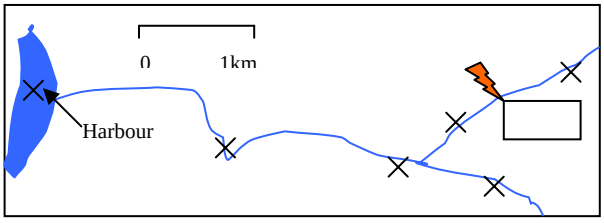
CH3041 Tutorial 5 Analytical A Answers

1. A new fungicide (organic chemical) has been approved by the *National Registration Authority* for use on sugar cane with a 6 month limited permit. Local members of *Sunfish* are concerned about the impact of the new product on aquatic life. A trial site is indicated in the marked area. You wish to confirm for *Sunfish* and the *NRA* that the fungicide is not entering the aquatic system. Plan a sampling protocol for the site, indicate what information you will need before you start sampling and what information you need to obtain from the sampling.



Samples are indicated at the X.

Information needed before the sampling includes:

1) What are the properties of the fungicide eg. H_2O-solubility, K_{OW}, mp, bp, p_{vap}, LC_{50}, $EC_{50,}$ toxicity band $t_{1/2}$, are there any secondary chemicals which could act cooperatively eg. emulsifier or surfactant.
2) What are the degradation products (metabolites) of the fungicide, what are their properties.
3) Have any toxicological studies been carried out, what are typical BCF values in an aquatic food chain.
4) Is the fungicide able to react in the environment with anything that will reduce the distance of transport (strong sorption onto clays) or the degree of biomagnification (metabolic conversion).
6) You will need to know the topography in detail (maps), are there any low lying areas in the catchment where the water will tend to pool, here any material adhering to sediment deposits are likely to be at their most significant levels. Are there field drains?
7) When will the spraying program take place. You will need to access the climate data from this date onwards and try to sample after periods of heavy rain. What is the quantity of the fungicide that will be introduced into the canefield per hectare.
8) What is the flow rate through the tributary and the main creek, these are used to calculate the dilution factors in the creek and tributary.
9) Safety aspects of sampling need to be estimated and access to the site.
9) Land use in the vicinity of the catchment (are there any other similar chemicals that are likely to be in the creeks).

What you need to get out:

1) The level of fungicide(+ metabolites) in the water of the creeks and harbour, including an estimate of the errors ie. the data quality.
2) The level of fungicide(+ metabolites) in the sediments of the creek having found the critical areas where contaminated sediments lie and in the sediments of the harbour directly at the creek mouth.

In principle there should be no fungicide detected in the water column or sediments. If there is then a check on the foodchain would be required where once the critical organism (eg. benthic organism) has been identified this could be used as a bioindicator for longer term ecosystem monitoring.
This will generate a set of data to aid in establishing if the fungicide under field conditions is indeed entering the aquatic environment.

Sampling protocol:

Fixed sampling sites would be used. Physical measurements will be taken at each sampling point (T, DO, pH) as well as collecting water and sediment samples.
The sampling regime will be as indicated on the map. Water samples will be taken in midstream under the surface into amber glass storage jars. In the harbour this will be in the creek mouth where the salinity has increased to 50% of the marine value. From there the water samples will be stored in an Esky on ice and then taken back to a freezer in the laboratory.

Sediment samples in the river and harbour can be collected using a coliwasa. The sediment would be stored in amber glass jars, cooled and transported to the lab for freezing.
Blanks: a control sample would be taken in the small side creek upstream of the confluence and directly above the cane field creek, an equipment blank would be taken at the end of each days sampling.
Replicates: 1 per every 5 samples. Spike samples at least one per days sampling.
Analysis will be carried out using either GC-MS, GC-ECD or HPLC-UV/Vis depending on the characteristics of the fungicide, the MDL will set the sample size based on the lower limit needed to class the water as safe. This is likely to of the order of 1ppb.
Total number of samples will be based on the above x 5%. The project will then be costed and the time for the project estimated. The frequency of sampling will be initially high perhaps every day (1 week), week (1 month) and after that at monthly intervals. A safety protocol will be needed. A quality assurance plan will need to be detailed. Then sampling can begin.

2. How would you collect the following blanks for soil samples containing DDT:
   1) Field blank
   2) Matrix blank
   3) Equipment blank

(1) Field blank: During sampling a sample of DDT-free soil taken to the site is treated as per samples. The DDT-free soil has been certified back in the laboratory.
(2) Matrix (background or control) blank :
Soil sample collected usually using a spade into glass containers or using a PVC pipe hammered into the ground.
A sample of soil similar to the test sample taken in the same run and at a nearby location where DDT is not expected to have impacted on the soil. Provides the background level of DDT in the soil.

3. Provide examples of sampling devices and storage containers for:
(i) Air (outdoor) : contaminant sulphur gases.
Sampling device could be real time analyser with no storage such as Fluorescence or UV spectrometer (SO_2) or a gas sensing electrode (SO_2).
Alternatively a gas sample could be either collected into SUMMA canisters, TEDLAR bags (SO_2, organosulphur gases) using a pump.
(ii) Water (estuary) : contaminant Sn from boat antifouling paints.
A peristaltic pump with seasoned teflon tubing used to transfer water to acid treated glass container (storage) or PET bottles.
(iii) Soil (A horizon) : contaminant PCBs from an old transformer site.
Spade or trier or auger, collect surface soil and place in amber glass container (storage) which will need to be cooled. Alternatively PVC pipe.

4. Describe an **analytical protocol** to determine the amount of mercury that remains in a soil sample 10 years after a mercury fungicide has been used on the site.

Extraction from soil matrix:
Extraction, separation of interfering substances, concentration.
Extraction : involves removing the Hg which will be present in three oxidation states Hg(0), Hg(I) or Hg(II) from the soil.
Of these the lower oxidation states Hg(I) may be found in covalent organometallic complexes while Hg(II) will commonly be found inorganic complexes bound to either O or S. The organometallic complexes can be removed by using a polar solvent such as dichloromethane.
The Hg(0) will need to be oxidised to Hg(II) to prevent loss of using strong acids and oxidants (H_2SO_4 / $K_2S_2O_8$) The inorganic mercury may be released by dissolving a quantity of the soil using a strong acid such as HF.

Separation : if AA is used then any interfering substances will be removed by selective complexation at this point.

Concentration : depending on the quantity of solvent used to remove the analyte from the matrix the solution may need to be concentrated by evaporation so that it meets the IDL.

Analysis of analyte:

Prepare a series of standards of known Hg concentration. Run Cold Vapour AA spectrometry on these standards and prepare a calibration curve. Run the unknown and determine if it is within the range of the curve. If it is calculate the concentration in the sample and then work back to the amount of sample to give Hg in ppm in the soil (mg / kg).

Alternatively if the sensitivity is sufficient then X-ray Fluorescence may be used directly on the solid without any extraction step. Again standards would have to be run.

Results:

Report the unknown concentrations in ppm including the error bars associated with the analyses.