Sampling strategies for contaminated brownfield sites

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Abstract. Brownfield sites often require a geochemical survey to assess the extent of contamination that is present as a result of previous industrial activities. These measurements are subsequently assessed to ascertain whether the site presents the possibility of causing significant harm to those who may use the site for specified purposes. The measurement process comprises both field sampling and chemical analysis, with sampling being of crucial importance, since previous studies have repeatedly shown that it is the sampling phase that generates the highest component of uncertainty. A variety of methods are currently available for sampling brownfield sites, such as different sampling patterns and the choice of depth and mass recovered. An investigator may also choose to employ more innovative sampling methods, such as in situ measurement strategies that can significantly reduce the overall time taken to complete the survey. The general aim of a sampling strategy is to take representative samples for chemical analysis, although this is rarely achieved due to the inherent heterogeneity of contaminants within any given site. Since it is practically impossible to sample an entire site, and thus achieve a truly representative sample, it is becoming increasingly understood that the uncertainty of the measurements should be estimated, to provide a more reliable interpretation of the survey. Various methods are currently available to estimate the measurement uncertainty that arises from both sampling and analysis, which vary in terms of complexity and cost. The level of uncertainty estimated during a site investigation should also be judged on its fitness-for-purpose (i.e. whether subsequent decisions based upon it are acceptable). The 'optimized contaminated land investigation' (OCLI) method is a new approach that can be used to balance the site-specific variables of any given investigation, such as the measurement costs against the level of uncertainty and costs that may arise from misclassification. This provides an objective and traceable judgement of whether the measurements are fit-for-purpose.

Keywords: Sampling, brownfield site, measurement uncertainty, fitness-for-purpose, contaminated soil

INTRODUCTION

The term ‘brownfield site’ has been defined in the USA as ‘real property, the expansion, redevelopment, or reuse of which may be complicated by the presence or potential presence of a hazardous substance, pollutant, or contaminants’ (United States Environmental Protection Agency 2004). In the UK, a brownfield site has been defined as ‘any land or premises which has previously been used or developed and is not currently fully in use, although it may be partially occupied or utilized. It may also be vacant, derelict or contaminated. Therefore a brownfield site is not necessarily available for immediate use without intervention’ (Alker et al. 2000). Land classified as a brownfield site does not indicate that it is contaminated per se; it is likely however, that a site investigation will be required to assess whether hazards are present and whether they pose a risk of significant harm. A key component in the assessment of the hazard concentration is the field sampling, where traditionally, samples are removed from selected locations and sent for chemical analysis to an external laboratory. Sampling in this context has been defined as ‘methods and techniques used to obtain a representative sample of the material under investigation’ (British Standards Institution 1999). The ability to obtain a truly representative sample is often limited by spatial variability in the range and extent of contaminants present at a site. It has been observed that ‘almost everything that is worth analysing is actually or potentially heterogeneous’ and ‘any sample is likely to have a composition that is different from the mean composition of the target [i.e. the site] and no two samples will have the same composition’ (Thompson 1996).

A practical consequence of this heterogeneity for most contaminated sites is that a duplicate sample, which is taken in close proximity to the original at the same nominal sampling location, might differ in contaminant concentration by a factor of ten or more. Indeed, it might be argued that a representative sample can only be achieved if the entire site is sampled, which clearly cannot be financially justified. Therefore, the choice of sampling design employed at a site, such as the number of samples, the depth and mass of the sample and the sampling pattern, will determine the degree of representativeness.

One important question might be ‘how representative is the sample that has been taken and analysed as a result of
a particular sampling design? This is approximately equivalent to asking 'what is the uncertainty associated with the measurements?' Measurement uncertainty has been defined (International Standards Organization 1993) as 'an estimate attached to a test result which characterizes the range of values within which the true value is asserted to lie.' Developers of brownfield sites and regulators would like to know the 'true' value of contaminant concentration. Given that this is not practically possible, it is therefore essential that the uncertainty of the measurement (i.e. the range in which the 'true' value lies) is estimated.

The judgement of measurement uncertainty has often mistakenly been restricted only to the chemical analysis that is performed upon the sample once it has been delivered to the laboratory. It is often assumed that using more precise analytical methods will ensure more reliable measurements (i.e. with lower uncertainty), upon which to base subsequent decisions. This is despite the adage that a measurement is only as good as the sample upon which it is made. Recent evidence indicates that the precision of 'very different' analytical methods contributes no more than 5% of the total measurement variation because of the limiting effect of contaminant heterogeneity within the topsoil (Crumbling et al. 2003). Other studies have shown that uncertainty generated by the sampling phase can generate measurement uncertainties of greater than 50% of the concentration value (Ramsey & Argyraki 1997).

The uncertainties generated by the primary sampling phase are especially important when considering the financial penalties that might arise as a consequence. For example, a site might be unnecessarily remediated following a site investigation due to a 'false-positive' misclassification. This occurs if an area of land is classified as 'not contaminated' when it is actually contaminated. Alternatively, failure to identify contamination, known as a 'false-negative' misclassification, might lead to substantial financial penalties running to millions of pounds, such as those due to subsequent litigation or from extra delays in site redevelopment.

The sampling phase of a site investigation, therefore, forms an important part of the characterization of the hazards that may be present. The main objective of this paper is to present the current approaches to sampling at potentially contaminated brownfield sites. The major sampling techniques that are used to assess pollutant hazard will be discussed with an overview of the more innovative methods of sampling, such as those used in conjunction with in situ measurement methods. The final section of the paper provides methods both for the estimation of measurement uncertainty that arises from sampling, and for the assessment of whether the measurements are fit-for-purpose based upon their uncertainty.

THE CONCEPTUAL SITE MODEL

Prior to sampling, the construction of an initial 'conceptual site model' is essential. The initial conceptual site model is created during a 'desk-top study' of the site using a variety of sources, which include: the site-use history; the geological, geochemical, hydrological, hydrogeological, archaeological and ecological setting of the site; and information provided by any previous site investigations. A site 'walkover' might also be conducted at this stage to inspect for any visual indicators of contamination, such as soil discoloration or lack or vegetation. Physical characteristics that might influence the subsequent sampling strategy, such as the presence of fencing, buildings and/or footings, may also be recorded. The conceptual site model is continually updated as additional information becomes available throughout the site characterization.

The information collected for the initial conceptual site model is also useful for assessing the pollutant linkages that are relevant to the site (Environment Agency UK 2000), that is, to develop a preliminary site risk assessment. The initial conceptual site model should consider whether any pathways exist between the contaminants and the potential receptors. This model, in conjunction with the risk assessment, drives the subsequent sampling strategy. The conceptual site model may also indicate which environmental medium needs to be sampled. If, for example, the risk assessment shows that human consumption of vegetables is the main exposure route (e.g. for cadmium), then analysis of vegetable matter may be more important than the sampling of soil alone. Similarly, if the main exposure route is via groundwater consumption, then the sampling of the groundwater at various depths may be essential. The end-use of the site, and its associated risk model, is therefore also important for the design of sampling strategies. This paper concentrates on sampling soil as an example, but the principles can be applied equally to the sampling of any other medium (e.g. herbage, groundwater or gaseous emissions).

SAMPLING STRATEGIES

Multi-staged sampling

The sampling strategy may involve a series of phased sampling surveys to satisfy all of the investigation objectives. An exploratory site investigation usually consists of a limited number of samples taken in sub-areas of the site where contamination is suspected, and may be implemented to validate the initial conceptual site model. The main site investigation is likely to contain the largest number of samples and aims to obtain all the information necessary for the assessment of contaminant concentration across the site. Supplementary sampling aims to produce more detailed information using a 'targeted' or 'judgemental' approach and may be applied if additional site information is required, such as the spatial delineation of a contaminant 'hotspot' discovered during the main investigation.

Judgemental sampling

Judgemental (or 'targeted') sampling strategies are designed using the information contained within the conceptual site model. For example, the number of sample locations may be increased within a particular sub-area of a site if there is historical evidence of a contamination event occurring there. Judgemental sampling may also be applied when
there are visible indications of contamination on the site, such as areas of soil discoloration or a lack of vegetation. Targeted sampling might be applied if the sampling protocol aims to assess the risk to human health posed by the contamination. If the main pathway of contamination is judged to be ingestion, for example, then the surface of the topsoil might be sampled in preference to the subsoil.

Variable density sampling. The term sampling pattern is used here to describe the spatial positioning of sampling locations in relation to each other. Variable density is one example of a judgemental sampling pattern. The variable density pattern allocates a different number of sample locations to each particular sub-area or ‘stratum’ within a site, by consideration of the expectation that the sub-area is contaminated (Figure 1). This variable density, or ‘stratified’ design, can employ a variety of different sampling patterns.

The main advantages of judgemental sampling strategies are that they have the potential to produce site-specific, spatially resolved information (British Standards Institution 2001) and are recognized as a cost-effective and time-saving approach (Environment Agency UK 2000). One disadvantage of using a judgemental strategy is that it is only as effective as the prior information upon which it is based. The conceptual model or previous site investigation may not have indicated the possibility of contamination if there is no prior evidence. The results of judgemental sampling will, therefore, tend to confirm the shortcomings of the model.

Non-judgemental sampling
Alternatively, non-judgemental strategies can be used if there is a lack of reliable information contained within the conceptual site model. The British Standards Institution (2001) suggests that non-judgemental sampling patterns should consist of a regular grid of sample locations (Figure 2).

Regular grid sampling pattern. The reasons given by the British Standard for selecting a regular grid (Figure 2) are that (i) the reliability of interpolation declines sharply as distance between locations increases, (ii) sampling locations are much easier to locate in the field, (iii) the detection of areas of contamination is simplified, and (iv) the design of further investigation is easier. One guide (International Standards Organization 2002) also comments that data from different stages of investigation, using a regular grid, can be readily correlated. The spacing between locations in a regular grid can vary between 50 m to 100 m for exploratory investigations and 20 m to 25 m for main investigations. If heterogeneous contamination is suspected, for example at a former gasworks, then 10 m spacing might be required (British Standards Institution 2001). A disadvantage of the regular grid pattern as compared to a herringbone pattern (Figure 3) is that it has a much-reduced ability to detect elongated sub-areas of contamination that happen to be parallel to the grid direction.

Herringbone sampling pattern. The herringbone pattern (Figure 3) has been shown theoretically, by computer simulation, to be the most effective strategy for locating a spatially coherent sub-area of increased contaminant concentration, or ‘hotspot’, for a given number of sampling locations. The herringbone pattern can be considered as related to a regular grid (Figure 2) in which alternate sampling locations are offset by one-quarter of the grid spacing.

The optimal number of sample locations is calculated by estimating the shape and size of a hotspot (for 95% probability) and is given (Ferguson 1993; Department of the Environment 1994) as:

\[
  n = k(A/a)
\]

where: \( n \) = the number of sampling points; \( A \) = the total site area; \( a \) = the hot-spot area; and \( k \) = the ‘shape constant’, which is 1.08 for a circular hotspot, 1.25 for plume-shaped hotspot and 1.80 for an elliptical one (aspect ratio 4:1 orientated at 0° or 90° to the grid).

This model (equation 1) predicts that the investigator can detect a contaminant hotspot with a high probability (95% confidence) when using the specified number of sampling locations. The application of the model is,
however, based upon the investigator’s prior belief in the hotspot’s shape, size, consistency and orientation, which cannot be exactly known beforehand. The physical characteristics of any hotspot may not be as well defined as the model expects, and may contain high levels of heterogeneity or smeared edges, for example. Furthermore, it is also possible that a hotspot does not actually exist at the site. The number of sampling locations calculated to locate a hotspot also does not consider the consequent cost of sampling or the inevitable uncertainty in the individual measurements.

Random sampling patterns. Another non-judgemental design is the random sampling pattern that distributes the sampling locations randomly across the site so that ‘any portion of the population has an equal (or known) chance of being chosen’ (Horwitz 1990). One possible example of a random sampling pattern is shown in Figure 4.

The random sampling pattern has been described as the most statistically sound approach; if executed correctly, it produces, on average, a representative (unbiased) sample (Thompson & Ramsey 1995). It has also been stated that to achieve representative sampling, one simply needs to take random samples (Myers 1997). While this might be true from a purely statistical viewpoint, one of the main problems associated with utilizing a random sampling pattern for the investigation of contaminated land is that it produces some sample locations that are too close to each other. This tends to give redundant information and the approach is therefore wasteful of resources (United States Environmental Protection Agency 1989), while other sub-areas of the site remain poorly characterized. Another practical limitation of random sampling designs is that on-site construction of the pattern is difficult and time-consuming, especially if the site is heavily vegetated or the surface is particularly uneven. A more practical alternative is to use a stratified random sampling pattern in which the coordinates of each individual location are selected randomly, within the squares of a regular grid (Figure 5).

Depth and mass of sampling
The choice of sampling depth is likely to be based upon the conceptual site model, such as the suspected depth of contamination, soil characteristics, or the risk assessment model. For example, if the pathway of contamination is judged to be indirect ingestion of soil by children using private gardens, it follows that the upper, contactable layer of topsoil should be sampled to assess exposure. A greater depth of soil might need to be sampled subsequently to determine the depth at which any subsequent remediation is conducted. Sampling of soil might also be conducted at a variety of depths to assess the vertical distribution, and perhaps previous mobility, of contaminants. A variety of intrusive sampling devices can be used which will determine both the depth and mass of sample taken (British Standards Institution 2001).

Sample mass. The choice of sample mass is important because it limits how representative the sample is at a particular sampling location. The mass may also affect the extent of sampling uncertainty, which is predicted to be inversely proportional to the square root of sample mass (equation 2). This relationship is important, because sampling uncertainty is predominately generated by the inherent heterogeneity of the contaminants at the location. Gy’s sampling equation (Gy 1979) indicates a proportionality where sampling variance ($s_{\text{samp}}^2$) can be reduced by increasing the sample mass:

$$s_{\text{samp}}^2 \propto 1/\text{mass}$$

For example, increasing the sample mass by a factor of two is predicted to reduce the sampling standard deviation by a factor of $\sqrt{2}$ (i.e. by a factor of 1.4). Interestingly, this relationship (equation 2) was initially demonstrated for sampling of coal (Bailey 1909).

Composite sampling
A sample increment has been defined as ‘a quantity of material taken at one time by one action from a larger body of material’ (International Standards Organization 1993). Sample increments are usually grouped together to form a composite sample which has been defined as ‘two or more increments/subsamples mixed together in appropriate

![Figure 4. A random sampling pattern, where the sampling locations are positioned randomly across the site.](image)

![Figure 5. The stratified random pattern indicates that the each sampling location is randomly distributed within each square of a regular grid.](image)
proportions, either discretely or continuously (blended composite sample), from which the average value of a desired characteristic may be obtained’ (British Standards Institution 2001). For example, the British Standards Institution (2001) in its Code of Practise for the ‘Investigation of potentially contaminated sites’ (2001) gives informative guidance for the ‘collection of a representative sample’ using a ‘nine-point sample’ (Figure 6). The investigator is directed to employ the nine-point sampling pattern when the material to be sampled is not homogeneous, or the material could be subject to local variation.

The collection of a ‘representative’ sample by the nine-point method involves taking nine increments that ‘are related to the points of a compass with an increment at the centre’ (Figure 6) and combining them to form one single sample. In a recent study, the removal of a five-fold composite sample at each location during a contaminated land investigation (Ramsey & Argyraki 1997) was seen to reduce the sampling variance by approximately $\sqrt{5}$, as predicted in equation (2) by Gy (1979).

The British Standard discourages the use of composite sampling from samples collected across a site at sample locations at distances that exceed those given for the nine-point sample. This is because of (i) the difficulty of comparing data with guideline threshold concentrations that relate to spot samples, (ii) the possibility of disguising isolated locations of high concentration by mixing with samples of lower concentration, (iii) the possibility of loss of volatile compounds during the compositing processes, and (iv) the difficulty of achieving an adequately mixed and representative sample.

Cost of sampling and acquiring spatially resolved information of contaminant concentration

The United States Environmental Protection Agency (USEPA) has recognized (Crumbling 2001) that there should be a balance between the resources spent on achieving an acceptable level of measurement quality (e.g. uncertainty) and the extent of spatial site information (e.g. the number of sampling locations). For example, allocating resources to a more accurate but more expensive measurement strategy might result in fewer sampling locations being investigated and hence less site information being gained (Figure 7). Alternatively, reducing the expenditure on each measurement could allow more samples to be taken across the site and gaining more site information. This approach can then improve cost effectiveness of the subsequent remediation. It has been demonstrated that allocating more financial resources for a more comprehensive site survey (e.g. more sampling locations) saved £870 000 (net) from the original remediation budget in the UK (Finnamore et al. 2000).

Chemical analyses of contaminant concentration

An extensive range of analytical methods is currently available for measuring the concentration of environmental contaminants. Traditionally, samples are removed from the site by what is known as ‘intrusive sampling’ and placed into suitable containers for transportation to an external laboratory for ‘ex situ’ chemical analyses. The samples are usually ground and homogenized prior to chemical analysis to minimize the effect of within-sample heterogeneity and enable subsampling. In order to increase ‘sample throughput rate’ (i.e. the time taken from field sampling to chemical analysis and data interpretation), the use of on-site (e.g. mobile) laboratories is advised as part of the USEPA’s current guidance on employing ‘dynamic workplans’ (Robbat 1997). The use of in situ (i.e. in the sample’s original place) or ‘field based’ measurement technologies to characterize contaminated land has several advantages and is becoming increasingly widespread.

In situ measurement of contamination

One significant advantage of in situ measurements is that they produce ‘real-time’ analysis of contaminant concentration. The desire to have quicker, and therefore more cost-effective, site characterization coupled with technological improvements has resulted in an increasingly widespread use of in situ measurement techniques. One such technique that is becoming popular for contaminated land investigations is in situ portable X-ray fluorescence.

In situ portable X-ray fluorescence spectrometry (PXRF). This has been demonstrated as an effective approach for measuring some forms of inorganic contamination as part of several published contaminated land investigations (Argyraki et al. 1997; Kalnicky & Singhvi 2001). X-ray fluorescence spectrometry detects the

![Figure 6. ‘Nine-point sampling pattern’ for the investigation of potentially contaminated sites (based upon British Standard Code of Practise 2001). The recommended distance between sample increments (arrows) is less than or equal to 1 metre.](image)
emission of X-rays from excited analyte atoms produced by high-energy electrons or a primary beam of other X-rays. The fluorescent wavelengths are indicative of individual elements and their intensity estimates the concentration of analyte atoms that are present within a shallow depth of the analysed sample (<5 mm).

One disadvantage of in situ measurements is that they tend to generate greater uncertainty than traditional ex situ techniques, predominately due to the smaller sample mass that is analysed. The difference between the analytical uncertainty generated by traditional ex situ and in situ techniques is, however, often overwhelmed by the effect of contaminant heterogeneity (e.g. the sampling uncertainty). Several methods can be applied to sample locations prior to the in situ measurements made by PXRF, such as removing loose stones and organic matter, homogenizing the soil and allowing the sample location to dry. Since PXRF analyses only the upper layer of the soil, it may be necessary to assess whether the extent of contamination differs substantially with depth. A previous study tested this hypothesis by measuring a soil core that was removed and showed that the results were not biased due to vertical variation in contamination (Argyraki et al. 1997). These findings may not be the case at other sites, and sampling at a variety of depths by PXRF may be required to establish the change in contamination with depth. Since this approach is likely to take additional time, negating one of the main advantages of in situ PXRF, it may be prudent to assess the variation of contaminant concentration with depth at only a selected proportion of sampling locations.

Another limitation of PXRF is that the current detection limits for certain elements may be too high for certain site investigations (e.g. total Cr = 1080 μg g⁻¹ for a 200 s count time). The presence of water within the topsoil sample can also cause a negative measurement 'bias' (Potts et al. 2002). The measurements can be corrected for this systematic error by assessing the water content of the topsoil. This value can be assessed either by a field moisture probe or by removing samples to be oven dried and re-weighed. A measurement of contaminant concentration in topsoil of 50 μg g⁻¹ can be adjusted for, say, 17% water content, by applying a correction factor of 1.20 (e.g. 50 / 0.83 = 60.24 μg g⁻¹). The irregularity of the sample surface can also cause scattering of the fluorescent X-rays, although a Rayleigh scatter correction can be applied to allow for this (Potts 1987). Sample preparation methods have been suggested to reduce the measurement error from surface irregularities, which include raking or sieving the sample area to reduce the effect of small-scale heterogeneity, compacting the soil to reduce the effect of soil surface irregularities, and removing any organic debris.

One important advantage of in situ PXRF is that it enables a rapid interpretation of the data, within minutes, which in turn allows further measurements to be taken quickly during the same site visit. These can often be of an ‘iterative’ sampling design that can focus on the delineation of contaminant hotspots that has been discovered during the initial survey. The potential reduction in overall time to complete a site survey enabled by in situ PXRF can easily be justified when costly delays in site development are thereby avoided. For example, a traditional site investigation may require several weeks before the results of the laboratory analysis are provided and a supplementary sampling survey can be completed.

**ESTIMATION OF MEASUREMENT UNCERTAINTY**

Applying a standard sampling protocol at every site does not guarantee representative samples or that all of the investigation objectives will be met, nor does it account for the site-specific geochemistry. In fact, the variety of methods that can be applied to characterize a potentially contaminated site reflects the site-specific nature of most investigations. Given the variation in sampling methods, and also the difficulty in acquiring a sample that is truly representative, it is important to estimate the uncertainty of the measurements. An estimate of measurement uncertainty will provide greater reliability in the interpretation of the measurements and reduce the likelihood of misclassification of the site. The measurements of contamination are usually compared against a national regulatory threshold value, such as a soil guideline value (SGV) in the UK. This comparison will largely determine any subsequent courses of action, such as whether further sampling, risk assessment or remedial action is warranted.
Two approaches can be used to allow for uncertainty in the comparison of measured concentrations values against a regulatory threshold. All of the measurements within a ‘decision area’ can be combined and the uncertainty on the mean concentration allowed for (DEFRA 2002). The 95th percentile of the uncertainty on the mean value is compared against the SGV for classification of the averaging area. Alternatively, the uncertainty on each individual measurement can be considered, in order to classify the soil for each sampling location (Figure 8).

Various methods are available for the estimation of measurement uncertainty, which vary in complexity and practicality; these are detailed elsewhere (Ramsey & Argyraki 1997). Perhaps the simplest and least expensive method implements the ‘duplicate method’ at some sampling locations (Figure 9). The duplicate method involves taking duplicate field samples, also known as ‘co-located’ samples by the USEPA (Figure 9). The duplicate samples (10% of total number of samples or \( n = \pm 8 \)) are taken at locations across the site in a random direction from the original sampling location. The duplicate samples are taken at a distance away from the original sampling location that represents the uncertainty of relocating the sampling location by the particular surveying technology used (typically 10% of the spacing between sample locations). For example, a sampling pattern using 20-m spacing might use a distance of 2 m for the collection of the duplicate. Both samples taken at each sampling location are analysed twice to estimate the analytical component of the uncertainty if required (Figure 9).

Analysis of variance statistics is used to separate the total variance into three components; sampling (\( s^2_{\text{samp}} \)), analysis (\( s^2_{\text{anal}} \)) and geochemical (\( s^2_{\text{geochem}} \)). The geochemical variance is due to variation in contaminant concentrations across the site (i.e. between sample locations).

Total variance (\( s^2_{\text{total}} \)) is calculated as:

\[
s^2_{\text{total}} = \sqrt{s^2_{\text{geochem}} + s^2_{\text{anal}} + s^2_{\text{samp}}} \tag{3}
\]

The measurement uncertainty (\( u \)) can be estimated by combining the analytical and sampling variance:

\[
u = s_{\text{meas}} = \sqrt{s^2_{\text{anal}} + s^2_{\text{samp}}} \tag{4}
\]

A confidence interval to the measurement uncertainty can be obtained by multiplying by a coverage factor (\( k \)) to give the expanded uncertainty (\( U \)):

\[
U = k u = 2 \times s_{\text{meas}} \quad \text{(for 95% confidence)} \tag{5}
\]

Expanded measurement uncertainty that is relative to the concentration (\( U\% \)) can be calculated by

\[
U\% = 200 \times \frac{s_{\text{meas}}}{\bar{x}} \quad \text{(for 95% confidence)} \tag{6}
\]

The calculation of relative uncertainty (equation 6) enables the uncertainty to be expressed as a percentage that is relative to each individual measured concentration, which can be used for a probabilistic classification (Figure 8). Further information regarding improving the reliability of contaminated land assessment using statistical methods and a comparison between the two approaches to handling uncertainty can be found elsewhere (CL:AIRE Technical Bulletin 2003).

**ASSESSMENT OF MEASUREMENT FITNESS-FOR-PURPOSE**

All measurements contain uncertainty and can only be considered as estimates of the ‘true’ analyte concentration. The uncertainty in individual measurements can never be entirely eliminated but can be reduced by implementing more stringent analytical methods or by increasing the sample mass (equation 2). A reduction in uncertainty, therefore, requires a corresponding increase in measurement expenditure. One important question is whether a particular level of uncertainty is acceptable for a particular objective. This is equivalent to questioning the ‘fitness-for-purpose’ (FFP) of the measurements. Currently, the judgement of measurement FFP is made by the analytical laboratory, based upon the results from the quality control solely on the analytical technique, for example, the monitoring certification scheme (MCERTS). This approach diminishes the importance of sampling variance, which is often the significant source of uncertainty. Sampling often generates up to 20 times more uncertainty than that

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**Figure 8.** Probabilistic classification of measurements, which allows for the estimated uncertainty (\( U \)) on either side of the measured concentration (\( c \)) to be compared against the threshold value.
generated by the analytical method, and can be significant for particularly heterogeneous sites (e.g. $U_{\text{amp}} = \pm 80\%$ of the measured concentration, at 95% confidence).

One example of a FFP criterion is that the measurement variance should not exceed 20% of the total variance. This is useful, but it does not explicitly address the issue of financial expenditure within contaminated land investigations that might constrain the purely scientific considerations. It is conceivable that a high level of uncertainty might be acceptable for some sites where the risk of exposure is low or when the site is of low financial value. Alternatively, a much lower level of uncertainty might be unacceptable at another site due to potential health affects and financial penalties that may arise from misclassification. The assessment of measurement FFP is currently often left to the subjective judgement of the investigator, which is not always scientifically traceable or defensible.

The optimized contaminated land investigation (OCLI) method is a recent innovative approach that provides a cost-based and objective estimation of measurement FFP. A full description of the OCLI method is given by Ramsey et al. (2002). The OCLI method is a statistical tool that balances the two main site-specific costs of any given investigation (i.e. the measurement expenditure and the potential cost arising from misclassification), using the estimated uncertainty, given a particular threshold value of contaminant concentration. The OCLI method provides the investigator with an ‘expectation of loss’ ($\ell$) for a range of uncertainty values, including the actual value estimated from the site investigation. The value of uncertainty that is likely to present the lowest expectation of loss value, known as the ‘optimal uncertainty’, can then be compared against the loss at a range of uncertainty values, including that at the actual uncertainty. A visual representation of the OCLI method, which allows for this comparison, is shown in Figure 10.

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CONCLUSIONS

Sampling is a crucial stage in the regeneration of a contaminated brownfield site because the decisions made following the site investigation are largely based upon the measured concentrations of contamination. Recent research has repeatedly shown that it is the sampling, and not the chemical analysis, that generates the greatest uncertainty. Failure to characterize a site correctly due to poor sampling can result in significant financial, and possibly health related, consequences.

Guidance for the sampling of contaminated land, such as British Standard 10175 (British Standards Institution 2001), aims to provide the investigator with a transparent and coherent sampling methodology. Generally, a site investigation is a phased process starting with the construction of a conceptual site model, which is based upon any existing site information. The sampling plan is designed to correspond with the conceptual model and to satisfy the objectives of the site investigation (i.e. the 'end-use' of the site). The sampling strategy will often be needed to provide information for an assessment of whether a significant risk is posed by the contamination. The conceptual model is continually updated as additional site information is obtained and guides any subsequent sampling conducted that may be conducted.

This paper has outlined some of the methods used for the sampling of contaminated land. It is unlikely, however, that most site investigations will employ the same methodology because each site will present site-specific characteristics and investigation objectives. It is also unlikely that a truly representative sample will ever be taken, regardless of the sampling strategy that is used. This is mostly because of the short-range contaminant heterogeneity, but also because of the finite time and financial resources available for a site investigation. Clearly, the entire site cannot be sampled to gain what would be a truly representative sample. Therefore, the measurement uncertainty should be estimated to provide the investigator with the opportunity to evaluate the measurements using a probabilistic approach which may reduce the likelihood of expensive misclassifications. The belief that only expensive chemical analysis will provide the 'true' contaminant concentration is becoming increasingly discredited. While good analytical methods are essential, a measurement can only be as good as the sample upon which it is based. The reluctance to acknowledge the importance of sampling and the difficulty in taking a representative sample have previously been due largely to the lack of practical methods with which to estimate and interpret the uncertainty that is always generated. This paper has shown that the ‘duplicate method’ can provide a simple and inexpensive method for the estimation of uncertainty. A cost-based assessment of the uncertainty can then be achieved by using the innovative OCLI method. The uncertainty estimates can also be fed through into the risk assessment to improve its reliability. As the contaminated land industry within the UK becomes more litigious, those willing to grasp the nettle of good sampling practise will be those most likely to succeed in providing more reliable site investigations of contaminated brownfield sites.

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