

PRACTICAL TIPS TO SHARE:

CONTROLLED WATERS RISK ASSESSMENT

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In June 2018, the Society of Brownfield Risk Assessment (SoBRA), The Geological Society Contaminated Land Group 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 this workshop has been the creation of a series of short tabular reports for each of the different discipline areas. 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 each author’s experience, 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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CONTROLLED WATERS RISK ASSESSMENT

PRACTICAL TIPS	Descriptor
<i>Think “Prevent and Limit”</i>	The Groundwater Daughter Directive (GWDD) and Article 6 of Directive 2006/118/EC (the Groundwater ‘Daughter’ Directive or GWDD) states that where a hazardous substance is present in the soil beneath a site but is yet to enter groundwater, no discernible entry of that hazardous substance is allowed into groundwater under the concept of “prevent”. This effectively requires the allowable concentration of the contaminant of concern to be only either background or the limit of detection within the groundwater body. The Environment Agency (2017) has produced a list of Minimum Reporting Values (MRVs) to support the assessment of ‘discernible entry’ similarly the Scottish Environment Protection Agency (SEPA, 2014) lists values in position statement WAT-PS-10-01. For hazardous substances that do not have an MRV, you should consider using the Limit of Detection (LOD).
<i>Include in your proposal for a visit to any nearby surface waters</i>	Several Environmental Quality Standards (EQS) are expressed as hardness dependent reflecting that their toxicity to aquatic life is influenced by this parameter. Groundwater and surface water chemistry are often markedly different. This is due to variations in residence times and the tendency of groundwater to move towards chemical equilibrium with the surrounding geology. However, too often hardness samples are scheduled on groundwaters and then applied in the selection of hardness related EQS in the surface water. Hardness should only be scheduled from the receiving surface water and NOT the groundwater on-site.
<i>Filtering samples in the field</i>	Several EQS for metals apply to dissolved concentrations (not total concentrations). Samples should therefore be filtered in the field and fixed using appropriate preservatives. Seek advice from the laboratory on the provision of appropriate filters and use of correct preservatives.
<i>Build the habit of sampling your receiving surface waters for, Calcium (Ca) Dissolved Organic Carbon (DOC) and pH (assuming safe to do so).</i>	The toxicity of metals is dependent on a range of water quality parameters that influence the amount of metal that is bioavailable. If you see exceedances of copper, lead, manganese, nickel and zinc in your Generic Quantitative Risk Assessment (GQRA) for leachates or groundwater against EQS always do metal bioavailability (m-Bat) calculations

(UKTAG 2014). These are an easy addition to your reporting, providing that surface waters have been sampled and scheduled appropriately.

Please note that these water chemistry parameters should, like hardness, be measured each time only from the receiving surface water and NOT the groundwater on-site. In addition, note that the EQS for bioavailable metals relate to dissolved concentrations.

Which leachate test?

Leaching tests do not simulate field conditions, but they may help to establish boundaries on leaching behaviour. The purpose of using leaching tests for land contamination applications is usually to estimate pore water concentrations of contaminants for use in groundwater risk assessment from soil samples. Environment Agency (2006) states that soil pore water concentrations can be determined from leaching tests, but does not expand on the method of derivation.

In the UK the traditional approach to leaching test data has been to use the output from an agitated batch test, usually at Liquid: solid ratio (LS) 10, as the pore water concentration. They are conducted at LS 10, primarily for practical reasons – to facilitate solid-water separation and derive sufficient sample for subsequent chemical testing. But the choice of an LS mass ratio for leaching should depend on the objectives of the study.

High LS ratio batch tests (e.g. LS = 10): can be used for a wide range of soils; they maximise the transfer of constituents (mg/kg); and produce enough volumes for performing the chemical analyses.

Low LS ratio batch tests (e.g. LS = 2): can be used where the objective is to achieve concentrations in the eluate (mg/l) as close to pore water concentrations as possible; or to make it less likely that concentrations are below the limit of detection for the analytical methods used. This test may not be appropriate for clay soils due to separation difficulties. If highly soluble constituents are present then the eluate may become saturated and lead to an underestimate of their leaching potential. There may also be insufficient sample available to conduct all chemical testing.

	<p>The Remedial Targets Methodology (Environment Agency, 2006) notes that pore water concentrations determined for samples using a 2:1 liquid/solid ratio is their preference. Experienced risk assessors may wish to consider alternative tests described in Environment Agency 2012.</p>
<p><i>Use Annual Average (AA) EQS in your GQRA</i></p>	<p>Avoid the use of Maximum Allowable Concentrations (MAC-EQS). They are designed to assess acute exposure of the aquatic environment to pollutants. They may be applicable in a one-off catastrophic spill or leak in an emergency response situation. However, be aware that for AA-EQS the Environment Agency states that monthly or quarterly monitoring with a minimum of nine samples over three years, and three samples per year, is required (Environment Agency, 2015). This is rarely practicable nor a typical expectation in the delivery of land quality projects by the regulator but should you have sufficient timeseries data consider averaging the results</p>
<p><i>Where an EQS has not been published consider using operational Environmental Quality Standards for Environmental Permitting</i></p>	<p>These standards are essentially the repealed Dangerous Substances Directive (DSD) substances. They have been advocated by SEPA for use in Scotland (2018) and, in the case of xylenes, by CL:AIRE (2017).</p>
<p><i>For EQS of Petroleum Hydrocarbons use proxy compounds in your GQRA</i></p>	<p>For petroleum hydrocarbons where no equivalent Volatile Organic Compounds (VOC), Semi-Volatile Organic Compounds (SVOC) or Polycyclic Aromatic Hydrocarbons (PAH) data are available use proxy compounds as per CL:AIRE (2017) Table 5.1.</p> <p>Do not use WHO (2008) Drinking Water Standards as a surrogate indicator of hazard to the environmental quality of a river. Only water quality standards relevant to the receptor should be used. A standard developed to protect ecosystems should never be used to protect human use or vice versa.</p>
<p><i>Consider your surroundings when in the field</i></p>	<p>When visiting a site that is likely to progress to GQRA or Detailed Quantitative Risk Assessment (DQRA) always consider your surroundings, and take note (and photographs, where applicable). Consider the topography of the site and the land around surface water courses in the vicinity and how they may interact with groundwater, land uses, etc. These influences can be much easier to interpret on the ground than when looking at sources on-line.</p>

<p><i>Consider capacity by including for upstream sampling in your cost proposal</i></p>	<p>Capacity defines the capability of a water body to assimilate pollutants. As a first pass you do not often consider capacity. If the observed concentration is below its respective standard at a location protective/adjacent to a receptor then traditionally risk is perceived as low. If in excess of its standard prior to entering a surface water, you should give consideration to any dilution capacity that might be available in the groundwater and in the surface water. To summarise:</p> <p style="text-align: center;">Surface water capacity = water quality standard – concentration in surface water.</p> <p>For existing and passive inputs if a surface water has capacity then dilution in surface waters may be considered up to EQS. If the surface water does not have capacity then the aim must be to meet the EQS in groundwater as it discharges to surface waters, i.e. no dilution allowed. Consequently, where surface waters can be accessed safely, you should always try to sample and retain up and down gradient samples from should the need arise to later assess the potential for capacity of the surface water (also to understand if the site is actively impacting the surface water).</p>
<p><i>Take photographs of your river</i></p>	<p>Conceptual uncertainty is one of the greatest contributors to model uncertainty. A few photographs shared with the modelling team can on occasion make a significant difference to conceptual understanding of whether there is a plausible pollutant linkage between affected groundwaters and a river, arising from hydraulic connectivity. Examples include recording whether the channel is concrete or clay lined, and its visual integrity! Also consider relative level of the river to the site/water level beneath the site and perhaps water level in the surface water relative to the bank / ground adjacent to the surface water.</p>
<p><i>Do not forget your site survey</i></p>	<p>A good borehole survey is required in the generation of hydraulic gradients. Hydraulic gradients can have order of magnitude effects on the outcome of your DQRA. The more spatial data the better in generating drawings of groundwater flow direction and gradients. The more rounds of monitoring water levels also the better to account for seasonality. Consider also sanity checking your hydraulic gradients and direction against topographic profiles. Commonly (although not always) hydraulic gradients reflect general topographic fall and direction.</p> <p>Furthermore, when the surveyor is already onsite build the habit of asking for the depth to water in any adjacent surface waters (think safety first). You can use this information to support your conceptual understanding of likely hydraulic connection between surface waters by comparing with groundwater levels.</p>

<p><i>Recording datum when gauging wells and checking the datum has been surveyed</i></p>	<p>Always record the datum of your measurement when recording dip data i.e. cover level, pipe level or ground level. It is good practice to always record to Ground Level (GL), where possible. Check that the survey data corresponds to the datum to which you are measuring or an accurate correction to m AOD will not be possible. This data is used to develop the groundwater configuration and hydraulic gradient across the site.</p>
<p><i>Dip to base</i></p>	<p>When repeat groundwater monitoring, continue to dip to the base of the well. This allows additional confidence that the correct well has been dipped but also informs silting up and potential well development requirements.</p>
<p><i>Consider tidal influence on groundwater level</i></p>	<p>Groundwater at sites located within proximity to tidal water bodies may be influenced by tidal fluctuations. Alterations to flow direction resulting from level changes may occur temporarily due to saline intrusion. At these sites it is important you accurately record the time of your water level dip. Where a strong tidal influence is anticipated, use down borehole pressure transducers to establish the groundwater configuration and gradients at different stages of the tidal cycle. If a tidal influence is anticipated, acquire additional chemical parameters to inform evidence of saline mixing, the minimum being Electrical Conductivity (EC). Where a tidal / coastal water body is the receiving water body coastal / transitional EQS are applicable for GQRA.</p>
<p><i>Consider your well installation and screen intervals</i></p>	<p>Water levels recorded in wells across a site are only directly comparable if measured within the same aquifer unit. If wells have been installed to target different aquifers vertically or horizontally, you should consider this when developing a groundwater configuration. In addition, if free phase Light Non-Aqueous Phase Liquid (LNAPL) is anticipated or dissolved phase concentrations indicate the presence of free phase but no LNAPL has been measured, you should consider whether the installation is suitable to enable free product accumulation (i.e. screened across the water table).</p>
<p><i>Think particle size?</i></p>	<p>Consider recording particle size gradings with depth in your boreholes. Effective porosity can have a multiplier effect upon the outputs of a DQRA. Understanding particle size alongside borehole descriptions can assist in the creation of a suitable model by identifying how likely preferential pathways vary with depth. Particle Size Distribution (PSD) data also can also be useful to provide estimation of hydraulic conductivity using Logan's approximation by an experienced risk assessor on those occasions site specific hydraulic conductivity data is unavailable/limited.</p>

<p><i>Initial concentrations, do you understand them</i></p>	<p>Initial concentrations can have order of magnitude effects on the outcome of a DQRA.. Risk projections are logically driven by initial source concentrations. Maximum worst case concentrations are often applied in our initial screening models. However, their use can result in overly cautious requirements for site clean-up. Representative concentrations should always be sought necessitating both time series and/or good spatial data.</p> <p>Having acquired such data, you will then have to decide on how best to include it in your model. You should be aware that the use of an average concentration may be misrepresentative if the data is not normally distributed. Consequently, you may wish to consider preparing a statistical assessment of the data identifying its distribution and seeking to find a representative concentration or range.</p>
<p><i>Consider solubility limits</i></p>	<p>On occasion you may receive analytical data from the laboratory that exists above its theoretical solubility limits. Typically, this arises due to accidental cross contamination and the presence of Non-Aqueous Phase Liquid (NAPL) in those samples delivered to the laboratory. Sometimes these concentrations are erroneously included within the parameterisation of a DQRA. You should be aware of the filtering requirements for most of the metals and the need to avoid NAPL contamination influence of suspended sediment on results for contaminants with low solubility and high K_{oc}* (heavy end TPH, PAH).</p> <p>If high concentrations are unexpectedly encountered consider initial comparison against their pure phase solubility (initial screen). However, when chemicals are released into the environment from a mixture like a petroleum hydrocarbon fuel, the water solubilities of the chemicals are typically far lower than their published solubility's. For example, the solubility of benzene is around 1750 mg/L, but typical maximum benzene concentrations resulting from equilibrium between fuel and water are only 20 - 40 mg/L. This occurs because the concentration (or effective solubility) depends on the abundance of the chemical in the fuel – Raoult's law.</p> <p>Exceedance of pure phase solubilities should be a trigger that you consider the possible wider presence of NAPL and the use of effective solubility limits as source concentrations within your as opposed to contaminated sample results.</p>

** the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution.*

Retain and schedule lots of Fraction of Organic Carbon (FoC) tests

Fraction of Organic carbon results can also have an order of magnitude effect on the outcome of a DQRA. Many organic pollutants are hydrophobic or lipophilic and are thus easily sorbed into fats, oils and organic carbon in the soil. The effect of sorption is to retard contaminants to the aquifer mineral surfaces. High rates of sorption slow the contaminant flow rate relative to water, increasing travel time and increasing the time during which degradation can take place; the resulting contaminant concentrations at the receptor(s) will be lower. Partitioning (Kd) between water and bulk soil can be determined by:

$$Kd = FoC \times Koc$$

where FoC is the fraction of soil that is organic carbon and Koc is the organic carbon-water partition, defined previously - See CL:AIRE (2017) Box 4.1.

Our models require values of fraction of organic carbon to be entered. Site data is important. For human health risk assessment, you acquire %SOM. Soil Organic Matter (%SOM) and Fraction/Total Organic Carbon are determined by the same laboratory method but reported as different numbers. They require conversion prior to input into our DQRA. Do not schedule just a single FoC test they are cheap. You should seek to schedule FoC testing from both the soil source and the aquifer pathway. Also avoid samples heavily impacted with non-volatile petroleum hydrocarbons – this carbon will wrongly - for use in DQRAs - be included in the result resulting in a high FoC and one that maybe misrepresentative of the pathway.

Check calibrations of your field Dissolved Oxygen (DO) equipment

Within our models is option to include the effects of biodegradation. The latter will reduce the flux of contaminant with time and distance towards a receptor. Turning on this option requires evidence that biodegradation is occurring, for example evidence of substrate loss, degradation products, geochemical indicators and, on occasion, direct micro faunal studies.

Initially you often wish to simply know whether you have aerobic or anaerobic conditions as certain contaminants are broken down preferentially under different conditions. Dissolved oxygen can therefore be a key parameter measured in the field in supporting the argument to turn biodegradation on in our models. Yet often field results are confusing due to poor field procedures. As a rough guide, oxygen values should be between 0.1mg/L (contaminated wells) and 10mg/L (clean wells), but, readings will depend on geological conditions. For example, as a rough rule of thumb, in uncontaminated aquifers with geologies that contain large proportions of organics, you may expect a low DO value, whereas in chalk aquifers for example, you may expect relatively high DO values under natural conditions. Dissolved oxygen concentrations of >1 mg/l are indicative of aerobic conditions.

Field multiparameter instruments have the ability to record DO in mg/l and %. Always set and record in mg/l. DO meters should be calibrated daily in the field.

Retain Oxidation-Reduction Potential (ORP)

ORP provides an indication of the process by which an organic contaminant is biodegraded: If we have an aquifer contaminated with Benzene, Toluene, Ethylbenzene and Xylene (BTEX) for example, as biodegradation progresses, the electron acceptors (which are what microorganisms use to breakdown BTEX) become progressively depleted according to a specific order, so the microorganisms are forced to use electron acceptors with a lower oxidising capacity. So it follows this progression from high ORP to low ORP. An environment that has a high concentration of electron acceptors is considered to be oxidising, and an environment that has been depleted of electron acceptors is considered to be reducing. But you cannot rely on an ORP value to provide evidence for specific electron acceptor use, it's purely qualitative. It can allow rapid delineation of a plume in the field. If you have a series of wells on a site, low ORP readings can be used as a quick indication that you have contamination in that area, where as a high ORP reading will generally indicate that you are away from the plume.

Note you should also retain as minimum pH, temperature and Electrical Conductivity (EC) if you know you will be progressing to DQRA to assist in understanding the likelihood of biodegradation. See also Environment Agency (2000) for an understanding of other parameters you may wish to consider in the assessment of biodegradation.

ORP vs Eh?

A common question is "what's the difference between ORP and Eh?" (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). ORP as you record it 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 to use in field measurements, and hence isn't practical. Typically, silver/silver chloride electrodes are more popular in multi-parameter water quality instrumentation because they are much more reliable and give a higher performance. You may also have a saturated calomel reference electrode, although this is uncommon in typical field equipment.

As we use a reference electrode other than the SHE in our field kit, what you have measured is termed ORP and not Eh. So before you do any comparisons of your data to redox potential values reported as Eh elsewhere, you have to apply a correction factor to convert the data. In most cases you need to add +200 mV to the reading to convert it to Eh, because you typically use the silver/silver chloride reference electrode, and that's the correction factor that it requires. Eh is a standardised way of reporting the redox potential, and it's how you should be reporting it, and this is something that quite often gets overlooked. This conversion can have large implications for the data analysis.

If you have a reference electrode other than the silver/silver chloride type, phone the hire company and ask them what correction factor you need to apply to the data.

Measuring pH (potential hydrogen and also a log scale)

What do we use pH for?

- 1) Provides an indication of the acidity and alkalinity of the groundwater; pH in itself if it is too high or too low can be toxic.
- 2) When viewed in conjunction with other parameters, it can be used as an indicator of natural attenuation of contaminants. The pH might be slightly lower in areas in which degradation is occurring relative to background areas, because of carbon dioxide from microbial respiration dissolving in the groundwater.
- 3) pH influences the stability of metals

It can also be used to determine the point at which purging has resulted in stability of the groundwater parameters, and you can start sampling. It is automatically corrected for changes in temperature, so, ensure that the temperature readings are sensible (i.e. between 11 and 14oC) if you're getting unusual pH values.

Be wary of highly alkaline or acidic readings. If you are getting such values, consider if they are realistic given the site conditions.

- As a rough guide, if the site is not contaminated, typically;
 - Chalk aquifer - pH of no less than 7 because of the calcium carbonate that makes up chalk
 - Upland peat – can have a pH as low as 4.5

Check your hydraulic conductivity (k) interpretations

This parameter has the potential to result in magnitude effects on the results of a DQRA. This parameter is often neglected and literature sourced in the parameterisation of DQRA. Yet this parameter can vary both vertically and laterally over short distances (aquifer permeability spans some 13 orders of magnitude in the UK), exerting a significant control on contaminant transport. Slug tests are most commonly used and can provide a useful means of estimating a formation's hydraulic conductivity in the near vicinity of the screened interval of the well. Slug tests have the advantage of being relatively rapid, inexpensive, and involve removal of little or no potentially contaminated water. In typical monitoring wells with partially submerged screen sections calculation of hydraulic conductivity may, however, be affected by drainage of the filter sand, resaturation of an unknown percentage of the filter pack, a dramatic reduction in the initial head drop due to filter sand pack drainage, and a non-constant screen intake length over the course of the test.

- Slug tests provide a weighted average conductivity that intersects the well screen provided that the screen section is submerged. This effect may be minimised by constructing wells screened only in discrete formations;
- You should allow slug tests to fully recover before a new test is commenced or the ongoing recovery of the formation will influence the new test;
- It is preferable that only fully submerged wells screens are applied;
- Finally, one further common mistake occurs within the interpretation of the data. Beware the filter pack. Water level recovery in a typical monitoring well in early time is often dominated by rapid draining of the filter sand evidenced by a steep portion of the recovery curve in early time. Hence, this early portion of the recovery curve should not be used in calculating hydraulic conductivity (K). Calculation of hydraulic conductivity using the early portion of the recovery curve may overestimate the formation conductivity by over an order of magnitude.

- The filter pack should have a higher conductivity than the formation, otherwise the test will only be measuring the K of the filter pack. Ensure your filter pack materials are suitable and of high conductivity.

Plan a downgradient well (s)

Risks assessments inherently contain conceptual, data and model uncertainty. Measured data will almost always carry greater weight and confidence than modelled data. The introduction of a downgradient well may be used for model validation (determining whether the model methodology is appropriate) or calibration (refining the model inputs such that the results match the measured values).

In designing your investigations think ahead and always try and include such a well or series of wells even if limited to the site boundary.

Total Porosity and Effective Porosity

Understand the difference between effective porosity and total porosity. Effective porosity is the interconnected pore volume or void space in a rock that contributes to fluid flow or permeability of an aquifer. Total porosity is the total void space in the rock whether or not it contributes to fluid flow. Effective porosity is typically less than total porosity. There are many literature sources for total porosity for different soil types (e.g. ConSim help files); however, DQRA requires input of the effective porosity. A rule of thumb (~50%) may be applicable as a first pass but must then be considered in the sensitivity of the model.

WQS versus LOD

Check the laboratory Limits of Detection (LODs) for your contaminants of concern and compare them to your WQS. If the LOD exceeds the WQS check if the laboratory can achieve a better LOD.

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