

WATER QUALITY MONITORING

PREPARATION & CONDUCT OF STUDIES
FOR THE TRACE ANALYSIS OF
CROP PROTECTION PRODUCTS IN WATER

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1. INTRODUCTION

This document describes procedures for the sampling of surface and groundwaters in order to subsequently determine concentrations of crop protection products that might be present. Prior to initiation of such monitoring work, detailed consideration must be given to the objectives of the study.

A protocol should be developed that defines the aim of the study, the substances (active ingredients and/or degradates) to be monitored, the analytical methods to be employed and the sampling sites and time points to be used. The protocol should also detail the sampling procedures to be followed, the sample size requirements, together with the sample shipment and storage needs. Geologic, hydrologic, agricultural and climatic information may need to be collected to allow interpretation of results and this should also be documented in the study protocol.

The development of such a protocol is fundamental to the success of a monitoring study and will require inputs from a wide variety of disciplines including analytical chemistry, hydrogeology, agronomy and engineering.

This monograph provides general help for the sampling aspects of a water quality monitoring study and may provide assistance for the preparation of the study protocol. More detailed information may be found in the literature referenced in the Bibliography section.

2. GENERAL MONITORING CONSIDERATIONS

Water quality monitoring programs are usually conducted with one, or sometimes both of the following objectives:

- a) Regulatory purpose: to provide a higher tier assessment of potential environmental exposures of parent and/or degradates resulting from normal product use in a local or regional setting. Data from such monitoring usually support higher tier ecological or human health risk assessments.
- b) Research purpose: to quantify the specific transport and degradation mechanisms of parent and/or degradates in actual field settings, typically focusing efforts on a single mechanism such as runoff/erosion, tile drainage or leaching.

The specific study objectives have important implications on the sampling strategies and it is therefore essential that the objectives be clearly defined prior to protocol development and study initiation.

2.1 Analytes of interest

Careful consideration should be given to which substances are to be measured in a monitoring study. The analytes of interest may be specific, but could include degradates or other compounds of similar chemical class or use-pattern. The early identification of the analytes of interest is essential since analytical methods may need to be developed or refined to achieve desired limits of quantification.

2.2 Sampling Methods and Containers

The choice of analytes also drives the requirements for sample size, collection method, and shipping/handling procedures. Generally, 0.5 – 1.0 litre amber glass bottles are accepted as appropriate for most water sampling needs. However, in some circumstances, Teflon™-coated or even plastic bottles may be appropriate, provided the sampling container is compatible with the analytes of concern. The sample volume required is dictated by the sensitivity of the analytical method and the desired detection level.

Containers may be re-rinsed at the laboratory and/or triple-rinsed with the sample water (ground or surface) prior to collection. If volatile organics are to be analysed, then sample vessels should be completely filled during sampling to prevent air spaces. Such samples should not be frozen since the sampling containers may rupture due to expansion.

Storage stability studies conducted under the conditions of shipping are generally used to ensure integrity of samples from collection to analysis. Sampling and shipping procedures should be developed, tested and documented. These procedures should then be followed exactly at each sampling interval. Modification to sampling procedures may change sample composition and lead to ambiguous results.

The overriding objective of a water quality monitoring program is to obtain representative and reproducible sub-samples and careful consideration should therefore be given to the size, number and frequency of samples collected. Often it will be necessary to confirm results with repeat analysis and therefore early consideration should be given to whether such confirmation work should be conducted on the remaining sample or from the analysis of a replicate sample. It should be remembered that water (even groundwater) is a dynamic medium and that no two samples are necessarily replicates unless a larger sample is taken and subsequently split into two small sub-samples.

2.3 Analytical method validation

The analysis of water samples for trace levels of crop protection products should be conducted only with validated analytical methods. Water samples from various sources can differ widely in physico-chemical properties, (e.g. pH, dissolved organic material, ionic strength and suspended solids) and prior to adopting an analytical method it is important that the method is validated for all analytes in the range of matrices that are likely to be encountered during the monitoring study.

As part of the method validation, recovery data should be obtained by analysing multiple fortified samples (typically five) at the method's limit of quantification (LOQ) and at a concentration exceeding those expected during the study (or 10 x LOQ). Mean recoveries for each fortification level should fall between 70 and 110%, ideally with the mean in the range 80 to 100%. The precision (relative standard deviation, RSD) of the method should be determined for each recovery level and the data set as a whole. The RSD should be less than 20% for each recovery level. A minimum of five calibration standards should be chromatographed to check the linearity of the detector. The calibration standards should encompass the expected analyte concentration range, normally 20% LOQ up to 120% of the highest expected concentration or 10xLOQ. The correlation coefficient (r) of the resulting calibration lines should be >0.99.

In a monitoring situation, it is often difficult to obtain true untreated 'control' samples for use in the validation and subsequent sample analysis. In these situations, it is advisable to select water samples for 'control' purposes from sources outside of the monitoring area. These samples should be free of the analytes of interest but as similar as possible to the physico-chemical properties of the water samples likely to be encountered during the monitoring.

During sample analysis, a minimum of one procedural recovery and one reagent blank should be analysed with each set of water samples to demonstrate acceptable method performance (70 -110%). Confirmation of positive residues is usually necessary if the monitoring method utilises a non-specific detection system (e.g. GC-ECD or LC-UV). No confirmatory analysis is normally conducted if the method of analysis is specific to the analyte or where selective detectors are employed (e.g. GC-MS, provided 3 fragment ions with $m/z > 100$ are monitored, GC-MS/MS, LC-MS and LC-MS/MS).

Further details of the validation and use of monitoring methods can be found in SANCO/825/00.

2.4 Siteselection

There are a number of procedures available for site selection for different types of studies, details of which may be found in the Bibliography section of this monograph. There are, however, some general principles that should be considered prior to selecting sites for monitoring:

- a) Is the study aimed at assessing water quality in general use or especially vulnerable conditions? Many monitoring studies are deliberately targeted to vulnerable or “worst -case” areas to assess the potential for water quality deterioration.

VulnerableGroundWaterSites:

These include sites with sandy soils, high rainfall, shallow depth to ground water, low organic matter, or areas prone to excessive preferential flow.

VulnerableSurfaceWaterSites:

These include sites with water bodies bordered by agricultural land with excessive slopes, heavy soils, intense rainfall, little buffer between treated field and the water body, or high density of field drain outlets.

More representative studies (surveys) may be conducted to assess ground or surface water quality on a regional or national scale. Such studies may include vulnerable areas but would be aimed at being representative of the areas in which the product(s) is/are used.

- b) When selecting sites it is essential that land use (both current and historical) is documented together with a thorough description/outline of the soil textures, topography, hydrology, geology, depth to ground water and/or flow rate of surface water and weather patterns. Only with an understanding of this information can the results of monitoring be understood, trends identified and environmental impact assessed.

2.5 Data recording

In all monitoring programs, it is essential that data be recorded accurately and legibly and that Good Laboratory Practice (GLP) principles are followed (whenever possible). In the site selection phase, however, it should be recognised that the collection of information to the rigorous standards of GLP may sometimes be impossible. For example, it is often impossible to validate crucial site -specific information like maps, GIS data layers, and expert knowledge. Therefore, this phase of monitoring studies is often conducted outside the scope of the GLP study protocol.

Once monitoring sites have been identified, a protocol should be written that describes in detail the sample collection, shipping, storage and analytical phases. It is usual to conduct these phases of the monitoring study to GLP standards of data recording and inspection. Where circumstances dictate that the specific requirements of GLP cannot be met, it is advisable that the study be conducted in the 'spirit of GLP'. Monitoring data should always be recorded accurately and legibly, with sample labelling, chain of custody, storage conditions and analytical records all documented and maintained to the highest standards.

3. SAMPLING OF SURFACE WATERS

3.1 General considerations

The nature of surface water bodies varies widely from small ponds to large lakes and from streams to large rivers, all of which can vary not only in size but also in flow rate.

Depending on the aims and the protocol for a particular study, a sampling programme will need to take into account many factors, the major ones being:

- a) Possibility and proximity to point sources of entry into the surface water body (i.e. drain outlets, run-off channels or sewage outlets).
- b) Horizontal distribution of sampling positions (i.e. the area to be covered).
- c) Vertical distribution of sampling positions (i.e. the depths from which samples are needed).
- d) Frequency and timing of sampling (i.e. annually, monthly, or in response to precipitation or run-off events, at average flow rates, etc.).
- e) Method of sampling.
- f) General observations such as turbidity, odour, colour, pH, temperature, conductivity, dissolved oxygen.

3.2 Horizontal distribution

Depending on the aims of a particular study, the area of sampling needs to be defined and the number of sampling points established. Protocols can vary from an investigation of point source contamination in a relatively confined area, to more general investigations of the presence of crop protection products in water bodies covering much larger areas, or the transport and fate of products through the watershed.

Sampling density and frequency will need to be adapted accordingly. In cases where the protocol requires samples to be taken upstream and downstream from a specific point of entry into a surface water body, the downstream site should be located where the input is homogeneously distributed within the water body.

3.3 Vertical distribution

The concentration of a crop protection product in water can vary with depth between the surface and the sediment, and the concentration profile can vary with time. For these reasons, the protocol for a study needs to take into account whether samples from different depths should be taken and with what frequency.

3.4 Methods of sampling

The simplest way of collecting sub-surface water samples is to immerse a sampling container, sealed with a plunger and attached to a length of stainless steel tube, into the water body. When under the surface, the plunger is removed to allow entry of water, and then re-sealed by means of a lever mechanism. Although this mechanical method is preferred, if essential samples may be taken by hand by carefully lowering an open glass jar into the water to effect sampling.

In some situations a peristaltic pump may be used to obtain samples from greater depths and from less accessible locations. A procedure for using a peristaltic pump is as follows:

Clean, medical grade Teflon™ tubing is installed in the pump head (following manufacturer's instructions) allowing sufficient tubing on the discharge side to allow easy transfer of water into sample bottles. A length of suction intake tubing to reach the required sample depth is attached to the intake side of the pump tubing. Several litres of water sample should be allowed to purge through the system before a actual sample collection. Low flow rates (typically <100ml/min) should be used to ensure minimal mixing of adjacent zones. Sample bottles are filled by allowing the pump discharge to flow gently down the side of the bottle with minimal turbulence.

4. **SAMPLING OF GROUNDWATER**

4.1 General considerations

The collection of representative ground water samples is more difficult and expensive than surface water, principally because of the relative inaccessibility of the sub-surface environment. Some general rules to follow when developing a ground water monitoring program are:

- a) Avoid introduction of contaminants during purging and sampling. Where possible use the same devices for both procedures.

- b) Where possible avoid the use of bailers as these need to be removed from the well continually during use and may cause contamination.
- c) Where possible use submersible or above ground pump together with "clean" sample tubing of Teflon™ or a compatible plastic.
- d) Avoid cross-contamination between wells or soil sampling holes. If possible, use different sampling equipment, or clean the equipment, between each sampling point. If the same equipment must be used, sample the cleanest well first and establish a cleaning procedure between wells and always decontaminate equipment between wells.
- e) Avoid sampling stagnant water by purging wells for 3-6 casing volumes or until pH, temperature and conductivity have stabilised. When wells de-aerate water, sampling should be conducted soon after the well recovers and within 24 hours of the well evacuation.
- f) Avoid aeration of water during sampling. This can especially affect the content of volatile products.

If the objective of a study is to determine the presence or absence of chemical residues in ground water that serves as an existing water supply, it may be possible (and inexpensive) to collect samples at one or more wells which use this supply, provided the existing wells are properly constructed and sited and can supply representative samples of ground water. However, if the objective is to define the horizontal and vertical distribution of agricultural chemical residues at a test location, then monitoring wells and/or special sampling equipment may be necessary, significantly increasing efforts and cost.

4.2 Hydrogeologic considerations for selecting a sample site

In deciding on a protocol for the development of any ground water monitoring program, a general understanding is needed of subsurface conditions in the sampling location and their relationship to chemical migration. In particular, it is important that the flow rate and direction of the ground water being monitored is determined, together with the nature of the aquifer (confined or unconfined) and the likely recharge area (not necessarily the overlying zone). This information is important in order to:

- a) Select sampling locations.
- b) Determine the scope of the monitoring program.
- c) Determine the number of sampling sites required.
- d) Determine the frequency and duration of sampling.

4.3 Sampling from existing wells

4.3.1 Site selection

In the case of existing wells there are two general elements for sampling which must be considered. The first is site selection. The wells best suited to meet the program objectives should be selected. In order to make this judgement, it will be necessary to review existing data on hydrogeologic conditions and conduct a survey and inspection of candidate wells.

The purpose of this pre-monitoring work is to:

- a) Determine those sampling locations which are representative of the ground water flowing through and away from the area of interest. This requires consideration of the vertical position of the well screen intake and the horizontal location relative to chemical use and anticipated ground water flow direction.
- b) Determine if the particular well is of suitable construction and remains in sound condition. Video cameras may be employed to check the integrity of the inside of monitoring wells. Generally, wells that are finished at ground level (flush-mounted) are unsuitable for monitoring purposes since they are prone to surface water infiltration.
- c) Determine the potential for contamination of the well and subsequent samples by sources other than the location of interest, such as old disposal sites, surface water run-off, septic systems or irrigation wells used for chemigation.

Unless all of these aspects of existing wells can be investigated and confirmed, then it is preferable to install new monitoring wells.

4.3.2 Sampling procedure

Generally, well water samples should be collected prior to any storage tank or water treatment. If the selected wells are in continuous use, pre-sample purging (pumping) may not be necessary. If the wells have not been in use during the 24 hours prior to sampling, pre-sample purging should be conducted. At a minimum, purging requires the removal of 6 casing volumes within 24 hours prior to sample collection. It is recommended to continue purging until constant pH, temperature and conductivity are obtained.

Samples can be obtained directly from the tap by simply filling the properly prepared and labelled containers.

4.4 New monitoring wells

In the development of a monitoring plan which uses wells installed especially for this particular purpose, it is of the utmost importance that the wells are located, designed and constructed properly. The well installation usually represents the most costly and non-repeatable portion of the monitoring plan. Primary objectives of monitoring wells are:

- a) To provide access to the ground water and usually to a discrete portion of the groundwater. This is usually achieved through relatively short intake screens.
- b) To determine the vertical and horizontal distribution of any detected chemical residues. This is usually achieved through clusters of wells with well intake screens installed at varying depths.

In order to accomplish these objectives the following general requirements must be taken into consideration.

4.5 Selection of monitoring well site

The general considerations for locating monitoring well sites are the same as for selecting existing well sites. The wells should be sited in vertical and horizontal locations anticipated to intercept ground water which flows through the use location under investigation, which cannot be impacted by other sources such as a disposal site or surface water runoff.

As with existing well site selection, consideration of hydrogeologic conditions through existing literature and consultation with experienced professionals is essential at this point. It is preferable that new wells are installed under the direction of a professional geologist and that a boring log is completed to fully describe the formation in which the new monitoring well is sited.

4.5.1 Well construction

Extreme care needs to be taken when installing a well in a treated field. Prior to drilling the surface soil (most likely to be contaminated) should be removed to a depth of at least 30 cm and placed aside. Drilling should then be conducted within the confines of the excavated area. Drilling equipment should be decontaminated by steam cleaning prior to each borehole advancement.

Material of construction

The material selected for well construction should have the least potential for affecting the monitoring results. There are several types of material used in well construction including carbon steel, galvanised steel, stainless steel, PVC and Teflon. All have been used successfully, but consideration of possible interaction between construction materials and the analytes of interest is essential and should be checked prior to well installation.

In addition to selection of appropriate materials, all casing and screen materials should be thoroughly cleaned prior to installation. This may, in the case of steel casing, require steam cleaning to remove any oil residues.

Well diameter

The diameter of the well need only be as large as necessary to allow for the introduction of the planned sampling equipment. A well diameter of 5 cm is normally recommended. The size of the hole in which the well is to be constructed should be approximately 5 cm in diameter larger than the planned casing to allow for placement of screen packing and grout seal. Excessively large holes should be avoided as they may affect water level readings and purging requirements.

Well depth

For regulatory monitoring studies designed to evaluate the leaching potential of normal product use on surficial ground water in a vulnerable hydrogeologic setting, the well depth is of particular importance. As a result, it is usually appropriate to select a site with a relatively shallow depth to surficial ground water (typically, 10 m or less). However, these criteria can vary depending upon the depth to ground water in the region of interest.

Well screen

The screen is part of the well through which water enters the casing and must be properly constructed and developed to avoid subsequent sampling problems. Commercial well screens for use in water supply wells are recommended for most monitoring wells even though well efficiency is not a primary concern.

Design criteria for the intake part of the well are:

- a) The screen of the intake part should have sufficient opening to permit sufficient inflow of water from the formation
- b) The slot openings should be just small enough to keep most of the natural formation out, but as large as possible to allow easy flow of water.
- c) The sand pack between the screen and the formation should prevent soil particles from clogging the screen.

Well screens for regulatory studies should generally range between 0.3 to 2.0 meters in length and be placed at or immediately below the top of the water table. This design permits sampling of the highest concentrations in ground water. It is generally recommended that clusters of wells be used with screens installed at two or more progressively deeper depths to provide information on the potential impact of leaching on deeper ground water. In certain situations, the use of multilevel samplers may permit the sampling of ground water from various depths within a single borehole.

Well development

Following well installation, the well should be 'developed' by pumping, until the well is free of fines/debris and the water is clear and sediment free. Well development is normally conducted using a large capacity pump and the process helps to settle the sand -pack surrounding the well -screen and ensure good hydraulic contact between the sand -pack and the surrounding aquifer material.

Well seal

All wells should be sealed at the surface to prevent contaminant migration from the surface. This is generally accomplished with a cement/bentonite seal of at least 1 meter in depth. The seal should be finished above grade by the widening of the seal to form a protective well pad to prevent direct run -in. In locations where winter frost damage is possible, the well pad should be reinforced with steel or fibreglass.

Wellhead protection

All monitoring wells should be protected above ground to prevent deliberate or unintentional damage or contamination. Wells should have a stick -up sufficiently high that the well cannot become engulfed during heavy rainfall or floods. All wells should be protected above ground by a steel casing and associated locking cap. Buffer posts should be positioned around the monitoring well to prevent damage by passing vehicles or wild animals. In certain situations, it may be impractical to finish wells above grade and it may be necessary to finish wells at the land surface or even below grade. In these situations it is imperative that special precautions are taken to avoid surface water or particulate contamination from entering the well.

4.5.2 Drilling methods

Selection of the drilling method best suited for a particular job is based on the following factors in order of importance:

- a) Hydrogeologic environment
 - Type(s) of formation(s).
 - Depth of drilling.
 - Depth of desired screen setting below water table.
- b) Location of drilling site -dry land or marshy.
- c) Design of monitoring well desired.
- d) Availability of drilling equipment.

Some of the methods commonly used for the installation of monitoring wells are listed below. All have advantages and disadvantages depending generally on site specific conditions and program objectives. A more detailed discussion of these and other drilling techniques is presented in materials listed in the Bibliography section.

- a) *Hollow-Stem-Continuous flight auger* -drilling is accomplished by rotating the auger into soil which acts as a large screw carrying cuttings to the surface on the rotating flights.
- b) *Mud Rotary* -Drilling fluid pumped down the drill stem, cooling the bit and returned to surface through the annular space, carrying cuttings. Care should be exercised to ensure that the mud does not contain a contaminant and “artificially” recharge groundwater.
- c) *Air Rotary* -Operates in the same manner as mud rotary except air is used for drill rotation.
- d) *Well Point* - Generally driven without prior hole drilling by a mechanical hammer or, under shallow groundwater conditions, by hand.

Issues to be aware of when choosing a particular drilling method are:

- a) How will the fluid be introduced during drilling affect future sampling and well hydraulics?
- b) Can samples of soil and rock be readily collected for descriptive purposes or residue analysis?

Care must be taken not to contaminate samples or monitoring wells. The evacuation and sampling equipment needs to be decontaminated prior to working on each well. Bailers, the submersible pump (outside), pump hose (outside), and other equipment must be thoroughly washed when moving from one well to the next.

Rope or wire used for bailers or pumps should be decontaminated before using on succeeding wells. Generally, simple washing with a detergent followed by rinsing with distilled water and one or two bailings of well water is sufficient. Alternatively, steam cleaning may be used.

5. SAMPLE PRESERVATION AND STORAGE

Close-capped glass, plastic or Teflon™ bottles may be used for collecting water samples, although compatibility with the analytes of interest should be confirmed prior to sampling. Compatibility tests should also be conducted to ensure no batch-to-batch variation when using plastic bottles

In most cases, rapid refrigeration of the samples has proved adequate for preservation of the samples for analysis. The samples may be shipped in an insulated container with ice. This method has proven effective for shipment with chemicals stored in a proper container. However, if the samples are to be shipped for long distances, dry ice should be used for suitable containers (i.e. not glass). The laboratory should then keep the containers refrigerated and protected from light until the analysis is performed. The primary exception to this general handling is extremely volatile chemicals that may require further protection against loss or cross contamination. Stability tests should be performed to ensure the appropriateness of the sample shipping and storage procedures.

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