

PRACTICAL TIPS TO SHARE: IMPROVING RISK ASSESSMENT - FIELD TO DESK

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In June 2019 the Society of Brownfield Risk Assessment (SoBRA) and RemSoc delivered a conference targeted towards early careers learning. Its aims were:

- To support technical excellence in the assessment, estimation & evaluation of risks and associated uncertainties from land affected by contaminants;
- To encourage “good practice” in the practical application of risk assessment to support decisions regarding the appropriate management of land contamination; and
- To facilitate and widen access to the dissemination of knowledge regarding land contamination risk assessment.

A commitment of the early career workshops has been the creation of a series of short tabular reports for the different discipline areas to bring together the points discussed during the workshop sessions if attendees feel it would be beneficial. These reports aim to:

- Direct early career professionals to what is considered important;
- Provide clarity as change is often easier when we understand why we are doing it; and
- Focus on identifying small changes that are easy to deliver.

This report is neither intended to present prescriptive guidance nor be exhaustive in content. It is simply a distillation of the author’s experience and represents contributions from those that attended the workshop including the facilitators. It is shared with the intention of directing both field staff and risk assessors in their early careers towards some good practices, and helping them to avoid common mistakes. It presents work conducted by a volunteer.

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IMPROVING RISK ASSESSMENT - FIELD TO DESK

PRACTICAL TIPS	Descriptor
INITIAL CONSIDERATIONS	
<p><i>Start with the CSM</i></p>	<p>The Conceptual Site Model (CSM) is the basis for all risk assessment; the term Conceptual Model (CM) is also used in other guidance. The CSM is formulated during the preliminary risk assessment in order to identify the potential sources, pathways and receptors (S-P-R). The CSM is refined and revised with a better understanding of the site as more information is obtained to establish and assess pollutant linkages.</p> <p>The following questions should be addressed: have the migration and exposure pathways been properly defined? Are there pathways that are unlikely to be active that have been modelled or are there non-standard pathways that have been excluded from exposure estimates, for example; diffusion of hydrocarbons through plastic drinking water pipes or consumption of homegrown foodstuffs other than fruits and vegetables? Has the appropriate type of receptor been modelled? A site may not be a risk to a receptor in its existing use but where a development is proposed, there might be a possibility that significant contaminant linkages will be created as a result of its future use. It is therefore important that low risks identified at an early stage are not discounted entirely from the remainder of the risk assessment process.</p> <p>The initial development of an outline CSM is fundamental to the design of an appropriate sampling strategy. The purpose of the site investigation is to reduce the uncertainty in the CSM to an acceptable level for decision-making. The CSM integrates what is already known about the site and identifies both what still needs to be discovered and how that information should be used. Underpinning the site investigation, therefore, must be a clear set of aims and objectives.</p>
<p><i>Be clear of your objectives</i></p>	<p>The setting of appropriate, well defined and relevant objectives is critical to all stages of risk assessment. The objectives should be set before the strategy of the investigation is designed and implemented. Lack of precision and or/clarity in setting objectives will inevitably increase uncertainties. This can lead to inappropriate conclusions</p>



being drawn and recommendations for further work which later turn out to be inadequate or unnecessary i.e. an appropriately scoped Phase 1 would have negated the need for, or reduced the extent of, further phases of intrusive investigation.

Always have clear data quality objectives. It is important that the rationale for collecting samples is understood at this stage so data can be collected which is fit for purpose. Samples should be taken which will be of use in a risk assessment. For example: it may not be relevant to take samples for asbestos in deep natural strata for a site which is not being redeveloped and a surface or shallow sample in made ground would be more appropriate; only one or two monitoring wells in an aquifer is unlikely to provide enough information for a DQRA. Choose the laboratory test that is most appropriate for the risk assessment you intend to undertake.

Choosing the correct sampling strategies

Targeted sampling is based on prior information collected during the preliminary investigation (desk study/documentary research) and may be used to confirm if an area is or is not affected by land contamination. It aims to confirm the presence or absence of a particular contaminant linkage established in the initial development of the CSM. This approach allows specific horizons to be sampled such as discoloured layers or odorous material as well as pockets of distinct materials such as ash and clinker. It is therefore important the sample is recorded as being targeted.

Non-targeted sampling uses a statistical approach to cover the site. This is normally undertaken on a grid or consistent shape of variable dimension and spaces dependent on the level of confidence or reduction of uncertainty that is required. The herringbone pattern, which uses an offset regular grid, is statistically more likely to identify linear contamination in two dimensions than a square grid pattern. The reliability of interpolation between sampling locations declines significantly as distances increase. BS 10175 identifies typical recommended densities of sampling grids, depending on the nature of the site investigation. Further information is also included in BS ISO 18400-104 on sampling strategies. In practice the number of sampling locations is often a balance between a sampling strategy that is sufficiently robust to meet the technical and risk management objectives, and project duration and budget constraints.

The application of statistical tests (for example, calculating upper or lower confidence limits within the current CIEH/CL:AIRE Guidance on Comparing Soil Contamination with a Critical Concentration), are only valid in relation to unbiased (i.e. non-targeted) sample data. Consequently, data collected from targeted sampling cannot



be used in the application of statistics. At the time of writing (June 2020) revised statistics guidance is being developed which may lead to the CIEH/CL:AIRE guidance being withdrawn.

Quality Control samples

Quality control (QC) procedures which can be used to identify errors associated with sampling and analysis should always be considered. This should be conducted with regards to the choice of sampling technique(s), numbers and types of samples, training of staff as well as storage and preservation of samples. The approach taken should be documented and a suitable system of record keeping needs to be established.

There are a range of QC samples that can be collected, typically these will be: duplicate samples to check the precision of sampling; the use of field blank and trip blank samples to monitor the sources of sample contamination; less common, the use of spiked samples as quality controls to assess sample stability during transport and storage. When collecting field blank samples, the de-ionised water provided by the laboratory which has already been subjected to a large-scale programme of testing to assure its quality should be used. A different source of de-ionised water must not be used; a common mistake is testing Benzene, Ethylbenzene, Toluene, Xylenes (BTEX) from de-ionised water purchased from a petrol station forecourt shop.

Stop and Check

It is all too easy to forget the ultimate objective of a site investigation and get wrapped up in the detail of the immediate task in hand. It is important to continually remind yourself, especially as you pass from office to field, and field to lab etc., to revisit your conceptual model, update it and check you are getting data of sufficient quality (fit for purpose) to meet your objectives.

SOIL SAMPLING

Sampling considerations for contaminants in soil

The risk driving pathway for a contaminant is dependent on many interconnecting factors. It is important to understand what impact the combination of sampling technique and analytical method may have on the data and the subsequent risk assessment so that the right matrix is sampled and handled.

For example, the concentration of a contaminant in the fine particle size fraction (PM10) is especially relevant for those contaminants where the inhalation of dust is a risk driving pathway. Finer particle sizes are also particularly relevant for dermal contact and soil ingestion pathways as such particles more readily stick to skin and are inadvertently ingested, than stones. Filling a sample jar with a large quantity of gravel and stones will not therefore generate large quantities of the important fine fractions for the laboratory to analyse. In addition, the laboratory sample preparation method for a given analytical technique (e.g. sieving and crushing, or drying) must be



understood as it can impact how representative the sub-sample tested is of site conditions and/or the assumptions made in its use in subsequent risk assessment.

Unless specific procedures are followed, losses of VOCs (Volatile Organic Compounds) during soil sampling are likely to be significant and will result in a possible under-estimation of vapour risk (further information on taking soil samples for determination of VOCs is available within BS 10176). Where there is a significant risk of vapour intrusion identified in the outline CSM, concentrations in the vapour phase should be measured rather than modelling being used to assess the risk solely from soil or groundwater data (also see BS 8576).

Record all visual and olfactory observations

Field observations should always be undertaken, documented and assessed in conjunction with laboratory data; correlations made should be included in your report. Site investigations also need to be adaptive, based on field observations, by allowing an element of flexibility rather than collecting samples at predefined depths following a rigid sampling procedure or specification, to allow for conditions found on site.

Although not all contaminants are visible, the use of photography is a useful line of evidence. Photography is often a contractual requirement. Even where it is not, the collection of photographic records should be carried out.

CONTROLLED WATERS

Always develop a monitoring well post-installation

The aim of groundwater sampling is to obtain water samples that best represent undisturbed hydrogeological conditions. Adequate well development is important to minimise the biases in sampling, for example, by ensuring the water sampled is representative of site conditions. Excessive turbidity, which can be present if a well is not sufficiently developed, may alter water quality and result in erroneous chemical analysis. Following installation, each monitoring well should be developed to remove silt and other fine materials from the lining, gravel pack and surrounding strata. Cross-contamination might occur at the point of installation. Well development procedures that have the potential to significantly alter groundwater quality should not be used.

Well development should be undertaken as soon as possible after drilling and installation, although sufficient time will be required to allow bentonite seals to fully hydrate and cement grouts to cure. The use of an improper technique can introduce the risk of collapse/failure of the screen or casing and therefore development must be planned and undertaken carefully.



	<p>The rate of pumping should be greater than that typically required for purging a well. Pumping will mobilise water, any dissolved materials and some of the finer sediment particles introduced during drilling, and will draw them through the screen. The pump used must be capable of dealing with sediment-laden groundwater. Surging can be carried out in conjunction with pumping. A surge block is a seal that closely fits the installation and is operated like a plunger beneath water level. Surging must be carried out at a rate that will not damage the casing or the screen. Damage can occur if surging creates a strong suction.</p> <p>Well development should continue until there is consistency in the water quality – both visibly and through measurement of on-site parameters e.g. pH and Electrical Conductivity (EC). Sufficient time should be allowed for equilibrium with the groundwater to be reached, this could be up to 14 days.</p>
<p><i>Follow laboratory requirements for filtering and preservation of metals</i></p>	<p>Water samples required for dissolved metals analysis require on-site filtering and preservation. They should be acidified to prevent precipitation of metals. Once precipitation has occurred there is no way of knowing how much metal was in solution, or in suspension, at the time of sampling. The only way of resolving this is to filter out suspended metals in the field, placing the filtered sample in a dedicated nitric acid bottle in which all the metal is known to be dissolved at the time of sampling.</p> <p>Ferrous iron, once sampled, will generally oxidise to ferric iron and precipitate as ferric oxyhydroxide. Hydrochloric acid must be used in the field to fix the ratio of ferrous and ferric iron. Adding the acid in the laboratory is not an acceptable alternative, since the ferrous iron is highly likely to have oxidised in transit. Similarly, samples should be filtered for Mn(II) to remove insoluble Mn(IV) compounds before adding to a bottle containing hydrochloric acid. The acid prevents the oxidation of Mn(II) to insoluble Mn(IV).</p>
<p><i>Other analytes requiring chemical preservation</i></p>	<p>Samples for ammoniacal nitrogen should be preserved with sulphuric acid to fix the NH₃ and convert it to NH₄, so this is measured and expressed as ammoniacal nitrogen. For cyanide, sodium hydroxide is used to keep the water alkaline and cyanide in solution. If water is slightly acidic, the cyanide may convert to hydrogen cyanide gas. Sulphide oxidises to sulphate, it needs to be preserved in zinc acetate to fix the sample.</p>
<p><i>On-site measurement of groundwater and surface water quality</i></p>	<p>Certain water quality parameters should be measured on-site (e.g. pH, EC, dissolved oxygen, redox potential and temperature). This is because these analytes change significantly in contact with the atmosphere, are also used for operational reasons to understand the effectiveness of purging and well development, and can be used as a line of evidence in further risk assessment. These measurements should be undertaken downhole using in-</p>



	<p>situ probes or performed using a flow cell in which a continuous flow of groundwater is in contact with the water quality meter.</p>
<p>Measurement of Dissolved Oxygen (DO)</p>	<p>The concentration of oxygen within groundwater is one of the most important parameters measured in groundwater sampling. It provides a first pass screen to identify conditions that are favourable for biodegradation. However, dissolved oxygen is often a difficult field parameter to acquire. The dissolved oxygen probe must be calibrated at the start of each day. Furthermore, probes that work via oxygen diffusion across a membrane can rapidly become fouled if hydrocarbons are present at concentrations approaching their saturation limit. In such cases, optical DO probes may provide more reliable readings.</p>
<p>Measurement of Oxidation Reduction Potential (ORP)</p>	<p>ORP is an indicator of electron activity, and it indicates the relative tendency of a solution to transfer or accept electrons. As groundwater contains a mixture of lots of different oxidising and reducing agents all reacting with each other, ORP is a measure of the net effect of all those oxidation and reduction reactions at that moment in time.</p> <p>The difference between ORP and Eh is frequently misunderstood (Eh being the way in which redox potential is reported in the literature). In essence, the two parameters are the same in that both quantify the potential of the medium to transfer electrons, however, Eh values are measured using a standardised reference electrode, called the Standard Hydrogen Electrode (SHE).</p> <p>ORP as recorded in the field, is a much less specific term in which the measurement can be made relative to any practical reference electrode. This is because the Standard Hydrogen Electrode is not easy or practical to use in field measurements. Typically, silver/silver chloride electrodes are popular in multi-parameter water quality instrumentation because they are much more reliable. Saturated calomel reference electrodes are also frequently used.</p> <p>As reference electrodes other than the SHE are used in field kit, what is measured is termed ORP and not Eh. Therefore, before any comparisons of data to redox potential values reported as Eh are undertaken, a correction factor must be applied to convert the data. Consultation with the instrument manufacturer is required to ensure the appropriate correction factor is applied.</p>
<p>Sampling VOCs in groundwater and surface water</p>	<p>Samples should be collected in 40ml glass vials with a septa cap. The samples should be taken with as little agitation or disturbance as possible. The vial should be filled so that there is a meniscus at the top and no bubbles or headspace should be present in the vial after it is capped. After the cap is securely tightened, the vial should be inverted and tapped to see if any undetected bubbles are dislodged. If a headspace is present, the vial should</p>



be topped off using a minimal amount of sample to re-establish the meniscus. If, after capping the vial, bubbles are still present, a new vial should be obtained and the sample re-collected. If samples are submitted for VOCs with a bubble, the analysis might be compromised as volatiles can preferentially migrate into the headspace.

GROUND GAS AND VAPOUR

Hydrocarbons can affect methane concentrations measured in the field by gas analysers

Methane is measured in the infra-red spectrum by gas analysers. They are calibrated using mixtures which give accurate readings providing there are no other hydrocarbons present. If other hydrocarbons are present, the methane reading will show a positive bias. The extent to which the methane reading is affected tends to be non-linear. Manufacturers supply filters which can reduce these cross-gas effects although they might not be effective in all situations. Samples should be collected and submitted to a laboratory and scheduled for permanent gas analysis if there are concerns that other hydrocarbons are interfering with the field results.

Correct use of Photoionisation Detectors

The Photoionisation Detector (PID) is a useful non-selective screening tool for VOCs. PIDs can detect a broad range of organic compounds including BTEX, ketones and aldehydes but also have a limited response to ammonia and other inorganic contaminants.

When using a PID, the correct lamp for the VOCs that are likely to be contaminants of concern should be used. The energy of the photons produced by the ultra violet (UV) lamp determines whether a specific chemical is detectable. If the ionisation potential of the contaminant is less than the electron volts (eV) output of the UV lamp, the contaminant will be ionised and detected by the PID. The standard lamp provided with most PIDs is 10.6 eV. This lamp will not detect dichloromethane or carbon tetrachloride, for example, which requires an 11.7 eV lamp. Higher energy lamps are subject to more physical limitations. In general, the higher the lamp energy the shorter the service life. The 11.7 eV lamp is less stable and deteriorates quickly. The 10.6 eV lamp will typically last two years depending on use and how well maintained it is, whereas an 11.7 eV lamp might only last 2-4 weeks. As a consequence, 10.6 eV lamps tend to be used by most of the instrument manufacturers.

PID manufacturers determine correction factors or response factors by measuring a PIDs response to a known concentration of a target gas, typically isobutylene. Correction factors tend to be instrument and/or manufacturer specific. Isobutylene is used because its responsiveness is about midpoint in the range of sensitivity of PIDs. No matter how comprehensive the list of correction factors, choosing the correction factor for the VOC never makes the reading exclusive or substance-specific. If the specific nature of the VOC or mix of VOCs is not known,



	<p>PID readings are not truly quantified. Unless the precise nature of the VOCs measured can be determined, readings should be thought of as “isobutylene units” or whatever measurement scale has been selected from the instrument’s library of correction factors.</p> <p>PID are susceptible to moisture and humidity. Water molecules can absorb UV light without becoming ionised and affect the performance of the PID. If an instrument is stored overnight in a vehicle or on-site in an unheated building it will take longer to warm up. If the moisture condenses inside the unit, a PID can give erratic, unstable or false readings.</p> <p>High concentrations of methane can quench the PID signal. Methane molecules are also capable of absorbing UV light. Because the UV photons are absorbed with the methane being ionised, the presence of high concentrations can reduce the ability of the PID to detect VOCs that are present at the same time. Where elevated concentrations are expected, methane should be measured in conjunction with measurements made with a PID. An assessment should then be made on the effect this had on the PID readings.</p>
<i>Use of appropriate vapour sampling techniques</i>	<p>Vapour sampling requires the use of silonite canisters or thermal desorption tubes. Tedlar bags and Gresham cylinders are not suitable for sampling VOCs because many of the target compounds are not stable in these environments. Gresham cylinders are simply a steel or aluminium tube with no passivated coating so are not suited to volatile analytes. Samples collected in Tedlar bags have very short holding times (48 hours or less) and analysis will have higher detection limits. VOCs can permeate the bag, in addition these bags are fragile and easily punctured.</p>
<i>Shut-in tests for canisters</i>	<p>The shut-in test is carried out to create a closed system between the canister, gauge and flow regulator to determine any loose connections in the sampling system prior to sample collection. The procedure consists of assembling the canisters, regulators and sample train and momentarily opening and shutting the valve in a clean area. Vacuum pressures on the regulator’s gauge are recorded and monitored. After the shut-in test has been validated, the sampling train should not be altered. If the shut-in test failed then specific measures are needed such as tightening all the fittings and repeating the test until it is validated before proceeding to the shroud/tracer test.</p>
<i>Consider the type of tracer gas used for well integrity tests</i>	<p>A tracer is used to test for an ambient air leakage into the sample system and monitoring well. The selection of leak detection compounds is site and analysis specific. Considerations include whether it is a known contaminant at the site or included in the laboratory’s list of analytes and whether it can be monitored with field equipment.</p>



There are generally two categories of tracers: volatile liquids (qualitative) and gases (quantitative). Gases include helium, sulphur hexafluoride and butane. Liquid tracers include alcohols (e.g. ethanol, isopropyl alcohol), solvent (e.g. hexane, pentane) or even consumer products (e.g. butane in shaving foam).

Helium is frequently used as a tracer because its presence doesn't interfere with the analysis of VOCs or petroleum hydrocarbons and can be measured in the field using a handheld detector. There is still a requirement for a high purity grade of helium to ensure there no cross-contamination. 'Party-grade' helium should not be used.

Tracers such as isopropyl alcohol have a direct impact on the quantification of petroleum hydrocarbons. If present at elevated concentrations (greater than 0.01%) they can cause (a) a false positive and (b) elevated reporting limits due to significant dilutions performed by the laboratory. Non-petroleum hydrocarbons such as limonene can still typically cause a high bias in the C9-12 hydrocarbon range.

ANALYTICAL TESTING AND DATA UNCERTAINTY

Deviating samples – what are they and how to avoid them.

Deviating samples are where the results may be potentially compromised by incorrect sampling, storage or inappropriate containers, for further information refer to TPS 63. The laboratory should always include a list of any deviating samples and the reason provided for the deviation.

As above, the correct containers and preservatives provided by the laboratory should be used. An awareness of the holding times of specific analytes especially time-critical parameters such as VOCs is important and these should be considered when scheduling analysis. Samples should be transported to the laboratory as soon as possible.

Sample temperature requirements

Samples should be stored in a refrigerated environment prior to transport. When in the field, samples should be placed directly in cool boxes or cool bags with a minimum of four frozen ice packs. Any headspace in the cool box before shipment should be minimised. The sample storage environment should maintain a temperature of $4.5 \pm 3.5^{\circ}\text{C}$ in accordance with the MCERTS Waters standard. The MCERTS Soils standard does not include a specific requirement for temperature although further guidance is provided in BS ISO 18512. When samples are submitted, the laboratory will measure the outside temperature of the bottle/container. If an accurate record of



	<p>the temperature from site to the laboratory was required, if requested, the laboratory should be able to supply a data logging thermometer to confirm any changes during initial storage and transport. When the samples are received at the laboratory, they will be stored in optimum conditions in a refrigeration area.</p>
<i>Speciated or non-Speciated hydrocarbon testing</i>	<p>Hydrocarbons are frequently found as complex mixtures of a large number of compounds. Consequently, it is not always possible to identify every compound present within such a mixture. Gasoline Range Organics (GRO) and Diesel Range Organics (DRO) are often applied as a cost-effective screen. Yet the approach developed for the analysis and assessment of hydrocarbons instead would typically involve separating hydrocarbons into aromatic and aliphatic fractions, then subdividing these into carbon bands. This approach has been widely accepted for use in human health risk assessment, for example, TPH Criteria Working Group, Volumes 1 to 5 and Environment Agency (2005) and is useful when considering the risks to controlled waters since the fractions can be assigned representative fate and transport properties. For further information refer to CL:AIRE (2017).</p>
<i>Consider the effects of sample preparation where there are marginal exceedances</i>	<p>Where contaminant concentrations are close to the assessment criteria, the effect of sample preparation on the laboratory results, and whether the preparation methodology could impact the critical exposure pathways should be considered. Depending on the contaminant of concern, it might be appropriate to carry out analysis on the <2 mm particle size soil fraction for human health risk assessment.</p>
<i>Tentatively Identified Compounds (TICs) – what are they and how do we assess the data?</i>	<p>These are non-target peaks in VOCs and Semi-Volatile Compounds (SVOCs) analysis. All non-target peaks detected with a concentration above the limit of detection are subjected to a mass spectral library search. This is normally limited to ten TICs but each laboratory may have a different approach. Non-target peaks with a library search confidence of >75% are reported based on the best mass spectral library match. When a non-target peak with a library search confidence of <75% is detected it is reported as “mixed hydrocarbons”. Non-target compounds identified from the scan data are semi-quantified relative to one of the deuterated internal standards, under the same chromatographic conditions as the target compounds. The result is reported as a semi-quantitative value.</p>
<i>Surrogate recoveries – what are they and how do we assess the data?</i>	<p>Surrogates are typically added to samples to monitor recovery of the analysis carried out. Typical recoveries for organics analyses are 70%-130% but are generally wider for analysis of VOCs, 50-150%. Recoveries for soils are affected by organic rich or clay rich matrices. Waters can be affected by high amounts of sediment. Labs only report results that have passed associated quality checks; all recoveries outside of the values will be due to matrix effects.</p>



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Note: Always ensure you are using the most up to date edition of any guidance document or British Standard.