross-contamination, inefficient extraction, and inappropriate methodology. Matrix spike samples, replicate samples, performance evaluation samples, and associated quality assurance evaluation of recovery, precision, and bias, can be used to distinguish analytical error from error introduced during sampling activities.

### **QA/QC samples**

This section briefly describes the types and uses of quality assurance and quality control (QA/QC) samples that are collected in the field, or prepared for or by the laboratory. QA/QC samples are analysed in addition to field samples and provide information on the variability and usability of environmental sample results. They assist in identifying the origin of analytical discrepancies to help determine how the analytical results should be used. They are used mostly to validate analytical results. Field replicate, collocated, background, and rinsate blank samples are the most commonly collected field QA/QC samples. Performance evaluation, matrix spike, and matrix spike duplicate samples, either prepared for or by the laboratory, provide additional measures of control for the data generated. QA/QC results may suggest the need for modifying sample collection, preparation, handling, or analytical procedures if the resultant data do not meet site-specific quality assurance objectives. The following paragraphs briefly describe each type of QA/QC sample.

#### *Field replicates*

Field replicates are field samples obtained from *one location*, homogenized, divided into separate containers and treated as separate samples throughout the remaining sample handling and analytical processes. These samples are used to assess error associated with sample heterogeneity, sample methodology and analytical procedures. Use field replicates when determining total error for critical samples with contamination concentrations near the action level. For statistical analysis to be valid in such a case, a minimum of eight replicate samples would be required

#### *Collocated samples*

Collocated samples are collected adjacent to the routine field sample to determine local variability of the soil and contamination at the site. Typically, collocated samples are collected about one-half to three feet away from the selected sample location. Analytical results from collocated samples can be used to assess site variation, but only in the immediate sampling area. Due to the non-homogeneous nature of soil at sites, collocated samples should not be used to assess variability across a site and *are not recommended for assessing error*. Determine the applicability of collocated samples on a site-by-site basis. Collecting many samples (more than 50 samples/acre) is sufficient to demonstrate site variation.

#### *Rinsate blanks*

Rinsate blanks are samples obtained by running analyte-free water over decontaminated sampling equipment to test for residual contamination. The blank is placed in sample containers for handling, shipment, and analysis identical to the samples collected that day. A rinsate blank is used to assess cross-contamination brought about by some improper decontamination procedures. Where dedicated sampling equipment is not utilized, collect one rinsate blank, per type of sampling device, per day.

#### *Performance evaluation samples*

Performance evaluation (PE) samples evaluate the overall bias of the analytical laboratory and detect any error in the analytical method used. These samples are usually prepared by a third party, using a quantity of analyte(s) which is known to the preparator but unknown to the laboratory, and always undergo certification analysis. The analyte(s) used to prepare the PE sample is the same as

the analyte(s) of concern. Laboratory procedural error is evaluated by the percentage of analyte identified in the PE sample (percent recovery). Even though they are not available for every single analyte, analysis of PE samples is required to obtain more definitive data.

#### *Matrix spike samples*

Matrix spike and matrix spike duplicate samples (MS/MSDs) are environmental samples that are spiked in the laboratory with a known concentration of a target analyte (s) to verify percent recoveries. MS/MSDs are primarily used to check sample matrix interferences. They can also be used to monitor laboratory performance. However, a dataset of at least three or more results is necessary to distinguish between laboratory performance and matrix interference.

MS/MSDs can also monitor method performance. Again, a dataset is helpful to assess whether a method is performing properly. Generally, interference and poor method performance go together.

MS/MSDs can also evaluate error due to laboratory bias (in the non-ISO traceable sense) and precision (when four or more pairs are analysed). Analyse one MS/MSD pair to assess bias for every 20 soil samples. Use the average percent recovery for the pair. To assess precision of recovery, analyze at least eight matrix spike replicates from the same sample, determine the standard deviation and the coefficient of variation. MS/MSDs are optional when the goal is to obtain screening data and required to obtain definitive data as one of several methods to determine analytical error.

#### *Field blanks*

Field blanks are samples prepared in the field using certified clean sand or soil and are then submitted to the laboratory for analysis. A field blank is used to evaluate contamination error associated with some of the sampling methodology and laboratory procedures. If available, submit field blanks at a rate of one per day.

#### *Trip blanks*

Trip blanks are samples prepared prior to going into the field. Trip blanks consist of certified clean sand or soil and are handled, transported, and analysed in the same manner as the other volatile organic samples acquired that day. Trip blanks are used to evaluate some of the error associated with sampling methodology and analytical procedures by determining if any contamination was introduced into samples during sampling, sample handling and shipment, and/or during laboratory handling and analysis. If available, utilize trip blanks for volatile organic analyses.

#### *Background samples*

Background samples are collected up gradient of the area(s) of contamination (either on or off site) where there is little or no chance of migration of the contaminants of concern. Background samples determine the natural composition of the soil (especially important in areas with high concentrations of naturally-occurring metals) and are considered “clean” samples. Although background samples are not considered to be “quality control” samples, they are best planned for along with other “QC” samples. They provide a basis for comparison of contaminant concentration levels with naturally occurring levels of target analytes in the soil samples collected on site.

If your objective does not involve determining whether a site is contaminated or not (for example, you may know that it is and are simply trying to comply with a regulatory action level) then you will not need background samples. However, if you do need background samples then at least one background soil sample should be collected; however, more are warranted when site-specific factors such as natural variability of local soil, multiple on-site contaminant source areas, and presence of off-site facilities potentially contributing to soil contamination exist (which is usually the case). Collect background samples as close as possible to the contaminated site, while making sure that they are not

contaminated, and make certain that the soil type is as similar as possible to the soil of the site under investigation.

If you do need to collect background samples, *always collect them first* so that you do not run any risk of contaminating the background samples, or the background sample location, with the target analytes that may be present in higher concentrations at the site under investigation.

### Evaluation of analytical error

The percentage and types of QA/QC samples needed to help identify the error and confidence in the data is based on the sampling objectives and the corresponding QA/QC objectives. The acceptable level of error is determined by the intended use of the data and the sampling objectives, including such factors as: the degree of threat to public health, welfare, or the environment; selected action levels; litigation concerns; and budgetary constraints.

The use of replicate samples is one method to evaluate the random component of the measurement uncertainty error. To evaluate the total error of samples with contaminant concentrations near the selected action level, prepare and analyze a minimum of eight replicates of the same sample. Analytical data from replicate samples can also be used for a quick check on errors associated with sample heterogeneity, sample methodology and analytical procedures. Differing analytical results from two or more replicate samples could indicate improper sample preparation (e.g. incomplete homogenization), or that contamination was introduced during sample collection, preparation, handling, shipment, or analysis.

It is usually desirable to try to quantify confidence since this a way to measure how “good” the data is for the ultimate decisions you will make based on it; however, quantification or analytical data correction is not always possible. A 95% confidence level (i.e. 5% acceptable error) should be adequate for most analytical measurement activities but it does NOT represent the sampling component, which usually is at a much lower confidence level. Thus, it is more important to express confidence as “total” instead of only from analytical measurements.

Confidence levels should be linked to the consequences of making incorrect decisions from the data. Thus, if incorrect decisions may seriously affect human health, the environment, or cost a lot of money then you will want to plan on obtaining data with reasonably high overall confidence levels; if incorrect decisions are less serious or less costly then it would be logical to accept data with lower confidence levels. If you are making a decision based on analytical data then you need to know if the values you are depending on to make that decision have an uncertainty of 10%, 50%, 100%, or more. Therefore, you need to establish some minimum confidence level (i.e. a statement of probability) that you are comfortable with (and can afford) to use the data to make decisions with.

Bear in mind that higher levels of confidence (representing a higher probability of making a “correct” conclusion) require larger numbers of sample data and thus increased project costs. Therefore, you do not want to select a higher confidence level than one that would be reasonable for the intended use of the data. The lower the confidence levels the fewer samples will be needed and the lower will be the sampling and analytical costs. Table V provides some general guidance on confidence level targets relative to the consequences of making incorrect decisions.

TABLE V. CONFIDENCE LEVEL GUIDANCE RELATIVE TO CONSEQUENCES OF MAKING INCORRECT DECISIONS

Human Consequences	Financial and Ecological Consequences			
	High	Moderate	Low	None
High	95%	95%	95%	95%
Moderate	90%	85%	85%	80%
Low	90%	80%	70%	60%
None	90%	70%	60%	50%



## **Correlation between screening results and definitive results**

One cost effective approach for delineating the extent of site contamination is to correlate inexpensive screening data and other field measurements (e.g. XRF, soil-gas measurements) with laboratory results. The relationship between the two methods can then be described by a regression analysis and used to predict laboratory results based on screening measurements. In this manner, cost-effective screening results may be used in addition to, or in lieu of, off-site laboratory sample analysis. An example of this relationship is shown in Section 3.1, Step Number 6.

Statistical regression involves developing a model (equation) that relates two or more variables at an acceptable level of correlation. When screening techniques, such as XRF, are used along with laboratory methods (e.g. atomic absorption (AA)), a regression equation can be used to predict a laboratory value based on the results of the screening device. The model can also be used to place confidence limits around predictions. Additional discussion of correlation and regression can be found in most introductory statistics textbooks. A simple regression equation (e.g. linear) can be developed on many calculators or computer databases; however, a statistician should be consulted to check the accuracy of more complex models.

Evaluation of the accuracy of a model in part relies on statistical correlation. Statistical correlation involves computing an index called the correlation coefficient  $I$  that indicates the degree and nature of the relationship between two or more sets of values. The correlation coefficient ranges from  $-1.0$  (a perfect inverse or negative relationship), through  $0$  (no relationship), to  $+1.0$  (a perfect direct, or positive, relationship). The square of the correlation coefficient, called the coefficient of determination, or simply  $R^2$ , is an estimate of the proportion of variance (standard deviation squared) in one variable (the dependent variable) that can be accounted for by the independent variables. The  $R^2$  value that is acceptable depends on the sampling objectives and intended data uses. As a rule of thumb, statistical relationships should have an  $R^2$  value of at least  $0.6$  to determine a reliable model; however, for health or risk assessment purposes, the acceptable  $R^2$  value may be made more stringent (e.g.  $0.8$ ). Analytical calibration regressions have an  $R^2$  value of  $0.98$  or better.

Once a reliable regression equation has been derived, the screening data can be used to predict laboratory results. The uncertainty of these 'predicted laboratory results' will however be high, and can be predicted by propagating the uncertainty of the screening values through the regression equation. These predicted values can then be located on a base map and contoured. These maps can be examined to evaluate the estimated extent of contamination and the adequacy of the sampling program.

## **Preparation of investigation plan**

Systematic planning is an essential part of organizing any successful field activity because it provides a logical framework for soil sampling and analysis activities. Without using some form of systematic planning important issues are certain to be overlooked, less effective sampling is likely, and the resulting data may not be of sufficient quality to be used for making the ultimate decisions for which it was collected. Therefore, it is important that a systematic plan be written and agreed to by all participants before the soil sampling activities begin. Time spent in preparing a good investigation plan will save both time and money later during the field and laboratory activities and also minimise the possibilities of wrong decisions taken on the basis of the resulting analytical data.

Seven essential elements of preparing a good investigation plan are described below. Although these essential elements are presented as a progressive, stepped process; in reality many of the elements are performed concurrently and in an iterative manner.

### *Steps for systematic planning*

There are seven steps to systematic planning. Many of these are iterative steps, i.e. once more information is obtained at a later step in the planning process then information in an earlier step must

be revised. These seven steps will definitively provide information on what, why, when, where, and how environmental data are to be obtained (including who is to obtain it at what cost).

(1) Step 1: Stating of the problem

The first step of the systematic planning process is to state the problem, as this step is vital to the success of any project. The problem should be clearly defined in readily understandable terms. All “stakeholders” i.e. the people who have an interest in the results of the investigation must agree to the statement of the problem, i.e. what is to be sampled and analysed, where, when, and (very importantly) why. Stakeholders may be nearby residents or community groups, government officials involved with decisions, and the technical leaders who are to conduct the sampling and analysis activities.

The purpose of the project is a critical part of the problem statement. For example, the purpose may range from an initial rapid and inexpensive screening of soil samples to the discovery of “hot spots” or to a thorough statistical investigation to determine mean values of target analytes in the entire site. Critical to the statement of the problem are the identifications of what pollutants are to be analysed for (e.g. all metals or only specific ones, volatile or semivolatile organics, oily hydrocarbons or chlorinated organic compounds, etc.).

(2) Step 2: Identification of the decisions to be taken

Sometimes this critical step is overlooked but it very important that everyone involved in a project understand what the data are to be used for. Improper understanding at the initial stage may lead to collection of too many or inadequate data, or data of the wrong kind or from the wrong places.

Examples of the kinds of information that are useful in decision statements include if data is being obtained to determine:

- whether remediation is required,
- whether the land-use is appropriate,
- whether pollutant concentrations conform to a regulation,
- whether there is a threat to groundwater,
- whether the data are to be used as input to risk assessment models,
- whether it is to be used for source identification (e.g. a point/non-point source),
- whether it is to be used for emission control, and/or
- whether it is to be used for some specific socio-psychological decisions.

Avoid general decision statements instead state decisions clearly and specifically. Include the specific pollutants, and the specific decisions that will be made once the data is available.

For example, a decision statement might read:

- Determine whether lead concentrations in soil surrounding drinking water wells for the town exceed WHO recommended levels and are contributing to unsafe levels of lead in the water.

Information in the above example would lead to a plan that will provide data on lead concentrations in soil at various areas around the subject wells. In addition, if there were potential sources of lead that are recognized then they also would be sampled.

When the resolution of a problem requires the definition of more than one decision, the decisions must be ranked in the order in which they are to be addressed. These decision statements need to be specific and comprehensive so that realistic cost and decisions can be developed.

### (3) Step 3: Identification of Inputs to Decisions

Inputs to the decision(s) need to be very detailed and thorough in order to ensure that the right kind and adequate data are obtained. Examples of the kinds of details that need to be identified include (but are not limited to):

- Sampling strategies to be used (i.e. judgmental, systematic, random, etc.).
- Site and soil characteristics will be obtained (e.g. weather, maps, descriptions, etc.).
- Sampling equipment needed.
- Sampling support equipment needed (e.g. surveying tools or meteorological equipment).
- Samples to be preserved and, the method of preservation.
- Samples to be composited and, the numbers per sample.
- Samples to be analysed in situ and in a mobile lab.
- The detection levels desired for each analyte and the reasons.
- The precision desired for the data and the reasons.
- The amount of bias acceptable for the data and the reasons.
- The forms of bias estimates desired (e.g. percent recovery, rates of false positive and false negative conclusions, or both).
- The degree of relevance of selectivity of the analysis with respect to correct pollutant identification (this affects the analytical methods that may be used).
- The safety equipment and protocols needed.
- The training and experience levels needed for project members.
- The methods of analysis to be planned for each target analyte and the capability of each method to meet the desired levels of sensitivity, selectivity, precision, and bias documented above.
- The budget available for sampling, analysis, and QA/QC activities.

### [4] Step 4: Defining of study boundaries

This step requires the project planning team to define realistic spatial and temporal boundaries (i.e. what should be studied, the location(s) where samples should be taken, and the time frame for both the sampling and analytical parts of the project. The boundaries should be defined as narrowly and clearly as possible by defining the subject of the study and its characteristics. Temporal boundaries may also specify how often the soil will be sampled in addition to the obvious ones of what months or seasons to sample.

As study boundaries are defined, practical constraints or potential obstacles that may impede the project should be identified, such as:

- Physical obstacles at the site (e.g. rock formations, inaccessible areas, size of the site, etc.),
- Availability of experienced and trained personnel,
- Availability of equipment (for sampling or for safety issues),
- Human activities (e.g. recent fertilization, spraying, paving, cultivation, heavy rain, etc.).

However, another boundary that is not usually considered in this step — but that has just as much influence as the boundaries of time and space — is the available budget. Often the budget is a limiting boundary with respect to the numbers and kinds of soil samples that will be able to be analysed. When numbers of soil samples that need to be analysed in order to provide a confidence level in the data that is desired (and relative to the consequences of making incorrect decisions) but can not be met because of the available budget then the budget is a fiscal boundary that limits the project.

#### [5] Step 5: Development of Decision Rules

Decision rules are concise descriptions of the actions to be taken based on the data collected. The decision rule is typically presented as “if/then” or “if/then/else” statements. For example, “if the concentration of lead exceeds 500 mg kg<sup>-1</sup> in any soil sample at the site, then three co-located samples, taken within 2 meters of the subject sample are to be analysed to determine the extent of this level of contamination unless analysis of other adjacent samples has shown that levels of lead typically exceed 500 mg/kg in this area of the project site.” For dynamic field activities (i.e. those where decisions for additional sampling and analysis are made based on *in-situ* or other time-relevant data), the decision rules may be used to develop a decision tree or logic flow diagram to facilitate decision-making during the mobilization.

In order to develop decision rules, the planning team needs to establish the action (threshold) levels using the documented decision inputs identified in Step 3. In addition, the planning team need to use the boundaries established in Step 4 and develop decision rules that are as specific as possible. Typical kinds of decision rules involve:

Actions that is to be taken if the target analyte(s) exceed the concentration levels documented in Step 2 (e.g. using the example in Step 2 a logical decision rule could be, “if lead concentrations in the soil exceed WHO recommendations then determine the source of the lead and, once known, decide if it can be remediated or whether the wells are to be moved.”

- Consequences for not achieving kinds and/or numbers of desired samples,
- Consequences for observing unexpected or unacceptable high or low target analyte concentrations,
- Consequences for obtaining unacceptable QA/QC results (e.g. higher than desired rates of false positive or false negative conclusions (or other forms of bias such as too low or too high percent recovery), insufficient precision, insufficient sensitivity, interferences, contamination of blanks or samples, incorrect preservation, incorrect sampling containers, exceeding recommended hold times before sample analysis, incorrect methods used, etc.).

#### [6] Step 6: Specification of Limits to Total Uncertainty

This is often the most difficult step, as it involves assigning of probability limits for the analytical data that is to be obtained. All environmental analytical data contain errors. Thus, this step assigns the amount of error that is acceptable in the data to be generated from the project. The largest source of error usually comes from variability in the data caused by inhomogeneity of the target

analyte distribution in the soil samples. The largest amount of QA/QC usually is focused on the laboratory and instrumental analysis of the target analytes rather than on the larger source of error in the sampling activities. The total uncertainty is the sum of the uncertainties from all of the sampling and analytical activities, not just the laboratory sources of error.

This step involves specifying the decision error limits of the project. Decision error occurs when a true hypothesis is rejected (i.e. false rejection) or an untrue hypothesis is accepted (i.e. false acceptance). This process requires that the planning team develop a hypothesis and then establish tolerable limits on decision error by evaluating the consequences that would flow from making an incorrect decision.

Once the project planning team has established the limits on decision error (e.g. plus or minus 20% relative standard deviation, or plus or minus 100 mg/kg-1, then they must design a data collection plan that allows them to stay within the prescribed decision error limits. The planning team can meet this requirement by examining the two factors that contribute to study error, and ultimately decision error.

These two factors are:

- Sampling design error — Error introduced when the data collection design is inadequate for making the desired decision; and
- Measurement error — The combination of random and systematic errors introduced in the measurement process by such activities as sample collection, sample handling, sample preparation, sample analysis, and data reduction.

When calculating decision error, the planning team must also consider the concept of the *grey region*, the region adjacent to the action level in which measurements are considered to be unreliable. Action levels are concentrations of the target analyte(s) that are determined in Step 2. They refer to the decisions that will be made once a designated event occurs. The grey region is also known as the area of uncertainty and represents the area near the action level that is too close for a definitive decision because of measurement and sampling error.

When the action level and the measured value of the parameter of interest are very close (relative to the inherent variability in the data), decision makers are confronted with a high degree of uncertainty in determining a course of action. Due to the inherent variability in the data little confidence can be placed in measurements that lie close to the action level. To reduce the potential error associated with the use of measurements in the grey region, highly accurate and precise measurements must be made in order to lower measurement error. Alternatively, a very large number of samples may be required in order to determine with acceptable confidence where the “true” value lies.

Either alternative, or a combination of both, will increase a project team’s level of confidence in the results. However, either using more accurate and precise methods and/or analysing more samples increase the cost of the project. When the budget does not permit sufficient samples or better methods to obtain the needed data, then the only alternative is to decrease the acceptable confidence levels in the data that will be obtained. Confidence levels may be thought of as the “probability” of a data point not exceeding a desired variability. For example, a desired measurement quality objective to have data with variability not exceeding plus or minus 10% at a 95% confidence level represents the case where the value of 450 to 550 mg kg-1 would be obtained in 95 out of a hundred times that a sample containing 500 mg kg-1 of the target analyte was analysed. Circumstances that do not permit sufficient samples to be analysed may result in either a lesser confidence level (for example, plus or minus 10% at a 60% confidence level) or a greater variability (for example plus or minus 25% at a 95% confidence level).

An advantage of using field analytical methods (to obtain data) is that they can help provide a large number of data points which can ultimately reduce decision error through the reduction in sampling design error resulting from the improved ability to describe a non-homogeneously distributed population. Consequently, with field analytical methods it is often possible to use more data points to increase confidence in decisions, even when individual data points are less accurate and precise than if fixed laboratory methods were employed. This situation is especially true in the heterogeneous environments of contaminated soils.

One way to avoid problems of working in the grey region is to select methods that are sufficiently sensitive that the action levels are considerably higher than the method detection levels. When values are significantly below an action level then less precise and more biased methods may be used and the data obtained still meets criteria defined for decision-making. The same is true when values are significantly above an action level; again, less accurate and precise methods are needed to provide data that is readily identified as concentrations above which there is little doubt that the action limit has been exceeded.

Various software programs can calculate the relationship between precision and numbers of samples that are needed to provide a desired confidence level. DQO-PRO, software distributed by the American Chemical Society Division of Environmental Chemistry (at <http://www.envirofacts.org>) is provided on a CD-ROM with this technical publication. It is accompanied by a PowerPoint tutorial.

#### [7] Step 7: Optimization of the Design of Investigation

This step is actually iteration and refinement of the previous six steps. It is an integration of all of the previous steps into a clear and resource-effective data collection design. This process may require revisiting previous steps to optimize the final plan. For example, this step involves calculating a baseline for the number of samples to be collected. If none of the data collection designs satisfies all of the decision performance criteria developed in earlier steps, then the planning team will need to increase the tolerable limits on decision error, increase the width of the grey region, change the study boundaries, or relax other project restraints. It is also at this point that the proposed sampling and analytical methods are evaluated in relation to their ability to provide the accuracy, precision, sensitivity and selectivity desired.

All of these criteria are then compared with the calculated number of samples needed to provide data having desired confidence levels and with the proposed methods and the budget that is available. If the budget would be exceeded then it must be increased or the number of samples must be decreased (also decreasing the confidence levels in the data), or less expensive methods must be selected.

The product of this activity is typically displayed in the form of a Sampling and Analysis Plan. This plan forms the basis for the development of the operational documents that are prepared after the systematic planning process.

#### **Documentation of sampling plan**

Documentation of a sampling plan is very important because it enables everyone to understand what the objectives of the study are and it provides a reference from which to measure the success of the mission.

One of the first and most important sections of the sampling plan is the one that documents the objectives — why the study is being conducted. Clearly stating the objectives is crucial to developing sampling plans that will provide useful information from the data that is planned to be collected. If the objective(s) are too general or vague, then time and money may be wasted collecting wrong data, or there may not be sufficient data, or the data may be of insufficient quality.

In addition to stating clear objectives they should also be *measurable*. If objectives are not measurable then no one can determine if the study was successful.

An example of a poorly stated objective is:

- To measure the concentrations of lead in the soil at site X in order to determine if there is widespread contamination.”

The problem with this objective is that it is too general and not measurable. For example:

- Will only surface soil be analysed or will soil at different depths be analysed?
- What is the measure of “widespread?” Is it half the site or 80% of the site?
- To what degree of sensitivity should the soil be analysed (down to what detection level)?
- What quality of data is needed in order to make decisions based on the data? For example, are data plus or minus 20%, 50%, or 100% desired?
- How selective should the method be? For example, is a 5%, 10% or 50% rate of false positive results acceptable? What rate of false negative results is acceptable?
- What confidence level is acceptable in the data (i.e. the probability of being correct)?

Thus, with the above questions in mind a measurable objective could be stated. The problem is to measure the average concentrations of lead in the soil at site X with a method that will provide a sensitivity of at least 100 mg kg<sup>-1</sup> and will provide data at 200 mg kg<sup>-1</sup> with tolerable error of plus or minus 20% with 90% confidence and at that concentration to produce false positive conclusions at a rate not to exceed 5% at 95% confidence level and false negative conclusions at a rate not to exceed 10% at a 95% confidence level. A second objective is to identify any areas of contamination with concentrations that exceed 500 mg kg<sup>-1</sup> and that are larger than 10 m in diameter if more than 10% of the samples have values that exceed 500 mg kg<sup>-1</sup> at a 90% confidence level.

It is important to note that although not all of the desired objectives may be met (because of budget or technical reasons), each of them can be measured and adjusted as necessary during or after the investigation. By clearly setting forth the measurable objectives everyone has a common goal that they are trying to reach and if it is not completely able to be reached then it can be documented why the objective could not be reached and what the consequences may be on the decisions that will be made when using the data.

### **Preparation of sampling protocol (instructions + record forms)**

#### *Sampling numbering scheme*

Annotating site map showing orientation (‘gate at north’), intended location and number of samples: number and design of increments (depending of design), sample amount, visual assessment of site variability

Instructions on surveying (how to set up the sampling grid, select sampling spots, site preparation, on-site sample manipulation (sieving, removing stones, roots, mixing of composites, subsampling, sample bags, sample preservation, sampling tools, sample collection, sampling depth, prevention of contamination, transfer to sample bags, labelling, depending on design: sampling points for background values / control, number, points and positions of duplicate samples).

#### *Suggested contents of record form*

- Name of sampling staff, date and time of sampling
- Site code with actual geographical position (also mark sampling point on site map), site/sampling point topography

- Weather conditions during sampling
- Description of location (soil type, e.g. finger analysis on texture, soil structure, skeleton content and size, soil bulk density (for conversion of concentration from mass/mass to mass/volume, if required) consistence, soil colour, organic matter content, vegetation cover (e.g. crop type), land-use, soil moisture, soil profile description (horizons)
- Potential sources of contamination (traffic, anthropogenic impact, agriculture)
- Sampled depth layer, sampling device (auger...)
- Anecdotal information on site (analysis history, pattern, previous land-use....)
- Additional remarks (observations, difficulties)

### Preparedness for the field visit

Table VI gives some suggestions for preparing the checklist.

TABLE VI. SUGGESTION FOR CHECKLIST

Materials		
Knife	sampling protocol	working gloves
Maps	sampling bags (e.g. freezer bags)	record forms
Measuring tape	sealing device	sticks / canes for laying out grid
compass	labels pre-prepared	strings
altimeter	waterproof marker-pen	field notebook
thermometer	sampling tools (auger, shovel...)	etc.
Munsell soil colour chart	bucket	
GPS		

#### *Activities in the field*

Activities in the field should support the proper collection and handling of the samples in a way that supports the measurable objectives. These may include quality control checks that samples are being labelled properly (for example independent verification of a portion of sample bottles for transcribed numbers, correct preservation materials if needed, maps were marked correctly, etc.

If background samples are needed then make sure, and document, that these were collected first (before the samples at the site). If difficulties occur with the planned sample collection (for example, if rocks or other obstructions do not allow samples to be taken at a planned location) then check to make sure that these have been documented properly.

Another activity in the field may include independent verification that the record forms are being completely filled out as accurately as possible.

#### *Transportation, processing and analysis of samples*

The sampling plan should detail any specific requirements for transporting, storing, and processing samples prior to their analysis. For example, soil samples containing volatile analytes may need to be stored at near zero degrees C and analysed as soon as possible. Other kinds of samples may need to have preservatives (for example nitric acid) added. And, some methods require sample



preparation operations (for example grinding to a specified mesh size before dissolution, etc.). If these details are included in the sampling plan then it helps ensure that they will not be overlooked during the intermediate steps between collection and measurement of the processed sample.

### *Interpretation of the investigation*

After the chemical analysis of the samples, the next step is the interpretation of the measurements in terms of the stated objectives of the investigation. However, one important step that is often missed out is to estimate the uncertainty of the measurements, including that arising from the field sampling. It is often assumed that if the measurements pass the QA/QC criteria of the analytical laboratory, then they can be assumed to be ‘correct’ and uncertainty can be ignored. This is untrue for two reasons. Even if the QC materials analysed in the lab show that the analytical methods are in an acceptable level of control, this does not mean that the measurements do not have uncertainty. It merely indicates that the uncertainty is probably at a level that the laboratory considers acceptable for their purposes. Secondly, the main source of uncertainty in the measurements usually arises in the process of field sampling.

The usual QA/QC schemes of analytical laboratories do not estimate uncertainty arising from this source. It is quite possible that a laboratory can pass a batch of analyses as having acceptable quality, whilst the actual level of measurement uncertainty is too large of some purposes of site investigation. The first step in interpretation of measurements should therefore be to make an estimate of the uncertainty of each measurement. Knowing this uncertainty, it is possible to make a reliable interpretation of the measurements with a stated degree of confidence.

### *Assessing reliability of measurements*

The best estimate of the reliability of a measurement is its uncertainty. This can be defined informally as ‘the interval around the result of the measurement that contains the true value with high probability’. The uncertainty ( $u$ ) is often expressed using estimates of the standard deviation of measurements ( $s_{\text{meas}}$ ), usually at the 95% confidence level ( $2 s_{\text{meas}}$ ), and as a percentage relative to the mean concentration ( $\xi$ ) of the pollutant concentration ( $U\% = 200s_{\text{meas}} / \xi$ ). There are four types of errors in measurement methods that contribute to uncertainty in estimates of concentration, which are:

- Random errors of sampling methods, estimated as sampling precision.
- Random errors of analytical methods, estimated as analytical precision.
- Systematic errors of sampling methods, estimated as sampling bias.
- Systematic errors of analytical methods, estimated as analytical bias.
- Well-established methods are available to estimate three of these four components (Table VII).

TABLE VII. THE FOUR TYPES OF ERRORS IN METHODS THAT CONTRIBUTE TO THE UNCERTAINTY OF MEASUREMENTS, AND METHODS FOR THEIR ESTIMATION. (RST = REFERENCE SAMPLING TARGET, IOST = INTER-ORGANISATIONAL SAMPLING TRIAL)

Error Type→	Random (precision)	Systematic ( <i>bias</i> )
Process ↓	Estimate using:-	Estimate using:-
Analysis	e.g. duplicate analyses	e.g. reference materials
Sampling	duplicate samples	RST, IOST

Analytical precision can effectively be estimated using duplicate chemical analyses. Sampling precision can be estimated similarly by taking duplicate samples at points separated in space by a distance reflecting the possible in the sampling protocol. Analytical bias can be estimated using certified reference materials that have a chemical composition that is well matched to the samples.

The estimation of sampling bias is potentially much more problematic, but two methods have been described. One method requires the use of a Reference Sampling Target (RST), which is the sampling equivalent of a reference material for the estimation of bias. The RST can either be created synthetically to have a known concentration of analyte, or it can be a routine sampling target selected for the purpose. The accepted or certified value of concentration (and its uncertainty) can either be taken from the known concentration of analyte added, for the synthetic RST, or established by the consensus of an inter-organisational sampling trial. The accepted value can also include a specification of the spatial distribution of the analyte, and its uncertainty.

The second method of estimating the contribution of sampling bias to the uncertainty of the measurement is to apply more than one sampling protocol to a sampling target, ideally with the involvement of more than one person for sample collection. One extreme example of this approach is the inter-organisational sampling trial in which eight or more persons independently collect samples from the same sampling target for the same specified purpose. If all specialists use the same protocol it constitutes a Collaborative Trial in Sampling (CTS), but if they all select their own protocols, based on their professional judgement, it constitutes a Sampling Proficiency Test (SPT). The variability of the estimates of analyte concentration between the sample units can then be used to estimate the uncertainty of the measurement procedure as a whole, as applied to a particular site. Any bias caused by the sampling of any participant then becomes part of the random error across the whole sampling trial, and hence is automatically included in the uncertainty. There are therefore four methods that can be identified for the estimation of the over uncertainty of measurement (Table VIII).

TABLE VIII. FOUR METHODS FOR ESTIMATING UNCERTAINTY IN MEASUREMENTS (INCLUDING THAT FROM SAMPLING). (CTS = COLLABORATIVE TRIAL IN SAMPLING, AND SPT = SAMPLING PROFICIENCY TEST).

Method No.	Method description	Specialist	Protocols	Components estimated			
				Panal	Banal	Psamp	Bsamp
1	duplicates + CRMs	Single	single	Y	Y	Y	No
2	protocols + CRMs	Single	multiple	Y	Y	between protocols	
3	CTS + CRMs	Multiple	single	Y	Y	between samplers	
4	SPT (+CRMs optional)	Multiple	multiple	Y	Y	between protocols +between samplers	

These four methods estimate the uncertainty with increasing rigour, but at increasing cost. Method 1 is the least expensive, and is the only method that will be considered further in this report. It does not include an estimate of sampling bias, although this can be added by the independent use of an RST. Separation of the main sources of uncertainty requires the use of analysis of variance, usually of the robust type, to allow for non-normal frequency distributions.

The estimation of the uncertainty relies on the availability of measurements made on some of a range of QC materials (Table IX).

The question of who calculates the uncertainty will vary according to circumstance. With the correct experimental design, it would be possible for the analytical laboratory to make reliable estimates of uncertainty, including that arising from field sampling.

TABLE IX. QUALITY CONTROL MATERIALS AND PROCEDURES THAT CAN CONTRIBUTE INFORMATION TO THE ESTIMATION OF UNCERTAINTY OF MEASUREMENTS

Type of QC material	Information Provided
Blank (reagent, field, preparation...)	identifies source of bias contributing to uncertainty, method diagnostics
Certified reference material	bias (traceable according to ISO 3534-1, 1993), diagnostics of chemical preparation and analysis
Reference material (e.g. secondary, internal)	informal estimates of bias between batch precision, diagnostics of chemical preparation and analysis
Duplicate analysis	analytical precision (only!)
Duplicate samples	sampling precision (after separation by ANOVA)
Reference sampling target*	sampling bias (s.s. site specific)
Interorganisational sampling trials*	uncertainty including sampling bias

\*Not recommended for routine applications (high effort)

However, this is not yet routine, and it may require the site investigator to make the calculation, once the laboratory has supplied the relevant QC information in an unrounded and uncensored format.

*Comparison with acceptable limits for uncertainty*

It is impossible to eliminate all uncertainty from measurements. It is also very expensive to reduce the uncertainty to very low levels. What is required therefore to specify the levels of uncertainty that will enable providing of a reliable interpretation of the contamination at the site to be made. In terms of sampling, this is equivalent to saying that the sampling, although not perfectly representative, is representative enough (or appropriate) for the specified purpose. Once the values of measurement uncertainty have been estimated, a comparison needs to be made with some specified limit. One approach is to express the estimated uncertainty as percentage of the concentration, and compare it with some predefined limit (e.g. 25% at the 95% confidence interval). A second approach is to compare the uncertainty of the measurements with the overall variability of the pollutant concentration across the site. If this variability is very high, then a relatively large value of uncertainty will not affect the basic map of how the pollution is distributed spatially. One suggestion has been that the variance due to the measurement ( $s^2_{\text{meas}}$ ) should not exceed 20% of the total variance ( $s^2_{\text{total}}$ ), where this is expressed as

$$S^2_{\text{total}} = s^2_{\text{geochem}} + s^2_{\text{meas}}$$

The use of Method 1 to estimate the uncertainty, involves the use of Analysis of Variance (ANOVA), which automatically gives estimates of these sources of variability and uncertainty. The large scale geochemical variability in the pollutant concentration across the site is quantified as the geochemical variance ( $s^2_{\text{geochem}}$ ). ANOVA also breaks down the measurement uncertainty into its two primary component parts, the analytical variance ( $s^2_{\text{anal}}$ ) and the sampling variance ( $s^2_{\text{samp}}$ ), by assuming

$$S^2_{\text{meas}} = s^2_{\text{samp}} + s^2_{\text{anal}}$$

It is also possible therefore, to identify the relative contribution to the uncertainty from the sampling and the chemical analysis. For the chemical analysis to contribute a negligible amount to the overall measurement uncertainty, it has been suggested that  $s^2_{\text{anal}} < 20\% s^2_{\text{meas}}$ . A third criterion has been suggested for selecting the optimum level of uncertainty, which also allows for the relative costs of the sampling and the analysis, and the financial consequences of misclassifying the extent of pollution at the site (Ramsey et al., 2002). Once the various contribution to the uncertainty are known, it is possible to decide how best to improve the sampling and analytical methodologies in any subsequent surveys.

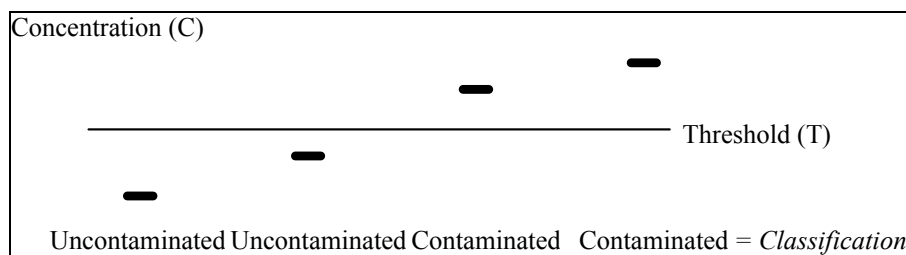
*Turning data into information*

One of the main advantages of reporting realistic estimates of uncertainty together with measurements of concentration is that end-users of the analyses can consider the implications of the uncertainty in the classification of contaminated land. The traditional deterministic approach is to compare the measured concentration values with an appropriate regulatory threshold value Fig 4(a).

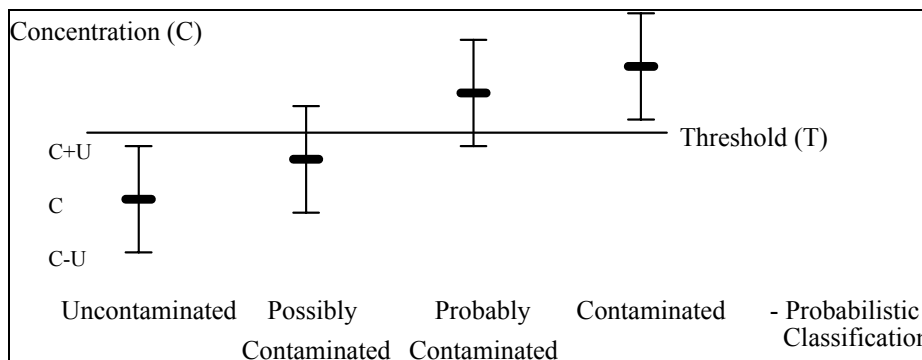
Any sampling point that has a reported concentration value below the threshold is classified as uncontaminated, and those above as contaminated. This approach ignores the presence of uncertainty, but once it is known a probabilistic approach can be taken (Fig. 4). If the measured concentration is below the threshold but the uncertainty interval extends above it, the point is classified as ‘possibly contaminated’ rather than ‘uncontaminated’. Similarly if the measured concentration is above the threshold but the uncertainty interval extends below it, the point is classified as ‘probably contaminated’ rather than ‘contaminated’.

*Reporting of measurements, uncertainty and investigation to end users*

From this discussion, it is clear that the manor of reporting estimates of concentration and uncertainty are central to enabling the reliable interpretation of soil contamination. For the estimation of uncertainty, the measured values of concentration need to be reported in a form that is unrounded. Once rounding occurs, the apparent precision improves. For example if two measurements on one soil sample were both reported as 2 mg kg<sup>-1</sup>, the method appears to have very good precision. If however the unrounded measurements were actually 1.7 and 2.4 mg kg<sup>-1</sup> this would give a very different estimate of the precision. Concentration measurements below the limit of detection need to be reported as the raw values. In this example, if these two measurements were both reported as <3 mg kg<sup>-1</sup>, then it would be impossible to use them to make a reliable estimate of uncertainty. Negative estimates of concentration need also to be reported in raw form.



(a)



(b)

FIG. 4. Comparison between (a) deterministic and (b) probabilistic classification of contaminated land, to show the effect of using estimates of uncertainty to improve the interpretation of measurements.

It is impossible to have true values of concentration that are negative, but it is to be expected that random and systematic errors will produce some negative estimates of concentration when the true value is close to zero. Suppression of such negative values will result in underestimation of uncertainty.

If the calculation of uncertainty is made outside of the analytical laboratory, then the laboratory will need to agree to give this raw information on QC materials to the site investigator. The best procedure for reporting the concentration values of the pollutant in the soils from the site will depend on the particular circumstances. Where simple reporting of pollutant concentration, and deterministic comparison with threshold values is all that is required, it may be acceptable to report concentration after rounding, zero suppression and censorship of values below some detection limit. If however, the concentration values are to be used for probabilistic calculations, such as those described above or for probabilistic risk assessment, then the most reliable interpretation will be made with unrounded, uncensored concentration estimates, accompanied by estimates of uncertainty for each estimate of concentration. At the end of the interpretation of the contamination at a site, it may be justified to round and censor the concentration values finally reported, but in that case there needs to be a full statements of the procedures of rounding and censorship applied to the values, and a statement of the estimates of uncertainty.

## 8. WORKED EXAMPLES

### Lead in contaminated soil

#### *Background Information*

A previously industrial site (300 × 300 m) was suggested for housing development, but lead contamination is suspected from historical records. There is a concern that the lead might affect the health of children playing around houses.

The allowable lead content in the country concerned is 500 mg kg<sup>-1</sup>. This is based on a range of typical values used by other countries (SAEFL, 1998)

#### *Steps for systematic planning*

##### 1. Step 1 — Stating of the Problem

The objectives of the project are

- to provide a sufficient number of samples/measurements to ensure that the mean concentration of lead in the topsoil across the site (i.e. 300 × 300 m (90,000 m<sup>2</sup>)) is less than 500 mg kg<sup>-1</sup>;
- to have an estimate on the frequency distribution (variability) of lead concentration within the sampling site;
- to assure that there are no “hot spots” larger than 20 × 20 m where lead could exceed 500 mg kg<sup>-1</sup>; and
- to complete the work in 100 person hours.

The overall measurement uncertainty (including sampling) acceptable to the investigator is 20% (less than 4% for analytical methods) at 95% confidence level.

##### 2. Step 2 — Identification of the Decisions to Be Made

Decision: If the mean concentration of lead across the area exceeds 500 mg kg<sup>-1</sup> (with 95% confidence) then the site will be remediated, otherwise only checks for hot spots will be made. If more than 10% of the measurements exceed the threshold (500 mg kg<sup>-1</sup>), then the objective will be reviewed.

### 3. Step 3 — Identification of the Inputs to the Decision (Table X)

TABLE X. INPUTS FOR DECISION MAKING

Decision on sampling strategy (judgemental sampling, random s., systematic., etc.)	<i>how</i> : systematic grid, with 30m spacing and 0-10 cm depth <i>why</i> : practical field method; a suggested technique for estimation of mean concentration in cases of presumed irregular occurrences of analyte (ISO 10381-1) sampling depth defined to address potential exposure of children (topsoil ingestion).
General soil & site characteristics (remoteness, infrastructure, accessibility, etc.)	easy access, 10% slope, weeds & bushes, anthropogenically disturbed, heterogeneous soil, clay-loam, Ph = 8 no buildings or foundations
Number of field samples (+QC scheme)	100, + 8 duplicated samples, to be discussed under section 6
Composite samples yes/no?	no; <i>why</i> : to fulfil objective b)
Sampling equipment needed (based on site characteristics and sampling strategy), sampling tools, sample amount (mass/volume)	<i>how</i> : stainless steel hand auger (0-10cm) or PTFE tubes, buckets, containers, labels, spot or site record form(s), approximately 100 g (dry weight) per sampling spot <i>why</i> : appropriate technology for obtaining surface soil, cheap, low contamination risk (no Pb in steel), usually sufficient mass for acceptable sampling precision and enough to provide archive samples
Surveying tools	<i>how</i> : measuring tape (e.g. 30 m), detail topography map (1:5000 or 1:10000), any kind of sticks to mark sampling points <i>why</i> : normal GPS is currently not accurate enough for this purpose
Sample preparation	<i>how</i> : dry sample < 40°C, (or as specified by local regulator), desegregate to natural grain size, sieve the material through nylon sieve 2 mm (10 mesh) size. Split representatively to create archive sub-sample. Store archive sample dry and contamination free. Grind one sub-sample in non-contaminating milling device to a particle size appropriate for the analytical method (150 µm for AAS ) <i>why</i> : meets analytical requirements and definition of soil
Analytical equipment/methods, (incl. <i>In situ</i> /On-site/off-site (laboratory)? detection limits, selectivity, precision (reproducibility / repeatability, bias, cost per analysis, needed analytical test portion),	<i>how</i> Flame-AAS (after acid digestion) in off-site laboratory acceptable analytical detection limit = 20 mg kg <sup>-1</sup> ; precision (repeatability) for concentration values > 200 mg kg <sup>-1</sup> <4% (95% confidence level) bias for concentration values > 200 mg kg <sup>-1</sup> ±4% needed analytical test portion is 3 g for AAS cost per analysis – 0.90 person hour per analysis) <i>why</i> : low costs, acceptable analytical characteristics
Number of false positives / false negatives classification	maximum false positives: 10% maximum false negatives: 5%
Logistics (constraints: time scale, capacity, quality system) Will chain of custody forms be required?	final results should be reported within 1 month lab capacity available, no accredited lab available, QC required for sampling & analysis (section 6) Chain of custody forms are required.
Personnel (qualification/training, safety precautions)	trained laboratory personnel available sampling: no soil scientist necessary, but people trained in sampling are necessary
Budget available	budget available for 100 person hours

#### 4. Step 4 — Defining of the study boundaries

- Time: One month from sample collection to reporting of measurements.
- Physical: 300x300 m, depth 0-10cm, no obstacles or access problem assumed. Experienced and trained personnel in sampling and analytical work available.
- Equipment for sampling, sample handling and preparation, and analytical measurement available.

#### 5. Step 5 – Development of decision rules

It is usually best to define decision rules separately for field sampling decisions and analytical measurement decisions because of the differences in their nature. Below are some examples of the kinds of decision rules that can and should be made during the planning process in order to clarify the project plans.

- *Field sampling decisions:*

- If you can't take the sample at the specified point, then move the point 2 m in a random, but recorded direction (e.g. obstruction at the sampling point, stone in the auger hole).
- If the weather conditions prior to sampling are unsuitable (according the sampling plan), then delay the sampling by 1 days (e.g. very heavy rain, sub-zero temperature).

- *Analytical measurement decisions:*

If a selected method of analytical measurement (excluding sampling) exceeds 4% uncertainty (at 95 % confidence level) at concentration level ten times above the detection limit (specified as 20 mg kg<sup>-1</sup> Pb), then the lab will reanalyse the samples and QC materials, by an alternative analytical method if appropriate.

If a selected overall method of measurement (including sampling) exceeds 20% uncertainty (at 95% confidence level) then we need to identify the dominant source of the uncertainty (from the QC materials), and reduce this source to acceptable level, if possible, or revise target level for overall uncertainty.

If the mean concentration of lead in soil samples exceeds 500 mg kg<sup>-1</sup> then remediation of the site is needed.

If the available budget is exceeded, then the resulting precision, bias, and overall confidence level targets will be calculated using the available data and compared to the original decision criteria. If data is too uncertain to base decisions upon (because of their consequences if they are wrong), then the budget, objectives and decisions will be re-evaluated and changed as necessary.

If confidence interval on estimate of site mean concentration is outside of the specified level, then review either the number of samples taken or specified confidence level.

Defining decision rules for consequences for true and false classification (false positives/false negatives) — derive financial, health implications.

If the 10% rate of false positives or 5% rate of false negatives (at the 95% confidence level) is exceeded then the analyses will be halted until the source of the problem is determined and solved.

TABLE XI. REQUIREMENT OF THE QC MATERIALS

Type of QC material	Information provided
blank (field, preparation, laboratory)	identifies source of bias contributing to uncertainty, method diagnostics.
certified reference material	bias (traceable according to ISO 3534-1, 1993), diagnostics of chemical preparation and analysis (See Appendix .....
reference material (e.g. secondary, internal)	Informal estimates of bias between batch precision, diagnostics of chemical preparation and analysis
duplicate analysis	analytical precision (only!) on all sample duplicates, see Fig 5.1.
duplicate samples	sampling precision (after separation by ANOVA) on 10% of number of sampling points but not less than 8 points at 2m from original grid points in a random direction (to reflect survey relocation error).

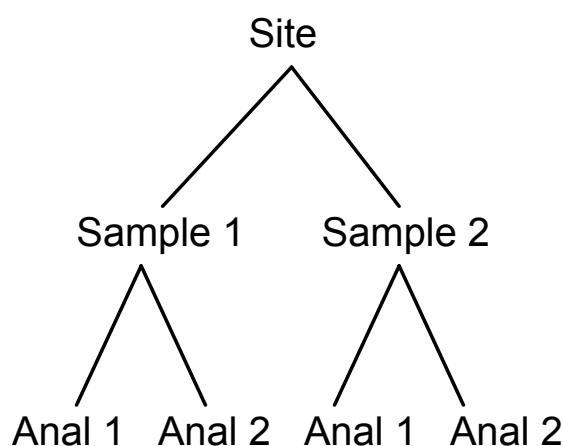


FIG. 5. Balanced design for analytical duplicate analyses on each half of the sample duplicate, taken at 10% of the sampling points, but not less than 8 points.

#### 6. Step 6 – Specification of the limits to Total Uncertainty

*Criterion 1.* Specified limit for measurement uncertainty (including that from sampling) is 20% (as a percentage of the mean, at 95 % confidence level). If this fails, then use criterion 2.

*Criterion 2.* Measurement uncertainty must not contribute more than 20% to the total variance at a 95% confidence level of the dataset. If the measurement uncertainty does contribute more than this 20%, then either the measurements have to be repeated with an improved protocol or the interpretation of the measurements has to allow for the extra uncertainty in the interpretation of the site for the stated objectives.

*Criterion 3.* For the analytical laboratory, the analytical precision specified needs to be less than 4% (at 95 % confidence level) at concentration level ten times above the detection limit (specified as 20 mg kg<sup>-1</sup> Pb). If this criterion is not met, then the lab will reanalyse the samples and QC materials, by an alternative analytical method if appropriate.

*Enviro-Calc* may be used as an initial estimate of the numbers of samples that need to be analysed to generate data with no more than 20% relative standard deviation at 95% confidence and with a tolerable error not exceeding 10%, in order to have the already specified target uncertainty (at 95% confidence) at concentrations more than ten times the detection limit (20 mg kg<sup>-1</sup>). The answer is



calculated to be 18 samples, but given the approximations made in this programme (e.g. that we are dealing with a Normal distribution), then the recommendation is to compare this sampling approach with others (for example systematic herringbone (grid) sampling).

#### Conclusions from Step 6 Initial Calculations

Eighteen samples would provide an average concentration that falls within a tolerable uncertainty of 20% (plus or minus 10% with 95% confidence) but they would not be sufficiently representative of the potential 'hot spots' within the site as a whole.

#### *Reiteration of Step 6 – Initial Calculations*

Ask the question in a different way. If the concentration of lead at any point across the site is greater than 500 mg kg<sup>-1</sup>, this would constitute a 'hot spot' and limit the possible development of housing. Excavation of the entire site would not be cost effective.

This then becomes the new objective of the investigation and the statistical equations in the programme.

A revised DQO based on systematic sampling would be: The objective is to ensure that the concentration of lead in any 20 x 20 m (400 m<sup>2</sup>) area of the site is less than 500 mg kg<sup>-1</sup> (plus or minus 150 mg kg<sup>-1</sup>) at a 95% confidence level. The site would require about 325 samples with a spacing of approximately 17m. This calculation with *HotSpot-Calc* would give 95% confidence of not missing a circular hot spot of radius 10m. However, this number of samples is more than three times the available budget.

In order to fit the budget of approximately 110 samples the size of the spot would have to have a radius of 18 m with a grid spacing of 30 m. Thus, the objective of not missing a smaller spot with a 10 m radius cannot be met without significantly increasing the budget.

#### 7. Step 7 – Optimisation of the sampling plan

However, the cost of taking and analysing the suggested samples exceeds the budget of a hundred person hours. The maximum number of samples that can be afforded on this budget is approximately 110 (calculated from 0.9 hours per sample). Using *HotSpot-Calc* this will give 95% confidence of not missing a circular hot spot of radius 18 m using a grid size of 30 m. Thus, a hot spot would have to be 36 × 36 m not to be missed instead of the desired 20 × 20 m spot.

We still need to know whether we have achieved specified proportions of < 10% false positives and < 5% false negatives (at 95% confidence level) for the method. This will be calculated when the measurements have been made. Using *Success-Calc* we can estimate that approximately 30 blanks (none of which exhibit false positives) and approximately 60 soil samples spiked near the acceptance criteria of 500 mg kg<sup>-1</sup>. However, since the method detection level of the selected method (flame-AAS) is 20 mg kg<sup>-1</sup>, there is no fear of meeting the false negative criteria because the method detection level is twenty five times lower than the acceptance criteria (unless the sampling was the dominant cause of the uncertainty).

If the laboratory runs a blank soil sample (containing lead at undetectable levels below 20 mg kg<sup>-1</sup>), each day for 30 days and pools the data into a set that can be treated statistically, then the false positive criteria may be evaluated. If all critical analytical conditions (e.g. analyst, instrument, calibration standards, AA lamp, etc.) remain unchanged over the 30 days of sample analyses AND if no false positives are detected in the blank soil samples, then the criterion of < 10% false positives will have been met (ignoring uncertainty arising from sampling). It is important to note that it is the unchanging analytical conditions that are critical, not the project samples.

Thus, over the 30 days of sample analysis the laboratory may use soil blanks that were associated with other project samples as long as the method and its analysis conditions and the soil blanks remained the same over this time period.

### Interpretation of measurement results

Estimates of concentration and data quality from laboratory or field measurements are given in Tables XI, XII and XIII. The measurements on the reagent blanks may have been subtracted from the measurements on the samples and CRMs by the laboratory. If not, you will need to correct these measurements yourself.

Assessment of the reliability of measurements Estimation of precision (random errors) of sampling and analytical methods

The four measurements made on the two duplicates for each of the ten sampling points (Table XI) resulting in 20 samples and 40 analyses. These measurements were analysed using robust Analysis of Variance (ROBCOOP) to give estimates of the uncertainty, and its components (Table XII).

Measurements of Pb concentration on duplicated samples, taken for the estimation of measurement uncertainty at the test site. Samples were taken at the 10 coordinates described by the Sample I.D. on the regular grid to the experimental design (Table XII).

TABLE XII. MEASUREMENTS OF PB CONCENTRATION ON DUPLICATED SAMPLES

SAMPLE I.D.	S1A1Pb ( $\mu\text{g g}^{-1}$ )	S1A2Pb ( $\mu\text{g g}^{-1}$ )	S2A1Pb ( $\mu\text{g g}^{-1}$ )	S2A2Pb ( $\mu\text{g g}^{-1}$ )
A4	787	769	811	780
B7	338	327	651	563
C1	289	297	211	204
D9	662	702	238	246
E8	229	215	208	218
F7	346	374	525	520
G7	324	321	77	73
H5	56	61	116	120
I9	189	189	176	168
J5	61	61	91	119

TABLE XIII. OUTPUT FROM ANOVA (CLASSICAL AND ROBUST) OF THE MEASUREMENTS FROM THE TEST SITE IN THE UNITS OF  $\text{MG KG}^{-1}$

Element	Pb
Number of duplicate samples n=10	
Classical results: Mean= 317.8000	
sigma values (geochem, sampling, analysis) – 197.552, 135.432, 17.990	
sigma (total) - 240.192	
Robust results: Mean= 297.3088	
sigma values (geochem, sampling, analysis) – 179.674, 123.814, 11.144	
sigma (total) - 218.488	

The output of the robust ANOVA (lower half of Table XII) shows that most of the variance (67.73%, [179.674]/ [218.488]) arises from the large scale geochemical variability in the Pb concentration across the site. The sampling procedure (including the physical preparation of the sample) contributes 32.10% to the total variance ([123.814]/[218.488]), and the analytical procedure contributes only 0.26% ([11.144]/[218.488]). The measurement procedure as a whole therefore contributes 32.36% to the total variance, but this is total dominated by the contribution from the sampling. Whether this is an acceptable level, will be discussed below.

*Estimation of bias (systematic errors) of sampling methods*

Experimental design did not allow for this. Sampling protocol has been designed to minimise the extent of sampling bias.

*Estimation of bias (systematic errors) of analytical methods*

Measurements of concentration made on reference materials are given in Table XIV. Reagent blanks were also analysed, and the average Pb concentration subtracted from all of the measurements, after the value was tested as being significantly greater than zero (using a t-test, - see example below for CRMs).

TABLE XIV. MEASURED AND CERTIFIED PB CONCENTRATION VALUES FOR CERTIFIED REFERENCE MATERIALS FOR THE ESTIMATION OF THE BIAS OF THE ANALYTICAL METHOD.

CRM name (n=4)	Mean (mg kg <sup>-1</sup> )	Std. Dev.s (mg kg <sup>-1</sup> )	Certified Value mg kg <sup>-1</sup>	Bias mg kg <sup>-1</sup>	Relative Bias %	Calculated t- value
NIST2709	19.7	3.2	18.9	0.8	4.23	0.5
NIST2710	5352	138	5532	-180	-3.25	2.6087
NIST2711	1121.4	14.7	1162	-40.6	-3.49	5.5238*
BCR141	34.4	3.9	29.4	5	17.00	2.5641
BCR142	36.2	4.6	37.8	-1.6	-4.23	0.6956
BCR143	1297.5	33	1333	-35.5	-2.66	2.1515

The six certified reference materials were selected to cover the full range of the possible Pb concentrations that might have been encountered at the site. The bias can either be estimated at each particular concentration, or estimated as a function of concentration. The individual estimates of bias from each reference material (Table XIV) are generally small, either in terms of absolute value at low concentration (e.g. BCR141) or when expressed as a percentage of the certified value at high concentration (e.g. NIST 2710). Whether the calculated value of bias is statistically greater than zero (at 95% confidence) can be checked by comparing the calculated t-value ( $t_{calc} = \text{Bias}/(s/\sqrt{n})$ ) with the tabulated value ( $t_{tab} = 3.182$  for  $n=4$ ). Only for one CRM (NIST2711) was statistically significant bias detected.

Expressing bias as a function of concentration can be achieved by a regression of the measured concentration value ( $c_m$ ) on the certified values ( $c_c$ ). The simplest technique, least squares regression, gives the regression equation:

$$c_m = 0.967 c_c + 2.542$$

The 95% confidence interval on these regression coefficients shows that the slope is significantly different from one (0.964 to 0.970), whereas the intercept coefficient is not significantly different from zero (-3.61 to +8.70). This indicates that the best estimate of the bias is a purely proportional factor of -3.3% (i.e.  $100 \times [1-0.967]$ ). In this case therefore there is evidence of 'rotational' bias of -3.3% on all of the measurements. The intercept value does not indicate that there is any 'translational' bias in this method, where the bias is a fixed concentration value across the entire

range of concentration. More sophisticated regression techniques can improve such estimates of bias by allowing for uncertainty on the certified concentration values, but do they not make a substantial difference in this case. When non-certified or in-house reference materials (HRMs) are used for the estimation of bias, the same basic techniques can be applied, with less weight being given to such estimates. The ‘bias’ values estimated in that way are not traceable, and are less reliable, and strictly not estimates of bias, by the ISO definition of the term (i.e. traceable according to ISO 3534-1, 1993).

### Estimation of overall uncertainty of measurements (including sampling)

Using the definition of uncertainty given above the random component of the uncertainty of the measurements can be calculated from the sum of the analytical and sampling variances. Using the robust estimates of the variance for the test site gives an estimated uncertainty of measurement as  $124.3 \text{ mg kg}^{-1}$ . When expressed relative to the robust mean concentration value, the relative expanded uncertainty (for 95% confidence) is given by

$$U = 200s_{\text{meas}} / \text{mean} = 200 \times 124.3 / 297.3 = 83.6 \% \text{ (Robust results)}$$

This includes the dominant contribution (99.2%) from the sampling process in this example. This equation assumes that the uncertainty is a fixed proportion of the concentration over a range of concentration values. This is generally true at the high concentrations generally found in contaminated land investigation, but breaks down where analyte concentrations approach the detection limit of the technique (ref. Lee & Ramsey Analyst, 2001)

### Comparison with acceptable limits for uncertainty

The uncertainty arising from the measurement procedures contributes 32.36% to the total variance, which is well above the suggested ‘fitness-for-purpose’ criterion of 20% (Criterion 2 of Step 6). This criterion was designed to ensure reliable geochemical mapping of contamination, and the further the value is exceeded, the less reliable the delineation of areas of contamination will become. If the actual value of uncertainty is known, it is however possible to identify areas which are definitely uncontaminated for example (Criterion 2 of Step 6).

The ANOVA has helped to identify sampling as the source of the largest component of the uncertainty. This contribution can be reduced by taking a larger mass for each sample. It has been shown that the sample mass is inversely proportional to the variance caused by the sampling. The sample mass could be increased by a factor of five, for example, by combining the masses of five increments taken from auger holes within a square metre at the sampling point. In that case the standard deviation contributed by the sampling (originally  $124 \text{ mg kg}^{-1}$ ) should be reduced by a factor of approximately  $\sqrt{5}$  ( $= 2.24$ ), to around  $55 \text{ mg kg}^{-1}$ . This would mean that the contribution from the sampling (and hence the measurement) would be expected to fall to approximately 8.5% of the total variance, which is well within the fitness-for-purpose criterion of 20%.

### Turning data into information

In terms of objective 1, the mean concentration across the site of  $291.9 \text{ mg g}^{-1}$  is less than the threshold value of  $500 \text{ mg kg}^{-1}$ . However, the best estimates of the lead concentration at each location on the sampling grid show that there are 8 points, where the Pb concentration nominally exceeds this regulatory limit.

Measured Pb concentrations at each point on the sampling grid ( $\text{mg kg}^{-1}$ ), shown by the actual coordinates used in the regular sampling grid (spacing 30 m). All values are concentrations measured on single samples except for the ten duplicated samples, for which the value given is the mean of the four values given in Table XV for that coordinate (e.g.  $787 \text{ mg kg}^{-1}$  at coordinate A4, is the mean of the first row) Values in **bold** indicate contamination over the regulatory limit of  $500 \text{ mg kg}^{-1}$ , and those in *italics* are ‘possibly contaminated’ when allowance is made for measurement uncertainty.

TABLE XV. MEASURED PB CONCENTRATIONS AT EACH POINT OF SAMPLING GRID

Row	A	B	C	D	E	F	G	H	I	J
1	474	287	250	338	212	458	<b>713</b>	125	77	168
2	378	<b>3590</b>	260	152	197	<b>711</b>	165	69	206	126
3	327	197	240	159	327	264	105	137	131	102
4	<b>787</b>	207	197	87	254	<b>1840</b>	78	102	71	107
5	395	165	188	344	314	302	284	89	87	83
6	453	371	155	462	258	245	237	173	152	83
7	72	470	194	82.5	162	441	199	326	290	164
8	71	101	108	<b>521</b>	218	327	<b>540</b>	132	258	246
9	72	188	104	463	482	228	135	285	181	146
10	89	366	495	<b>779</b>	60	206	56	135	137	149

In step 2 it was stated that if more than 10% of the measurements exceed the threshold ( $500 \text{ mg kg}^{-1}$ ), then the objective has to be reviewed. The objective in the above example therefore need not be reviewed in view of only 8% points being the threshold. This interpretation is however deterministic, and ignores the uncertainty in the measurements of concentration ( $U\% = 83.6\%$ ). We can calculate from this how low a measured concentration ( $c$ ) must be, for there to be a less than a 97.5% probability that the true concentration does not exceed the threshold value ( $T$ ). This case is shown as 'possibly contaminated' on Fig. 4.4 (page 44?). At that limit we have

$$c + U = T$$

For this example, the upper limit of the uncertainty interval ( $c + U$ ) is equal to  $1.836c$ , and  $T$  is equal to  $500 \text{ mg kg}^{-1}$ , and hence  $c$  is equal to  $272 \text{ mg kg}^{-1}$ . Inspecting the measurements made on soils taken from the site, there are now an extra 25 of the sampling points that fall into this category of 'possibly contaminated', where the true Pb concentration may exceed the threshold (with a probability of  $>2.5\%$ ) (shown in italic on Table 5.8). Overall therefore there are 33% of the sampling points that may have true concentration above the threshold value, and the objectives of the investigation must therefore be revised. New objectives could include delineation of areas within the site where the Pb concentration exceeds the threshold value, and therefore requires selective remediation.

It is possible to apply this probabilistic approach to classifying all of the points at the site, into the four classes, of uncontaminated ( $c < 272 \text{ mg kg}^{-1}$ ), possibly contaminated ( $c = 272$  to  $500 \text{ mg kg}^{-1}$ ), probably contaminated ( $c = 500$  to  $3049 \text{ mg kg}^{-1}$ ) and contaminated ( $c > 3049 \text{ mg kg}^{-1}$ ). This lower limit for the classification of definitely contaminated ( $3049 \text{ mg kg}^{-1}$ ) is the concentration where there is only a 2.5% chance of the true concentration being lower than the threshold value of  $500 \text{ mg kg}^{-1}$  ( $c = 500/(1 - 0.836)$ )

This treatment of uncertainty did not include systematic errors in either the chemical analysis or the field sampling. The later cannot be addressed by the approach used in this investigation (Method 1, discussed above). The estimate of analytical bias can either be incorporated into the estimate of uncertainty, or else considered separately. If all of the measured Pb concentrations are low by 3.3%, then measured values of  $483.5 \text{ mg kg}^{-1}$  (i.e.  $500 \times [1 - 0.033]$ ) represent an un-biased Pb concentration of  $500 \text{ mg kg}^{-1}$ , equal to the threshold value. Similarly, allowing for the random component of the uncertainty, a measure Pb values of  $263 \text{ mg kg}^{-1}$  (i.e.  $272 \times [1 - 0.033]$ ) represent a bias-free Pb concentration of  $272 \text{ mg kg}^{-1}$ . One extra sampling point (F3) has a measured Pb concentration (of  $264 \text{ mg kg}^{-1}$ ) that could therefore represent a true above the threshold value, and should be classified as 'possibly contaminated'. This bias correction can be applied to each of the classification boundaries applied, giving boundaries of 263, 484 and  $2948 \text{ mg kg}^{-1}$  respectively in this example.

Another alternative option is to 'correct' all of the analytical measurements by the estimate of the known analytical bias, before the interpretation takes place. This option assumes that the estimate

of the bias is reliable (e.g. that the reference materials suffered the same interference effects as the samples). It is possible to estimate the uncertainty in estimate of the bias (nominally 0.094% from the regression) but this is very likely to be an under-estimate. Moreover once values have been 'corrected', information on the method of correction, and the extra uncertainty caused, are often lost. The most transparent option is therefore to state the analytical bias and allow for it in the probabilistic interpretation of the measurements, as described above.

### **Reporting of measurements, uncertainty and investigation to the end users**

As discussed, all of the measurements used in the estimation of uncertainty are to be left unrounded to the point where there was at least one digit of random variation. There has to be no suppression of negative estimates of concentration (e.g. in estimation of bias from reagent blanks).

Similarly, there was no censorship of measurements that were nominally less than the detection limit at this stage. In the reporting of the estimates of concentration to the end user all values are rounded to the nearest integer mg kg<sup>-1</sup>. An overall estimate of the random component (83.6%) and the systematic component (-3.3%) of the measurement uncertainty are supplied, as single values applicable to all concentration values. A set of unrounded concentration and uncertainty estimates is to be made available to any end-user that requires them for use in further data interpretation (e.g. risk assessment or geostatistics). This could take the form of estimates of concentration and uncertainty (at a specified confidence level) for each sampling point.

### **The assumptions made in the interpretations need to include**

- That the estimates of uncertainty made on selected samples and reference materials are representative of the uncertainty on the other samples taken.
- That the uncertainty (random and systematic) is taken to be a fixed proportion of any concentration value.
- That no estimate or allowance is made for any bias caused by the processes of sampling or physical preparation of the samples.
- That errors are assumed to be either normally distributed, or to have less than 10% of outlying values (for the robust ANOVA).

The measurements apply only to the top 10 cm of the soil at selected points within the survey area, and no inference is made about contamination between the sampling points or at a greater depth (i.e. small 'hot spots' of contamination may have been missed).

The example described in this report is intended to help explain the general principles, and it not intended to be taken as a recommended method. Every site requires specific considerations for an optimal sampling design depending upon the objective of concerned investigation.

### **Possible modifications to the work example**

A similar area of suspected contamination will be used to aid comparability with the worked example.

#### *Atmospheric deposition of <sup>137</sup>Cs*

Differences between Worked Example and requirements for investigation of a new atmospheric deposition of <sup>137</sup>Cs.

Step 1:

- Replace analyte of lead by <sup>137</sup>Cs, atmospheric deposition. Threshold value for <sup>137</sup>Cs activity (5.21 kBq m<sup>-2</sup>).

Step 3:

- Use in situ measurement with gamma-ray detector (counting time per measurement, detection limit, measurement uncertainty 30%, counting time fixed (how long?) using the same sampling design (random distribution of points).
- No sampling or laboratory analytical equipment needed.
- No chains of custody forms.
- Highly trained personnel necessary for quantitative measurements.
- Review QC material required.

Step 6:

- Criteria 2 and 3 are not needed decide if 10 samples are enough.

Step 7: probably smaller budget needed (justify later)

### **Pesticides**

Differences between Worked Example 1 and requirements for investigation of Pesticides

- Step 1: replace analyte of lead by Clorpyrifos, threshold value?
- Step 3: measurement uncertainty 30%, using the same sampling design (random distribution of points) surface contamination, sampling depth 0-10 cm, hand auger as sampling equipment sample transportation.
- Step 4: in brown glass bottles instead of plastic bags sample preparation: keep at  $\sim 4^{\circ}\text{C}$  from time of sampling, totally different sampling preparation and analysis (GC-MS?) detection limit? highly trained personnel necessary for quantitative measurements.
- Step 5: Review QC material required, reference material, spiked samples?
- Step 6: criteria 2 and 3 are not needed decide if 10 samples are enough.
- Step 7: time budget will be too small.

## **9. CONCLUSIONS**

Conclusions (on basis of objectives):

- It is not possible, or even a requirement, to describe perfectly the extent of contamination in an area of soil.
- The first requirement is to specify the particular objectives of the investigation. It is then necessary to design an investigation that aims to meet these objectives with a specified degree of confidence.
- It is important to measure not just the concentration of the contaminants but also to estimate the uncertainty in those measurements. Once the uncertainty is known, the reliability of the interpretation of the contamination can be expressed.

- The objective of the measurements is not to aim for the lowest uncertainty, or use methods with the best precision and the lowest bias. The requirement is to have a level of uncertainty in the measurements that is low enough to achieve the stated objectives. If the measurement procedure is designed to allow identification of the sources of uncertainty, then it will be possible to target where improvements need to be made if the uncertainty does need to be reduced.



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## Annex A

### CONTAMINATION THRESHOLD VALUES RECOMMENDED BY VARIOUS AGENCIES (ISO/WHO/DIN/BSI/EURO/EPA)

TABLE XVI. CRITICAL LIMITS OR MAXIMUM ALLOWABLE CONCENTRATION OF HEAVY METALS IN SOILS IN SEVERAL COUNTRIES\*

Country	Critical limits (mg Kg <sup>-1</sup> )**						
	Pb	Cd	Cu	Zn	Ni	Cr	Hg
Denmark	40	0.3	30	100	10	50	0.1
Sweden <sup>1</sup>	30-60	nv	nv	nv	nv	nv	0.2-0.3
Finland	38	0.3	32	90	40	80	0.2
Netherlands	85	0.8	36	140	35	100	0.3
Germany <sup>1</sup>	40-100	0.4-1.5	20-60	60-200	15-70	30-100	0.1-1.0
Switzerland	50	0.8	50	200	50	75	0.8
Czech Republic	70	0.4	70	150	60	130	0.4
Eastern Europe <sup>2</sup>	32	2	55	100	85	90	2.1
Ireland	50	1.0	50	150	3	0100	1.0
Canada	25	0.5	3	050	2	02	0.1

\*Source: [www.epa.gov/oerrpage/superfund/programs/risk/ecorisk/exhibits/exhibit1.pdf](http://www.epa.gov/oerrpage/superfund/programs/risk/ecorisk/exhibits/exhibit1.pdf)

\*\* Values are for protection of all land uses

1. The first value is for sandy soil, second value for clay soil

2. Eastern Europe includes Russia, Ukraine, Moldavia and Belarus

nv = no value



## Annex B

### ACTION, TRIGGER AND PRECAUTIONARY VALUES FOR SOIL PROTECTION

#### Federal Soil Protection Act, 1998, Germany

The Federal Soil Protection Act on protection against harmful changes to soil and on rehabilitation of contaminated sites in Germany covers a wide spectrum of the aspects concerning soil contamination due to environmental pollutants. The definitions of the various relevant terms as well as the limits of the contaminants in respect of the different uses of the soil summarised in this act and published on March 17, 1998 can be used as a guiding reference in understanding the uses relating to soil contamination. The definitions of various terms and the concentration of the contaminants relating to various action of soil use/remediation given in this act are summarised in this annex.

#### Terms and Definitions

##### *Trigger Values*

Values which, if exceeded, shall mean that investigations with respect to the individual case in question required, taking to relevant soil use into account, to determine whether a harmful soil change or site contamination exists.

##### *Action Values*

Values for impact or population which, if exceeded, shall normally signal the presence of a harmful soil change or site contamination, taking the relevant soil use into account, and to mean that measures are required.

##### *Precautionary Values*

Soil values which, if exceeded, shall normally mean there is a reason that concern for a harmful soil change exists, taking geogenic or wide-spread, settlement-related pollutant concentrations into account.

#### Soil Uses - Human Health Pathway

##### *Playgrounds*

Places for children that are generally used for playing, without the play the sand in sandpits. If necessary, officially designated playgrounds must be evaluated on the basis of public health standards.

##### *Residential Areas*

Areas serving housing purposes, including back gardens or any other gardens of similar use, including where they are not represented or specified under planning law within the meaning of the Building Use Ordinance, except for parks and recreational facilities, play grounds as well as paved traffic surfaces.

##### *Parks and Recreational Facilities*

- Facilities serving social, health and sports purposes, in particular public and private green areas as well as unpaved areas that are regularly accessible and used in a comparable way.
- Plots of Land Use for Industrial and Commercial Purposes
- Unpaved areas within workplaces or manufacturing plants, which are used only during working hours.

## Soil Uses - Plant Pathway

### *Agriculture*

Areas for the cultivation of varying field crops, including vegetables and field forage plants, this also includes areas used for commercial gardening.

- *Vegetable Garden*
- Back garden, small garden and any other garden areas used for growing food crops.
- Grass Land
- Permanent green areas.
- Limiting Values

TABLE XVII. ACTION VALUES FOR SOIL-HUMAN HEALTH PATHWAY

Substance	Action Values (ng I - Teq/kg TM*)			
	Play grounds	Residential areas	Parks and recreational facilities	Land use for industrial and commercial purposes
Dioxins/furanes (PCDD/F)	100	1,000	1,000	10,000

\* sum of the 2,3,7,8- TCDD- toxicity equivalents (according to NATO/CCMS)

TABLE XVIII. TRIGGER VALUES FOR SOIL- HUMAN HEALTH PATHWAY

Substance	Trigger Values (mg/kg TM)			
	Play grounds	Residential areas	Parks and recreational facilities	Land use for industrial and commercial purposes
Arsenic	25	50	125	140
Lead	200	400	1,000	2,000
Cadmium	10 <sup>1</sup>	20 <sup>1</sup>	50	60
Cyanides	50	50	50	100
Chromium	200	400	1,000	1,000
Nickel	70	140	350	900
Mercury	10	20	50	80
Aldrin	2	4	10	-
Benzo(a)pyrene	2	4	10	12
DDT	40	80	200	-
Hexachlorobenzene	4	8	200	200
Hexachlorocyclohexane (mix or beta HCH)	5	10	25	400
Pentachlorophenol	50	100	250	250
Polychlorinatedbiphenyls <sup>2</sup>	0.4	0.8	2	40

- in back gardens and small gardens where children stay and food plant are grown, the trigger value 2.0 mg/kg TM must be applied.
- where PCB total contents are determined, the measured value must be divided by a factor of 5.



TABLE XIX. ACTION AND TRIGGER VALUES FOR AGRICULTURE AND VEGETABLE GARDENS.- WITH REGARD TO PLANT QUALITY (IN MG/KG DRY MATTER)

Substance	Method <sup>1</sup>	Trigger value	Action value
Arsenic	KW	200 <sup>2</sup>	-
Cadmium	AN	-	0.04/0.1 <sup>3</sup>
Lead	AN	0.1	-
Mercury	KW	5	-
Thallium	AN	0.1	-
Benzo(a)pyrene	-	1	-

- Extraction process for arsenic and heavy metals: AN- ammonium nitrate, KW- aqua regia.
- In case of soils with temporarily decreasing conditions, a trigger value of 50 mg/kg dry matter must be applied.
- In areas that are used for growing bread wheat or strongly cadmium-accumulating vegetables, an action value of 0.04-mg/kg dry matter must be applied; otherwise, the action value is 0.1-mg/kg dry matter.

TABLE XX. ACTION VALUES FOR GRASSLAND (IN MG/KG DRY MATTER)

Substance	Action Value
Arsenic	50
Lead	1,200
Cadmium	20
Copper	1,300 <sup>1</sup>
Nickel	1,900
Mercury	2
Thallium	15
Polychlorinatedbiphenyls (PCB6)	0.2

Where sheep are kept on grassland, the applicable action value is 200 mg/kg dry matter.

TABLE XXI. TRIGGER VALUES FOR AGRICULTURE - WITH REGARD TO GROWTH IMPAIRMENTS OF CULTIVATED PLANTS (IN MG/KG DRY MATTER)

Substance	Trigger Value
Arsenic	0.4
Copper	1
Nickel	1.5
Zinc	2



## Annex C

### REGULATORY STANDARDS ACTING AS TRIGGER VALUES FOR Pb IN CHILDREN'S PLAYGROUNDS (SAEFL, 1998)

TABLE XXII. REGULATORY STANDARDS

Origin	Regulatory standards for Pb (mg/kg DM)
Hamburg (Schuldt, 1988)*	500 (trigger value)
Baden-Wuerttemberg (Jaroni and v.d. Trenck 1996)*	100 (trigger value)
Bavaria (AGU 1994)*	300 (tolerable pollutant concentration in the soil)
Berlin (Anonymous 1996a)*	400 (risk value)
Bremen( Ewers et al. 1993b)*	400 (intervention value)
North Rhine-Westphalia( Anonymous 1991)*	1000 (guide value II)

\* cited in SAEFL, 1998.



## Annex D

### SOIL REFERENCE MATERIALS

TABLE XXIII. AVAILABILITY OF SOIL REFERENCE MATERIALS

S. No.	Name of the Agency	Soil Reference Materials Available
1.	International Atomic Energy Agency, (IAEA) Wagramer Strasse 5, P.O. Box 100, A-1400 Vienna, Austria	IAEA-SOIL-7 - Soil – Trace elements IAEA-326 - Soil – Radionuclides IAEA-327 - Soil – Radionuclides IAEA-312 - Soil – Radium-226 IAEA-375 - Soil – Radioactive isotopes IAEA-SOIL-6 - Soil – Radioactive isotopes
2.	Institute for Reference Materials and Measurements (IRMM) Retieseweg, B-2440 Geel, Belgium Phone +32(0)14 571-272 Fax +32(0)14 584-273 E-mail <a href="mailto:doris.florian@irmm.jrc.be">doris.florian@irmm.jrc.be</a>	BCR-141-143 Toxic metals BCR-690 Rare earth metals CRM -143R Major and trace elements CRM - 524 PAHs CRM - 529, 530 PCDDs and PCDFs CRM - 143 R Major and trace elements CRM - 483, 484 Extractable trace elements
3.	Federal Institute of Material Research (BAM), D-12200, Berlin Phone +49-30-81 04-0 and heavy metals Fax +49-30-8 11 20 29 E-mail <a href="mailto:info@bam.de">info@bam.de</a>	BAM CRM 5001 Organochlorines Pesticides BAM CRM 2001 Pentachlorophenols and heavy metals
4.	Laboratory of Government Chemists (LGC), Queens Road Middlesex TW11 0LY Phone +44 (0)20 8943 7000 Fax: +44 (0)20 8943 2767 E mail <a href="mailto:info@lgc.co.uk">info@lgc.co.uk</a>	LGC6138(RM) - Contaminants LGC6144 - Contaminants LGC6135 - Leachable and total metals LGC6141(RM) - Extractable metals LGC6113(RM) - PCBs
5.	National Institute of Standards and Technology (NIST) Gaithersburg, MD 20899 Phone : +1 301 975 6439 Fax: + 1 301 948 3825 E mail: <a href="mailto:srminfo@nist.gov">srminfo@nist.gov</a>	SRM2710 - Trace and constituent elements (highly elevated) SRM2711 - Trace and constituent elements (intermediate levels) SRM2709 -Trace and constituent elements (low levels) SRM4353a - Flats soil No. 2 - In prep SRM4355 - Radioactivity
6.	National Research Centre for Certified Reference Materials (NRCCRM) No. 7 District 11, CN-100013, Beijing, China Phone : +86 10 4213149 Fax: + 86 10 4228404 E mail: <a href="mailto:nrccrm@public3.bta.net.cn">nrccrm@public3.bta.net.cn</a>	GBW07402 - Composition including trace elements GBW07403 - Composition including trace elements GBW07404 - Composition including trace elements GBW07405 - Composition including trace elements GBW07406 - Composition including trace elements GBW07407 - Composition including trace elements GBW07408 - Composition including trace elements GBW07409 - Composition including trace elements GBW07410 - Composition including trace elements GBW07411 - Composition including trace elements GBW08302 - Trace elements GBW07418 - Composition including trace elements GBW07419 - Composition including trace elements

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		GBW07420 - Composition including trace elements
		GBW07421 - Composition including trace elements
		GBW07422 - Composition including trace elements
		GBW07412/500 - Available nutrients
		GBW07412/1000 - Available nutrients
		GBW07413/500 - Available nutrients
		GBW07413/1000 - Available nutrients
		GBW07414/500 - Available nutrients
		GBW07414/1000 - Available nutrients
		GBW07415/500 - Available nutrients
		GBW07415/1000 - Available nutrients
		GBW07416/500 - Available nutrients
		GBW07416/1000 - Available nutrients
		GBW07417/500 - Available nutrients
		GBW07417/1000 - Available nutrients
		GBW07401/ 07411-Composition including trace elements
		GBW08303 - Trace elements
7.	Slovak Institute of Metrology (SMI) Dept. of Measurements in Chemistry, Karloveska, Bratislava Slovakia E.mail: <a href="mailto:info@smi.cz">info@smi.cz</a>	CMI7001 - Trace elements CMI7002 - Trace elements CMI7003 - Trace elements CMI7004 - Metals

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Note: All the above mentioned soil reference materials can also be purchased from LGC.

## Annex E

### CHECKLIST FOR SYSTEMATIC SAMPLING

#### Calculation Checklist for IAEA's Soil Sampling Advisor (ISSA)

1. Are your decisions based on authoritative sampling and analysis?

Yes. Enter the number of samples you will take and go to Number 9.

No, they are based on probabilistic sampling and analysis.

2. List the overall (sampling + analysis) confidence level from Segment 1 of ISSA

3. How many different methods are needed?

4. A. How many statistical samples are needed?

Calculate statistical samples for each matrix and method based on the average estimated concentration of the analytes with the lowest probable concentrations, minimum acceptable tolerable error, and the estimated precision of the method with that matrix and analyte using *DQO-PRO's EnviroCalc* for this calculation.

If the precision values are only available for the analytical errors (i.e. they do not contain sampling component errors) then use advice in ISSA's Explanation Box to estimate sampling precision.

4. B. What is the cost of each analysis?

Multiply the cost of each analysis by the number of site samples.

5. A. How many systematic samples are needed?

Calculate systematic samples for each method based on the minimum size of a contaminated area that is acceptable to be missed, the minimum acceptable probability of missing it, and the size of the site area. *HotSpot-Calc* will be used for this calculation.

How many depth layers will be sampled? If only the surface will be sampled then enter "1" on this line.

If systematic samples will be taken at various depths multiply the number of samples above by the number of depth layers to obtain the total number of systematic samples needed.

5. B. What is the cost of each analysis?

Multiply the cost of each analysis by the number of site samples.

6. A. How many method blanks will be needed for false positives?

Calculate the number of method blanks from the maximum tolerable rate error, the desired minimum confidence level, and the maximum tolerable number of false positives in the data pool.

*Success-Calc* will be used for this calculation.

B. What is the cost of each analysis?

Multiply the cost of each analysis by the number of site samples.

7 A. How many method spikes will be needed for false negatives?

Calculate the number of method spikes from the maximum tolerable rate error, the desired minimum confidence level, and the maximum tolerable number of false negatives in the data pool.

*Success-Calc* will be used for this calculation.

B. What is the cost of each analysis?

Multiply the cost of each analysis by the number of site samples.

8. How many other types of QC samples will be needed (answer from Segment 1 of ISSA)?

List each type of QC sample that will be needed:

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QC samples needed for procedural bias: \_\_\_\_\_

QC samples needed for contamination bias: \_\_\_\_\_

QC samples needed for each kind of precision \_\_\_\_\_

9. What is the cost of sampling and analysis?

Multiply the cost of each analysis by the number of site and QC samples.



10. Is the cost of sampling and analysis less than the budget?

If yes, then you are finished.

If no, then decide whether to lower confidence levels, find less expensive methods, or increase the budget.

If lower confidence levels are selected, recalculate numbers of samples needed.

If different methods are selected, recalculate numbers of samples needed based on new values for detection and quantification levels.