GENERAL PROCEDURE FOR THE SAMPLING OF SURFACE WATER AND GROUNDWATER

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1. INTRODUCTION

This document provides general procedures for the sampling of surface waters from streams and small rivers and groundwater from purpose-built monitoring wells. Samples collected according to these procedures are intended for the characterisation of waters contaminated from olive oil wastes.

The procedures assume that sampling shall be undertaken by suitably trained and qualified personnel and that widely accepted standards of sampling and laboratory practice shall be followed at all times.

Procedures for health and safety and quality assurance are not within the scope of this document. However, it is recommended that all sampling is undertaken in accordance with:

- *A health and safety policy*
- *A quality system*
  The quality system should provide clear and precise guidelines at all stages of the sampling process to ensure that good practice is followed at all times. Quality control measures should be included to quantify and if necessary control sampling errors (for example the collection of blanks and replicate samples).

2. PRELIMINARY SURVEY

A preliminary survey shall be undertaken prior to the commencement of sampling to detect likely sources of contamination and existing environmental information. Site reconnaissance may be necessary.

3. SAMPLING STRATEGY

Sampling should always start by defining the purpose of the measurement. If the different stages are under the responsibility of different people, there needs to be good communication between all parties involved (Stoeppler, 1997).

A detailed sampling strategy shall be formulated for each site to be sampled. The sampling strategy shall define: the number of sampling points; locations of sampling points; number of samples; sample type; time and frequency of sampling; sampling equipment.

The design of the sampling strategy shall be specific to the site being sampled and shall be formulated in the light of information gained during the preliminary survey. A detailed strategy for each site is not within the scope of these procedures. However, guidance on the formulation of an appropriate strategy is provided in Sections 3.1 and 3.2 below.

3.1 SELECTION OF SAMPLE LOCATIONS

Selection of sampling locations shall be determined primarily by the objectives of the sampling program, although it is good practice to consider the following:

- *Accessibility*

- *Obtaining a representative sample*

  Collecting a representative sample may be problematic where the water to be sampled is heterogeneous (for example sampling of a river downstream of an effluent discharge or tributary should be undertaken at a sufficient distance from the tributary to ensure complete mixing of the waters).

  Sampling locations near the boundaries of systems (for example banks or bottoms of rivers or lakes and the walls of pipes or channels) should be avoided except when these regions are of direct interest.

- *Rate of flow*

  Where it is necessary to know the rate of flow at the time of sampling, the sampling locations should generally be chosen so that the corresponding discharges are known or can be estimated (for example selection of sampling locations adjacent to a weir).

A larger number of sites will always provide more information than a smaller number. However, in practice, the number of sampling sites will usually be determined by the budgetary constraints (Madrid and Zayas, 2007).

3.2. TIME AND FREQUENCY OF SAMPLING

3.2.1 Frequency of sampling

Sampling frequency is an important factor in terms of representativeness. Low sampling frequency could underestimate the occasional presence of samples with high analyte concentration. Sampling frequency is subject to influence (e.g., by transport, access to the sampling site, the availability of test organisms and financial constraints) (Madrid and Zayas, 2007).

Where environmental conditions are not stable, then more than one sampling effort may be required. Where this is the case, the frequency at which repeat sampling is required should be determined by considering:

- The variability of the environment
- The objectives of the sampling program
- Cost of sampling and analysis

Samples may be collected periodically or continuously.

3.2.2 Time of sampling

Where environmental variations are cyclical (for example seasonal variation of flow in rivers), the times at which samples are collected should be determined such that the samples represent adequately the parameter of interest. Where repeated samples are collected the samples should be timed such that each part of the cycle is evenly represented (eg MEWAM, 1996). Timing may also be important where samples are taken before and after a pollution event.

4. SAMPLING OF SURFACE WATER

4.1 SAMPLING TECHNIQUE

Sampling shall be undertaken from within the watercourse (in-stream sampling) (Section 4.1.1) or from the bankside (Section 4.1.2). Where it is not possible to collect samples using these methods (for example where the river is too wide or too deep) the sample may be collected using an alternative method agreed in advance.

4.1.1 In stream sampling

The Sampler shall enter the stream slightly downstream of the sampling point and approach the sampling point with the minimum disturbance to vegetation or bottom deposits.

When the sampling point has been reached, the Sampler shall face upstream into the flow of the water. The sampling container shall be placed under the surface of the water to a depth of approximately 30 cm so that the neck of the container is submerged. The container shall be tilted such that it points slightly upwards towards the surface, allowing the container to be filled. When full, the container shall be removed from the water.

When sampling static water, once the container has been submerged and the neck tilted upward as described above, the container shall be filled by moving it away from the Sampler in a forward motion with the mouth of the container pointing upstream, avoiding any disturbed material.

If the sample becomes contaminated with disturbed material, for example sediment or vegetation, the sample shall be discarded downstream of the site. A fresh sample shall be collected.

4.1.2 Sampling from the bankside

Samples shall be collected from the bankside by extending the sampling container into the centre of the stream, using an extension arm where necessary. Care shall be taken to avoid sample contamination by either disturbance of the bed or the bank of the watercourse. The container shall be filled as described above.

4.2 SAMPLING EQUIPMENT

The collection of samples of surface water shall be undertaken utilising:

- A plastic bulk sampling container (for example polyethylene, PTFE, PVC or PET)[1] to collect the sample from the watercourse. The container shall be of appropriate volume to fill all the sample bottles (where a water sample is to be analysed for a number of parameters, it is likely that a number of separate sample bottles, each with different preservation techniques, will be required).

- Appropriate sample bottles. Sample bottles shall be cleaned thoroughly before use. For general trace analysis, the bottles should be filled with a 1 mol/L solution of nitric or hydrochloric acid and left to soak for at least one day followed by rinsing with distilled or deionized water. Alternative cleaning methods may be appropriate (for example where analysis of different parameters is required). The cleaning method shall be agreed in advance with the laboratory undertaking the analyses.

- A plastic funnel [1]

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[1] The use of plastic containers is not appropriate where the sample is to be analysed for organics.

- A pH meter, dissolved oxygen meter, conductivity meter and/or thermometer.

Samples collected by direct sampling into sample containers (Section 4.3.2) do not require the use of special sampling equipment. Appropriate sample bottles that have been pre-cleaned shall be used.

4.3 SAMPLE COLLECTION

Water samples shall be collected by either collection of a bulk sample and sub-sampling into separate sample bottles or direct sampling into sample bottles. Direct sampling into bottles shall be undertaken where shallow water is to be sampled, making filling a container impractical; where very clean water is sampled and the use of a sampling container presents an unnecessary potential risk of contamination; or where only one bottle needs to be filled. It shall not be employed for bottles which contain preservatives or where sample filtration is required.

4.3.1 Collection of the bulk sample and sub-sampling

(i) Rinsing container and funnel

Using the sampling container, sufficient of the body of water shall be taken for a thorough rinsing of the container and funnel. The rinse water shall be disposed of downstream of the site or in such a way that it does not contaminate or disturb the site to be sampled. Disposal of rinse water or excess bulk sample shall not itself be a source of pollution.

(ii) Taking the bulk sample

After the rinsing process, a sample of the body of water shall be taken in the sampling container without causing undue disturbance of the surrounding site which might change the nature of the sample. Extension handles shall be wiped if necessary between successive samples using non-contaminating absorbent paper. The sample shall be carried to the place where the bottles are arranged for sub-sampling.

(iii) Sampling by increments

In conditions of low flow or where the source of water is difficult to access, the sample container shall be filled by increments (that is small individual portions using a smaller sampling container). This technique shall also be employed where a large volume of sample is needed.

(iv) Sub-sampling into bottles

The sample bottles shall be thoroughly rinsed with the sample (unless the sample bottles contain preservatives in which case rinsing shall not be undertaken). The sample shall be divided into those types of bottles required using a funnel to guide the flow as necessary. Care shall be taken to avoid aeration of the sample.

When the bottle caps or tops are removed prior to sub-sampling they shall be handled, placed and stored in such a way that contamination or loss is avoided. Care shall be taken that the nature of the sample does not change during sub-sampling and the sample shall be agitated to prevent settlement of suspended solids. After sub-division the bottle caps or tops shall be replaced securely to prevent leakage, loss or contamination of the sub-sample.

When sub-sampling into bottles containing preservatives, the funnel shall be rinsed inside and out to prevent contamination of subsequent samples.

4.3.2 Direct sampling into bottles

Where direct sampling into bottles is appropriate (see Section 4.3 above), it shall be undertaken using the collection method described in Section 4.1.1. The sample bottle shall be rinsed thoroughly before collection of the sample.

5. SAMPLING OF GROUNDWATER

5.1 SAMPLING TECHNIQUE

The sample shall be collected from the monitoring borehole by use of a sampling pump. Where it is not possible to collect samples using this technique, the sample may be collected using an alternative method (such as a bailer) agreed in advance.

5.2 SAMPLING EQUIPMENT

The collection of samples of groundwater shall be undertaken utilising:

- A sampling pump which is appropriate for the parameters of interest in the sample (sampling pumps vary in their suitability for sampling of different chemical constituents). The appropriate sampling pump should be selected.
- A plastic bulk sampling container (see Section 4.2)
- Appropriate sample bottles (See Section 4.2).
- A plastic funnel (The use of plastic containers is not appropriate where the sample is to be analysed for organics).
- A pH meter, dissolved oxygen meter, conductivity meter and/or thermometer.

5.3 SAMPLE COLLECTION

5.3.1 Borehole inspection

The borehole shall be inspected to ensure it is suitable for groundwater monitoring. A description of the borehole including completion details (eg casing, diameter and type) and the full depth of the borehole shall be recorded on the sample report.

5.3.2 Water level dipping

The water level will be measured using a dip meter. Water level measurements shall be taken by lowering the probe down the well or borehole until it encounters the water, causing the buzzer to sound (or light to activate). When this happens, the tape shall be pulled back slowly out of the water until the signal stops. The exercise shall be repeated several times to accurately locate the water surface. The position on the tape shall be accurately marked against a fixed datum point, such as the top of the casing.

5.3.3 Well purging

Purging of the borehole is undertaken to eliminate the standing water in the borehole so that a sample representative of the groundwater is collected. The borehole shall be purged by pumping to waste a volume of water equivalent to at least 4 to 6 times the internal volume of the borehole itself. The pumping time required can be calculated approximately from the volume of water in the borehole and the pumping rate. The well volume (litres) can be calculated from the formula $3.14 \times r^2 \times L \times 1000$, where r is the radius of the well (m) and L is the height of the water column (m).

Prior to purging and at intervals during purging, the pH, temperature and/or electrical conductivity of the pumped water shall be determined. Purging shall be continued until no significant variations ($< \pm$ 10% in terms of conductivity and pH or $\pm$ 0.2^{o}C in terms of temperature) are observed.

Records of purging shall be kept including the rest water level, volume purged, duration of pumping, purging rate, the water level at the time of sampling and the pH, temperature and conductivity readings (if taken). All information shall be recorded on the sample record sheet.

If the maximum aquifer yield is less than the minimum practicable purge rate, the procedure for purging and sampling shall be agreed.

5.3.4 Sample collection

Once purging is complete, the bulk sampling container and funnel shall be rinsed thoroughly with the sample. The rinsate shall be disposed in such a way that it does not contaminate or disturb the site being sampled.

A bulk sample shall be taken, with sample transfer from the well undertaken at a rate less than 100 mL/min. Sub-sampling from the bulk sample into sample bottles shall be undertaken as described in Section 4.3.1.

6. SAMPLE FILTRATION

Filtration is an important factor that needs to be accounted for during both sampling and subsequent sample-preparation steps. Filtration is going to depend on the water-monitoring program, e.g. whole water (dissolved + sediment-bound fraction) or dissolved fraction (Coquery et al., 2005). It is expected that, for priority metals, monitoring will focus on the dissolved fraction, while, for organic pollutants, the whole water should be considered.

Where the determination of "dissolved" species is required, the samples shall be filtered through a 0.45 μm filter paper. Filtration shall be undertaken at the time of sampling or as soon as possible after sampling. The procedure for filtration provided below is intended for filtration using a syringe and disposable filtration cartridge. Filtration may be undertaken using an alternative method agreed in advance.

(i) Preparation

The filtering equipment shall be prepared for use before commencing sampling and shall be placed in a clean dry area to avoid any possible contamination.

The bulk sample shall be collected and those sub-samples/bottles that do not require filtering shall be filled first. If the bulk sample appears to have high suspended solids, it shall be allowed to settle before filtering.

The barrel of the syringe shall be filled completely with the bulk sample and then run to waste away from the bulk sample, other bottles and equipment. This procedure shall be repeated twice to ensure the syringe is thoroughly rinsed.

(ii) Filtration

The syringe shall be filled from the bulk sample to a point above the volume required for the sub-sample (by approximately 10 ml). The filter unit shall be attached to the syringe and then a sufficient volume of sample shall be passed through the filter in order to rinse and wet the filter (approximately 10 ml). This filtrate shall be run to waste away from other bottles and equipment.

The cap/stopper shall be removed from the bottle and placed in a safe area. The required volume of sample shall be filtered into the bottle. If there is difficulty in filtering the sample, the filter shall be disconnected from the syringe and replaced with a new filter. When the new filter unit or assembly has been connected to the syringe, the filter shall be rinsed (discarding the rinse water). Filtration shall be continued until the required volume of the sub-sample has been collected in the bottle.

After filtering, the filter shall be disconnected from the syringe and discarded. If the syringe is to be used only once, it shall be discarded. If the syringe is to be re-used, it shall be rinsed thoroughly and shaken dry before storing in a clean dry place.

7. SAMPLE LABELLING AND RECORDS

7.1 SAMPLE IDENTIFICATION

A unique identification number shall be allocated for each sample and labelled at time of sampling. The system of labelling separate sample bottles intended for different analyses shall be determined before undertaking fieldwork.

7.2 SAMPLE RECORDS

A sample report shall be filled in at the time of sampling. A check-list of information should be provided on a sample report for collection of samples.

8. SAMPLE PRESERVATION

Sample preservation is undertaken to ensure that the concentration of the parameters of interest in a sample do not change significantly in the period between sample collection and analysis. The initial composition of the sample must be maintained from sampling through to analysis. Handling and storage of collected samples is of a great importance during sampling. There are several problems that could appear during sampling and storage of samples such as losses from volatilization, decomposition by means of temperature, UV irradiation, microbial activity or chemical reactions (with e.g. external agents, O_2, CO_2, etc). In order to prevent changes in sample composition, it is good practice to:

- Store samples in the dark
- Keep samples cool (at minimum no warmer than the temperature at the time of sample collection)
- Avoid agitation
- Use appropriate sample containers
- Fill containers completely and seal tightly
- Add preservatives which should not interfere during the measurement step

Techniques generally suitable for the preservation of individual parameters or groups of parameters should be used. The agreement of the analytical laboratory shall be obtained prior to selection of preservation techniques since the appropriate technique varies according to the method of analysis used. Where the addition of chemical preservative is recommended, the chemical shall be of sufficient concentration that the volume added does not affect the concentrations of parameters of interest in the sample due to dilution.

Since preservation techniques vary according to the parameter of interest, where several different analyses are required, it may often be necessary to fill several containers which are preserved in different ways.

Where possible, samples shall be preserved in the field, either by adding chemicals to the sample or by sub-sampling into appropriately labelled sample bottles containing the preservative. When adding chemicals in the field, appropriate laboratory practice shall be followed (for example to ensure cross contamination of samples or stock solutions do not occur). Following the addition of preservative chemicals, the sample shall be gently agitated to mix the sample and preservative.

Where preservation in the field is not possible, the preservation shall be undertaken as soon as possible after sampling.

9. SAMPLE HANDLING AND TRANSPORT

Good practice for the transport of samples shall be followed, including:

- Containers holding samples shall be protected and sealed in such a way that they do not deteriorate and do not lose any part of their contents during transport.

- Packaging shall protect the containers from possible external contamination and breakage and shall not itself be a source of contamination.

- During transportation, the samples shall be kept as cool as practicable (utilising insulated cool boxes and ice packs as appropriate) and shall be protected from light.

- Each sample shall be placed inside an individual waterproof bag or container.

Samples shall be transported to the laboratory in good time for analysis to commence within the maximum recommended holding time for all parameters of interest.

10. FIELD TESTS

Procedures for the measurement of temperature, dissolved oxygen, conductivity and pH using portable field instruments are described below. The procedures are suitable for measurements undertaken in situ and from discrete portions of sample removed from the water.

Measurements on surface waters shall be undertaken in situ wherever possible. In cases where measurement of surface waters in situ is not possible and when measuring groundwaters, the measurement shall be taken from a sample in the bulk sampling container, filled according to the procedures in Section 4 and 5. When taking measurements in a discrete portion of sample, the probes shall be rinsed in distilled water and dried with non-contaminating absorbent paper before placing in the sample container, taking care not to handle the probes directly with the fingers.

10.1 TEMPERATURE

The thermometer shall be placed directly in the body of water to take a reading. After one or two minutes have elapsed and the reading has stabilised, the temperature shall be recorded to the required accuracy.

10.2 DISSOLVED OXYGEN (INSTRUMENTAL)

The dissolved oxygen meter shall be calibrated according to manufacturers' instructions. This usually involves a two point calibration - a zero point calibration with sodium sulphite solution for 2 to 3 minutes and a 100% calibration either in air saturated water or in water saturated air. Calibration in water saturated air involves placing the probe loosely in a bottle containing a small amount of fresh water. The probe membrane should be wiped dry with a tissue and should not touch the water in the bottle. The reading normally takes at least 5 minutes to stabilise.

To measure the dissolved oxygen of the water, the probe shall be gently agitated within the water manually (in a discrete sample, care shall be taken to avoid entraining air). The probe shall be allowed to attain the water temperature and the reading shall be stabilised before being recorded (approximately 2 minutes is usually sufficient).

10.3 CONDUCTIVITY

The conductivity meter shall be calibrated according to manufacturers' instructions.

The reading shall be taken by immersing the conductivity probe in the sample. Temperature compensation shall be undertaken if necessary (although this may often be automatic). The meter shall be allowed to reach thermal equilibrium before the reading is noted. Where a multi-range meter is used the most appropriate range shall be selected.

10.4 pH

The pH meter shall be calibrated according to manufacturers' instructions. Calibration shall typically involve the use two pH buffers which differ by at least 3 pH units and bracket the expected pH range of the test sample.

The measurement shall be taken by gently moving the electrodes in the water until the probe attains the water temperature and a stable reading is given. Once stable, the reading shall be recorded to the desired accuracy.

11. DETECTION LIMITS

Analytical suites and detection limits shall be specified for all samples before commencing analysis.

Analytical suites and detection limits shall be specified for each sample when the sample details are known and shall be appropriate for the objectives of sampling, the nature of the samples collected, the standards to which the samples will be compared, the capability of the laboratory and the budget available for analysis.

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