

## **Appendix 2 Geochemical Sampling Protocol**

### **1. Stream sediment sampling and analysis**

#### **General Information**

Sampling protocols will *essentially* follow those described for the FOREGS programme ([www.gsf.fi/foregs/geochem/fieldman.pdf](http://www.gsf.fi/foregs/geochem/fieldman.pdf)). However, this programme is designed for regional geochemical studies rather than contamination studies so some modifications will be required in respect of the number and location of sub-samples collected. The <150µm size fraction is particularly useful for regional geochemistry sampling, especially where common ore metals are of interest, but other size fractions may also be considered for contamination studies.

Regional geochemical studies sample the active stream sediment, i.e. the fine- to medium-grained bed-load material (silty-clayey-sandy) that is transported by running water. Studies into the distribution of trace elements in relation to the size fraction of stream sediments generally show that several elements including Mo, Cu, Zn, Mn and Fe are concentrated in the finest fractions of the sediment. Typically, the <150µm size fraction is analysed, as this is fine enough to include only the very fine sand, silt, clay and colloidal fractions, but is coarse enough to yield sufficient fine material in the majority of situations. However, the possibility that some elements of interest may be preferentially bound to coarser, sandy material in the vicinity of the mine site could also be considered. The potentially complex physico-chemical conditions prevailing in streams around mine sites may warrant a more detailed sampling and analytical approach than that adopted for FOREGS. However, as GSI has already completed regional studies in southeast Ireland, Longford-Down and Inishowen in which the <150 µm fraction was collected, it would be desirable, in order to allow comparison with and/or use of this data, that samples of this size fraction be collected for the HMS-IRC project. This does not preclude collection of coarser samples if desired or necessary in some instances.

The emphasis in FOREGS protocols on collecting enough sediment to produce at least 0.5kg of <150µm sample is less relevant in contamination studies as there is no requirement to collect a sample that is representative of a much larger area.

It is important to avoid metal contamination at every stage of the sampling process:

- No hand jewellery or medical dressings should be worn during sampling. Heavy duty rubber gloves should be worn at all times to avoid contamination of the samples.
- Metal-free polyethylene scoops will be used.
- Metal-free nylon or polypropylene sieve-mesh housed in inert wooden frames will be used.
- Metal free funnels and sample collection containers (Kraft bags, plastic bags or bottles) will be used.

#### **Site selection**

Whereas regional stream sediment samples comprise material taken from 5-10 points over a stream stretch of 250 - 500 m, sampling of streams around mine sites will, for obvious reasons of scale, be more focused. The aim will be to demonstrate the spatial extent of any stream sediment contamination around the mine site and,

depending on the scale of the site, sampling sites may be relatively closely spaced. Individual samples should still be aggregated from a number of sub-sites but the sub-sites will ideally be chosen to ensure the width of the stream is sampled over a limited length. A decision about the length of the stream over which sub-samples are collected will be made for each site separately on the basis of detailed mapping. *Accessibility will play a significant part in determining sample locations.* Because sampling points used for regional geochemical studies are relatively widely spaced, sub-sites can be spread over a wide area. In contrast, sub-sites for contamination studies will be tightly constrained thereby limiting site selection opportunities. If water is being collected simultaneously from the same stream, then stream sediment sampling should start from the water sampling point and the other sub-samples should be collected up stream. A composite sample should not be made from samples taken from beds of different nature.

Vertical profiling of stream sediment should be considered in those cases where initial sampling has indicated that contamination has occurred. A suitable vertical sampling device would have to be acquired for this purpose.

### **Standard Equipment**

Not all of the equipment listed will necessarily be employed.

1. Kraft paper bags
2. Polythene bags
3. Heavy duty elbow length rubber gloves
4. Plastic wash bottle
5. Sieve set with wooden frames, nylon or PPP 2.0 mm and 0.150 mm mesh screens
6. Metal-free gold pan
7. Metal free plastic buckets or containers with lids
8. Trenching tool - metal free, polyethylene (PE) or polypropylene (PP)
9. Permanent drawing ink marker (preferably black or blue)
10. Permanent ink pen
11. Maps (OS maps, site map, aerial photo)
12. Field observation recording sheet
13. GPS
14. Camera

### **Sampling procedure**

This procedure assumes that samples are being sieved through a very fine (<0.150 mm) mesh. This may not always be the case in the course of this project.

Mark the sample identifier on the outside of the plastic bucket using permanent ink marker. Mark the exact site location of the first (downstream) sub-sample on the field map and note distance upstream over which other sub-samples were collected. Record GPS reading. Complete the details of the field observation sheet (below).

Samples will be sieved using wet sieving whenever it is possible. Rubber gloves are recommended for protection throughout sampling. Following collection of any water samples, prepare the equipment for stream sediment sampling:

- wash all stream sediment sampling equipment (buckets, sieves, gold pans, gloves and scoop) with stream water downstream of the sampling point;
- set-up the gold pan in a stable position;

- if using two sieves, place the sieve with the finer mesh in a stable position resting on the gold pan;
- place the sieve with the coarser mesh over the first sieve;
- because fine sediment can lodge in spaces between holding rings and mesh used in GSI sieves, it is desirable to pre-contaminate the sieves - load some sediment into the top sieve and work it through both sieves before washing again in stream water downstream of the sampling point;
- load sediment into the top sieve with the scoop;
- rub the material through the top sieve wearing rubber gloves for protection;
- take care to remove large stones from the sediment by hand;
- once the bottom sieve contains a reasonable quantity of sediment, remove the top sieve and discard the material in it;
- fill wash bottle with stream water;
- the finer sediment in the bottom sieve is washed and rubbed through the sieve with the aid of stream water;
- it is very important at this stage that coarse material that would bias the sample does not enter the collection pan – ensure no such material is adhering to bottom sieve or is introduced to the finer material during the collection process;
- the sample should be repeatedly washed until all the fine material has passed through the sieve;
- transfer the contents of the pan to the plastic bucket, using water from the wash bottle if necessary, a replace lid on bucket;
- the whole sieving process should be repeated until the bucket contains sufficient fine-grained sediment;
- seal bucket with lid and store in vehicle;
- the sediment should be allowed to stand until all the suspended material has settled and clear water sits on top of the sediment – this may be at end of the day or following day in field base or GSI laboratory;
- once the suspended material has settled, excess water on the surface of the sediment should be carefully decanted - care should be taken to remove only water and not sediment at this stage;
- the remaining sediment should be thoroughly homogenised and mixed using the plastic stirring rod before being transferred into Kraft bags;
- write the sample identifier on enough 10 x 22 cm Kraft paper bags to hold all the sample volume - this size of Kraft bag allows ease of drying the samples;
- if sample is bagged in field or at field base, the number of bags for each sample site should be recorded on the field sheet and on a sample check-list sheet.
- once the sample has been homogenized, carefully transfer the sample into the Kraft bags using a clean plastic funnel;
- the Kraft bags should be air-dried for as long as required;
- if moving the samples from field base place each Kraft bag in a 15 x 40 cm polythene bag and secure the top of the bag with a knot to prevent loss or cross contamination of samples during transport;
- the samples should be secured upright in a plastic crate or box and transported carefully to the next location or to the GSI laboratory base for further drying;
- at the GSI laboratory, the samples should be completely dried at < 40°C. Freeze drying is a recommended as this helps to disaggregate the samples;
- all sampling equipment must be thoroughly cleaned between each site to avoid cross contamination.

In dry conditions where there is no flow in the stream bed, samples will have to be dry-sieved. Since water is not available to wet sieve the stream sediment to the required <0.150 mm fraction, collect a bulk composite sample from the 5-10 sampling points. Collect material of finer grain size or if possible only the top thin layer of silt on the sand bar, from the centre of the stream. Care should be taken to sample stream sediment with as little as possible organic matter, and to avoid the reduced material, identifiable by its typically dark colour and bad odour, that occurs at greater depths. Also, in the case of narrow channels take care not to collect material that has fallen from the banks.

The removal of stones and other coarse-grained material could be achieved by sieving through a 5 mm nylon sieve and collecting the material in a plastic bowl. Collect equal amounts of material from the 5-10 sub-sites. The use of the 2 mm nylon sieve is not recommended for dry sieving, because it is too small for clay agglomerates and slightly moist samples.

Transfer the fine-grained sample to the Kraft paper bag and seal. Place the sealed Kraft envelope within a polythene bag, and tie a loose knot in the polythene bag to prevent loss or cross contamination during transportation.

Air dry the sample, disaggregate if necessary in porcelain bowl and sieve it through a 2 mm (or other) aperture nylon sieve.

At each stream sediment/water sample site take two photographs, the first to show general upstream topography from the lowermost sub-site and the second the nature of the stream bed at the best sub-site.

### **Sample processing**

Samples will be dried in Kraft bags either in air or at 30°C in the oven. If caking occurs during drying, grinding with a pestle and mortar may be required. Samples will be placed in plastic bottles for storage prior to analysis.

### **Quality assurance and control**

The likely heterogeneous nature of contaminant dispersion in stream sediments around mine sites presents particular issues for QA / QC protocols. Potentially large differences in composition between samples emphasize the need to take measures to avoid inter-sample contamination. Inherently large variations in composition also cast doubt on the value of collecting field duplicates. Other areas that need to be addressed in respect of QA / QC are:

- homogenization of samples prior to analysis and
- analytical accuracy / precision for samples with anomalously high concentrations of metals and other elements.

Specific QA / QC measures proposed for stream sediment sampling and analysis are:

1. adherence to FOREGS sampling protocols, particularly those relevant to contamination of samples by sampling equipment;
2. pre-contamination of sieves with sample followed by washing in stream water to reduce risk of inter-sample contamination;
3. analysis of replicate samples (splits taken from final prepared sample) to monitor sample homogenization and preparation;
4. analysis of standard sample to monitor analytical accuracy and precision.

## Analysis

- Analysis will routinely be carried out by portable XRF, using a bench-top docking station;
- Approximately 5 - 10% of all samples will be analysed in a commercial laboratory by ICP techniques to provide a check on the XRF results.

## 2. Surface water sampling and analysis

### General Information

Surface water will include streams, adit discharges, run-off from solid waste and ponded water on mine sites. Water sampling should be repeated at different times of the year to assess the effects of variations in flow rates.

A number of parameters will be measured in the field rather than the lab. These will include:

- temperature
- EC
- pH
- dissolved oxygen
- flow rate (where relevant / possible)

Field-based measurements allow an initial, rapid assessment of water quality and can be used as part of a reconnaissance study to help identify sites for laboratory-based water analysis.

In addition to the parameters listed above, acidity / alkalinity will be measured using a Hach titrator kit either *in situ* or at the field base at the end of the day. In the latter case, samples should be kept in a fridge / cool box after sampling.

The sampling protocol will essentially follow that of FOREGS ("Stream Water"). Filtering of water samples will be done *in situ*, using disposable syringe filters, rather than subsequently in the lab, given the limitations of GSI's lab facilities.

### Water samples to be collected

Both filtered and unfiltered samples will be collected, as follows:

- 1 x 1000 ml PE bottle of unfiltered water for major ion and trace element analysis;
- 1 x 100 ml Nalgene trace element-free bottle (or equivalent as supplied by the laboratory) of filtered water, preserved with conc. HNO<sub>3</sub>, for dissolved ion and trace element analysis;
- 1 x 500ml PE bottle of unfiltered water for alkalinity / acidity testing.

Sample bottles will be supplied by the laboratory for both total and dissolved element analyses. Bottles will have to be purchased for storing samples for alkalinity / acidity testing.

### **Equipment to be used**

Sample bottles for total major and trace element analyses of unfiltered water and analysis of dissolved elements in filtered water will be provided by the laboratory. Other recommended equipment includes:

- 500 ml new polyethylene bottles (for non-filtered water samples for alkalinity / acidity analysis);
- disposable gloves (vinyl gloves, powder free);
- disposable syringes;
- disposable cellulose syringe filters 0.45  $\mu\text{m}$  (pyrogen free);
- deionized water;
- HPLC water for preparation of lab / travel blanks;
- washing bottles;
- permanent drawing ink markers;
- cool boxes / fridges and ice packs / batteries for them;
- rubbish bags for discarded filters, etc.;
- pH-meter;
- buffer solutions for calibration of pH-meters;
- EC-meter;
- buffer solutions for calibration of EC meters;
- two polyethylene (500 ml) beakers for sample water to measure pH and EC;
- alkalinity / acidity measurement kit (Hach or equivalent);
- dissolved oxygen meter and calibration material.

### **Water sampling procedures**

Where stream sediment is also being collected then the water sample should be taken first, from the lowermost stream sediment sampling point, as stream sediment sampling will cause sediment to enter into suspension.

The sampling procedure closely follows that of FOREGS, with some modifications. GSI's temperature, pH and EC meters are integrated in one device and thus field measurements of these parameters are carried out simultaneously. The procedure is:

1. write the sample number on sample bottles;
2. complete sample card and mark location and sample number on the map;
3. rinse temp / pH / EC meter thoroughly in stream / adit, etc., to be sampled to remove any trace of previous sample or storage solution;
4. rinse twice and fill the polyethylene beaker with stream water, place the temp / pH / EC meter in water and measure the temperature, pH and conductivity – record on field data sheet;
5. alternatively, the measurement can be made directly in the stream / adit, etc., if flow and /or chemical homogeneity allow stable reading to be achieved;
6. wearing vinyl gloves rinse a disposable syringe with sample water and fill it up with water;
7. put filter on syringe;
8. discard the first 10 ml of filtered water from each new filter unit used;
9. take a 100 ml marked sample bottle for acidified sample fill the bottle up to its neck with filtered water (change filter if needed) and close it tightly; note that the filtered sample water should go straight into the bottle without contact with hands;

10. rinse the marked 1000 ml sample bottle with sample water twice and fill it up so that the bottle is completely submerged in the water and no air bubbles are left in the bottle. Fill the bottle as full as possible and close it tightly below water level;
11. rinse the 500ml alkalinity / acidity sample bottle twice and fill to brim before replacing cap;
12. after recording the temp / pH / EC readings on field data sheet, rinse the meter and beaker with deionized water and keep the meter in its cap with storage solution;
13. the filled sample bottles are placed in the cool box / fridge;
14. alkalinity / acidity measurements should be carried out either in field or at field base at end of day as per instructions in Hach kit – samples to be stored in cool box prior to analysis;
15. record alkalinity / acidity titration results and computed alkalinity / acidity (mg/l CaCO<sub>3</sub>) on field sheets;
16. a lab blank (HPLC water) should be enclosed with each batch returned to the lab – sample is prepared in lab using same techniques as in field.

#### **Treatment of water samples**

1. After return from field, place the bottles in a cool unit, e.g. refrigerator;
2. Complete Chain-of-Custody forms;
3. Place water samples in cool box and send to the laboratory.

#### **Quality control and assurance**

1. Duplicate water samples should be taken at regular intervals.
2. Lab blanks, made up using HPLC water should be included with each sample batch.
3. Trip blanks, containing HPLC water, can also be included.

### **3. Solid Mine Waste**

#### **General Information**

Solid mine waste can be analysed either by portable XRF or by standard wet chemical methods in a certified commercial laboratory. The portable XRF offers rapid *in situ* semi-quantitative analysis and, in a laboratory environment, quantitative analysis of prepared samples; wet chemical analysis offers potentially greater accuracy but is a relatively slow process. The high initial cost of the XRF will be offset to a degree by the savings on laboratory analyses.

There are two issues in relation to mine spoil, particularly, that are directly relevant to the choice of analytical technique. Firstly, the typically very heterogeneous nature of mine spoil, both compositionally and in terms of grain size, poses significant problems for analysis since it is virtually impossible to obtain a truly “representative” sample. Secondly, even if a representative sample were found, achieving true homogenization of the sample would be very difficult. Standard laboratory analytical techniques rely on analysis of a small sub-sample of a homogenized sample. Tailings are generally much less heterogeneous and have a finer grain size and would not, therefore, pose so severe a problem.

The difficulties posed by sample heterogeneity apply to whatever analytical technique is employed. Since these difficulties make truly accurate analyses of mine

spoil at least problematic, it is suggested that the semi-quantitative portable XRF method is preferable as the rapid *in situ* analysis will allow detailed mapping of contamination “hot-spots” on and around mine sites – the perceived relative lack of absolute accuracy of the method would be outweighed by the large number and wide range of samples analysed. A number of wet chemical analyses of spoil could also be carried out on selected material to establish concentration ranges for elements of interest. Such samples would be selected on the basis of initial XRF analysis.

### **Portable XRF analysis**

EPA/GSI acquired a Niton XLt 792Y for use in the HMS-IRC project. An account of the analyser’s analytical performance is provided in Appendix 4. The XRF’s portability means it can be used to analyse most solid material provided it can be positioned so that the X-ray window lies flat against the surface being analysed. Material should be raked over to disaggregate it and then smoothed and compacted for *in situ* analysis. The window of the Niton XLt has a diameter of 20mm so for coarse material it is desirable to analyse a number of points on the surface to achieve a representative analysis. Given the inherent compositional variation in solid mine waste, such an approach, i.e. analysing several spots at each sample site, is desirable in any case, regardless of grain size. Approximately 10% of sites should be sampled for laboratory analysis both by XRF on prepared samples in the GSI lab and by wet chemical methods in a certified commercial laboratory.

### **Spoil Sampling protocol**

For single spoil heaps of relatively homogeneous appearance, where the aim is to obtain an estimate of the range and median element concentrations in the heap, a minimum of 5 points should be analysed, one at each corner of the grid, the other in the centre. The more spots analysed the better so the grid can be modified to include 6, 9 or more spots in a regular array. The general approach to analysis is:

- mark the outlines of a grid, the size of which will depend to some extent on the areal extent of the spoil heap - a 10m x 10m area can be considered a standard area but larger or smaller areas may apply depending on size and time available for analysis;
- use a trowel to mark out a 20 x 20cm spot, turn over and rake the top 5cm of material, smooth and compress it to form a flat surface;
- analyse for 90 seconds using the “soil” mode, 60 seconds on the main filter and 30 seconds on the light-element filter;
- during the 60 seconds on the main filter, move the XRF twice to a different point in the sample site so that three spots are analysed, each for 20 seconds – the movement should be swift to avoid analysis of “air” for any significant length of time;
- do the same when using the light-element filter except reduce the interval to 10 seconds;
- record all observations for each sample analysed on appropriate field sheets – data to be transferred to digital file at earliest opportunity;
- for every 5 to 10 sample spots, and ideally at least once for each spoil heap, collect a 0.5 – 1kg sample of material from the 20cm spot analysed, place in plastic bag, seal and return to GSI lab for processing;
- samples returned to the lab should be passed through a 2mm nylon sieve before quartering, if required, and grinding in an agate or equivalent contaminant-free mill;



- milled samples should be placed in labelled bottles for storage;
- quartered remains of sample material not milled should be stored for potential future use.

Where the spoil is heterogeneous in appearance, distinctive parts of the spoil heap should be analysed, with the number of spots in each distinctive part reflecting its relative size. Apart from attempting to determine the range and median composition of heaps, the portable XRF should be used to help identify “hot spots” or parts of waste heaps with anomalously high element concentrations.

#### **Tailings sampling protocol**

A similar approach to that for spoil heaps can be applied to tailings although grain size variation, at least, will be smaller than for spoil. In order to sample at depth, a pit should be dug to the required depth using a stainless steel spade. Alternatively, a sample can be cored using a manual coring device. The sample can then be analysed either *in situ* or in the lab / field base on the XRF stand.

### **4. Leachate testing**

#### **General Information**

The protocol for leachate testing follows that of the U.S Geological Survey’s field leach test for mine wastes and other materials (Hageman 2007). This rapid test was originally devised specifically for mine wastes and compares favourably to the US EPA’s 18-hour leaching procedure (Method 1312) (Hageman 2007). It uses a 20:1 leachate:solid extraction ratio, the same as the US EPA method, which ensures the readily soluble components of a sample can be taken into solution without exceeding leachate saturation limits. Use of this ratio also allows direct comparison with results obtained using the US EPA test and it ensures that there is sufficient leachate to allow complete geochemical analysis and characterization.

#### **Laboratory equipment required**

1. 2mm-mesh nylon sieve;
2. laboratory or field balance capable of weighing 50g of sample;
3. 1000 ml wide-neck PE bottles;
4. 500ml or 1000 ml graduated cylinder;
5. deionized water;
6. pH, EC meter;
7. beaker for pH, EC tests;
8. alkalinity / acidity kit (Hach);
9. 50-60ml plastic syringe;
10. disposable cellulose 0.45µm capsule syringe filter;
11. 100ml plastic bottles with 10% nitric (laboratory-supplied) for sample storage.

#### **Procedure for extracting leachate**

Once a representative sample is available, the procedure below is used to extract the leachate for analysis. Collection of a “representative” sample entails collecting a series of samples from sub-sites within a waste heap, using a grid or other non-biased method of sampling. The recommended number of sub-sites (Hageman 2007) is 30 where the aim is to collect a truly representative sample. The final

composite sample should weigh at least 1kg. Mixing and homogenization of sub-samples can be carried out using large buckets.

1. Samples should be air-dried in the laboratory;
2. dry samples are passed through a 2mm-mesh nylon sieve;
3. 50g of the composite sample is added to a wide-necked 1000ml PE bottle;
4. 1000ml of deionized water is added to the PE bottle which is then capped;
5. the PE bottle is then clamped to a laboratory shaker along with other bottles if more than one sample is being processed;
6. the shaker is run for 5 minutes at highest speed possible;
7. after shaking, the sample is allowed to settle for 10 minutes;
8. after settling, the syringe and filter are used to fill the acidified bottle with supernatant liquid from PE bottle;
9. part of the remaining supernatant liquid is poured carefully into a beaker for pH, EC and temperature measurement;
10. remaining supernatant liquid can be used for alkalinity / acidity test either immediately or later after storing in 250ml plastic bottle in fridge;
11. the filtered leachate sample should be stored under refrigeration until returned to the laboratory for analysis.

### **References**

Hageman, P.L. (2007) U.S Geological Survey field leach test for assessing water reactivity and leaching potential of mine wastes, soils and other geologic and environmental materials. U.S. Geological Survey Techniques and Methods, book 5, chapter D3, 14p.