Water sampling: Traditional methods and new approaches in water sampling strategy

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This article outlines the issues that need to be considered when planning water sampling for chemical monitoring and provides guidance on the work required. In addition, it considers the limitations associated with current monitoring practices based on spot sampling and presents some existing technologies that may used to complement standard spot sampling.

Keywords: Biological early warning system; Chain of Custody; Chemical monitoring; Emerging tool; Passive sampler; Uncertainty of measurement; Water Framework Directive; Water sampling; WFD

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1. Introduction

The Water Framework Directive (WFD) of the European Union (EU) is one of the most important pieces of environmental legislation produced in recent years. The objectives of the WFD are to improve, protect and prevent further deterioration of water quality across Europe. The term ''water'' within WDF includes most types of water body – not only groundwater, but also surface waters (lakes and rivers) and coastal waters. Monitoring is required to cover a number of ''water-quality elements'' including [1]:

- physicochemical properties (temperature, density, color, turbidity, pH value, redox potential, conductivity, surface tension, suspended solids, total/dissolved organic carbon);
- hydromorphological status (erosion and bench river characteristics);
- biological (distribution and composition of the species and biological effects); and,
- chemical monitoring (with particular emphasis on the contaminants in the list of priority pollutants).

A measurement almost invariably involves the process of taking a sample (i.e. sampling is an important step within the water-monitoring process). Although significant efforts have been made in designing procedures for analytical measurements, very little attention has focused on the sampling stage. Historically, measurement scientists have primarily been concerned with measurements made within laboratories, and the process of sampling has been conducted by different people, who often work in separate organizations. The measurement scientist's knowledge of the sampling process is sometimes limited.

This article discusses the issues that need to be considered when planning water sampling for chemical monitoring and provides guidance on the work required. In addition, it considers the limitations associated with current monitoring practices based on spot sampling and presents some existing technologies that may be used to complement standard spot sampling.

2. Sampling and monitoring

Sampling could be defined as a process of selecting a portion of material small enough in volume to be transported conveniently and handled in the laboratory, while still accurately representing the part of the environment sampled. The main difficulties in sampling are representativeness and integrity.

Many people think that the analysis starts when the sample arrives in the laboratory. However, sampling is an integral part of the analytical process, so analysis starts with sampling. Sampling is so important that, in some cases, it

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represents the main contribution to the error of the whole analytical process, especially when trace contamination is being measured. The relative error, as well as the absolute possible error due to sampling, sampling preparation and instrumentation analysis, differs from matrix to matrix and it depends greatly on the range of concentration of analytes. In general, the possible error of instrumental analysis is relatively low. For analytes in water at the sub-μg/kg level, the possible errors due to sampling and sample preparation are both relatively great [2].

Sampling should always start by defining the purpose of the measurement [3,4]. If the different stages are under the responsibility of different people, there needs to be good communication between all parties involved. Sampling planners and analytical scientists need to optimize the whole measurement procedure (including the sampling step). Both need to discuss the objectives of the measurements with the customer. Once the purpose of the analysis has been established, a sampling plan should be developed to achieve the purpose. This plan should be written as a protocol (standard operation procedure, SOP) that includes the following aspects (Fig. 1):

1. when, where and how to collect samples;
2. sampling equipment, including its maintenance and calibration;
3. sample containers, including cleaning, addition of stabilizers and storage;
4. sample-treatment procedures (e.g., drying, mixing and handling prior to measurements);
5. sub-sampling procedures; and,
6. sample record-keeping (e.g., labeling, recording information, auxiliary information, and chain-of-custody requirements).

The sampling plan should be written according to the purpose of the analysis and in advance of performing field sampling. Development of a sampling plan offers several advantages:

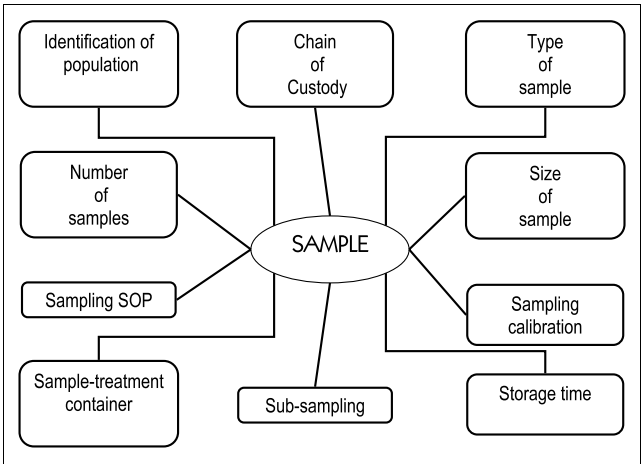

Figure 1. Items to be considered in developing a sampling plan.

1. it forces constructive thinking and stimulates suggestions and criticisms;
2. it avoids misconceptions, misunderstandings and problems if there are changes in personnel;
3. it offers guidelines and SOPs to sampling personnel; and,
4. it provides documentation for quality assurance (QA).

3. Sampling as a source of uncertainty of measurement

The act of sampling introduces uncertainty into the reported measurement. The sources of errors are quite numerous and they appear even before performing field sampling because of inadequate design of the sampling plan. Even when procedures are nominally correct, there will be slight variations in the procedures due to ambiguity in measurement protocols and to minor adaptations that are made to protocols in real-world sampling. Whether high levels of uncertainty lead to unacceptable levels of reliability in the decisions based upon them depends upon rigorous evaluation of fitness for purpose. Sampling-uncertainty estimation is outside the scope of this article, but it has been described in many papers [5–9].

Table 1 gives a summary of the potential sources of errors during sampling and the issues to be taken into consideration when performing sampling.

Sampling location is important in water-sampling strategy. The sampling site should represent the environment under study. The optimal selection of sampling sites is related to the objective of the program (e.g., whether it is trend detection, regulatory enforcement, or estimation of pollutant loadings). The placement of sampling sites can be considered on three levels [10]:

1. macrolocation is concerned with the selection of which length or tributary of a river should hold a sampling station;
2. microlocation is concerned with where in a selected length of river a station should be placed; and,
3. representativeness determines where and how a sample may be taken at a chosen site.

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 of the program.

The location, in space (or time), for sampling is rarely specified exactly. The sampler has to make such decisions, hopefully on objective criteria. However, as heterogeneity is inevitable (in space or time), such decisions will affect the estimated concentration. It is well known that sampling may be biased (e.g., by inappropriate timing where temporal fluctuations occur, or by access restrictions). Heterogeneity always gives rise to

Table 1. Sources of error in sampling

Sampling stage (decision making)	Possible sources of error
Definition and sub-division of the field	Heterogeneity of the sample; spatial and/or temporal change of pollutants: hot spots
Sampling method	No representative statistics; skew distribution; contamination or analyte loss
Number of samples	Few replicates; absence of representativeness
Sample mass	Absence of representativeness
Moment of sampling	Seasonal changes; climatic conditions
Sampling	
Experimental conditions	Matrix effects; lixivation or irreproducible deposits
Bottling	Contamination or extraction by the equipment or container material; volatilization
Storage during sampling	Contamination or losses by volatilization; chemical reactions (change of species)

uncertainty. If the sampling target was perfectly homogeneous, this contribution would be minimal. If the test portion is a few milligrams, then nearly all material will be heterogeneous and the sampling step will contribute to the uncertainty in measurement of analyte concentration.

Hydromorphological and hydrological conditions and intermittent chemical releases [11,12] associated with industrial or urban wastewater effluents, bed-sediment re-suspension and diffuse pollution (e.g., run-off from periodic application of pesticides to agricultural land) lead to spatiotemporal variations in the physico-chemical characteristics of water. Sampling frequency is therefore 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).

Apart from representativeness, one of the main difficulties in sampling is preservation of the sample [2–4]. The initial composition of the sample must be maintained from sampling through to analysis. If this is not the case, the final conclusions will not reflect the initial situation. For all of that, 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:

- losses from volatilization;
- decomposition by means of temperature, UV irradiation, microbial activity and chemical reactions (with, e.g., external agents, O_2, CO_2, sample containers or container walls).

Several approaches have been applied to preserve sample integrity:

- protecting samples from external agents (e.g., using brown-glass containers);
- addition of preservatives (in this case, the selected preservative should not interfere during the measurement step); and,
- storage of the samples at low temperature (e.g., for trace-metal analyses, waters are typically stored at 4°C, while sediment and biota have to be frozen).

Storage at higher temperatures can enhance bacterial growth in solution and on the container surfaces, resulting in losses of metals. Acidification of water samples will inhibit bacterial growth, but it is only recommended if total acid-soluble metals are being measured, because of the solubilization of particulate metals. For filtered samples, acidification is appropriate, unless speciation measurements are going to be performed. For sediments, frozen storage is preferable because, at higher temperatures, samples are readily oxidized. Biota samples are also better preserved by freezing.

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 programme [13]:

- whole water (dissolved + sediment-bound fraction); or,
- dissolved fraction.

It is expected that, for priority metals, monitoring will focus on the dissolved fraction, while, for organic pollutants, the whole water should be considered. Filtration is usually performed with 0.45-μm filter-pore size of different materials (e.g., glass fiber or cellulose acetate). Unless the membrane filter and filtration apparatus used for water samples is rigorously cleaned by soaking in dilute acid followed by distilled water, contamination can be a major problem. For ultratrace analyses, test filtrations of distilled water are recommended to ensure that no contamination is present. Concerning the water volume to be filtered, the effective filter-pore size can change during the filtration of large volumes, especially if there are appreciable amounts of suspended solids [2]. Following filtration, appropriate water-sample-preservation techniques are required to prevent further losses or changes.

Of special importance in sampling is the nature of the sample containers. The material should be resistant to the preservative conditions and not interact with the analytes as that could lead to sample contamination or losses of analytes. The influence of the container increases as the concentration level decreases. There are several materials available: glass (not for trace elements, except for mercury, as it is very fragile and heavy to

transport), plastic (polyethylene could react with organic solvents and is not suitable for pesticides) and polytetrafluoroethylene (Teflon). The closure should safely seal the container, while remaining inert with respect to the contents. Both container and preservatives are going to depend on the type of analyte and the technique used for further analyses.

Contamination of the samples can occur from several sources (e.g., adsorption of atmospheric gases, container and surroundings). To determine the extent of contamination or losses during field sampling, the process should include field blanks, container blanks and trip blanks. Field blanks are bottles filled with distilled water indicating the potential contamination sources during sampling and travel to the laboratory.

From all the above, sampling can produce high levels of uncertainty simply through the routine application of an accepted measurement protocol to a highly heterogeneous material. These errors are quite numerous and cannot be controlled by applying Certified Reference Materials (CRMs).

4. Traditional methods in water sampling

Currently, the most commonly used method for measuring levels of chemical pollutants for all three modes of monitoring is spot (bottle) sampling, followed by extraction and instrumental analysis. This methodology is well established and validated, so it has been accepted for regulatory and legislation purposes. However, this approach is only acceptable if it is representative of the chemical quality of water at a particular sampling site. We need to consider that spot samples are collected at a given location and time, and that the information obtained is unique to the place and the time selected.

For surface waters, samples are often collected by directly filling the sample bottle. For deeper water layers, below about 0.5 m, these methods do not work any more, so dedicated water samplers are used. They are lowered in an open condition on a rope or steel cable and remotely triggered to close. A third option is the use of pumps (e.g., peristaltic pumps offer the option of collecting larger amounts of water, and may be used together with in-line filtration, thus avoiding contamination (air dust) in the field). In most sampling operations, there will be measurements carried out on site, possibly even in situ. This is necessary as several parameters (e.g., pH, temperature and dissolved oxygen) cannot be analyzed adequately after transport to the laboratory [14]. Portable instruments should be properly cleaned and calibrated before starting the measurements.

One approach to obtaining a more representative picture of the water quality over time is by using automatic samplers. They comprise either a set of small bottles that allow , e.g., collection of a discrete sample every hour, or one big bottle that collects sub-samples at different time intervals. The collection regime is either time-dependent, when samples are collected at regular pre-set time intervals (e.g., 24 h) or they can interface with flow-measuring devices to sample in response to discharge changes (e.g., a sudden increase in the flow following a storm). These devices are very suitable for protected areas (e.g., drinking-water-intake sites) for protection against accidental pollution. Some of them can incorporate alarm or early-warning systems in order to generate an alarm if accidental pollution takes place. The main disadvantages of these systems are cost and maintenance.

The WFD states that water quality is also determined by biological characteristics, so-called ''ecological status''. Indicator organisms to be collected include algae, bacteria, fish and macro-invertebrates. Benthic macro-invertebrates (e.g., mussels and worms) are bottom-dwelling organisms that live in or on the sediment of streams, rivers, lakes and the sea. They are more or less stationary, they do not migrate like fish, and are therefore a good indicator of the pollution status of the site investigated.

For shallow waters, where it is possible to walk through the stream, collection is done by hand picking, or using a net held against the stream. For deeper waters, one needs to use samplers (e.g., a van Veen or Patterson grab sampler). After collection, sediments are sieved over, e.g., a 2-mm-mesh sieve. Analysis includes identification of the species and counting.

All samples collected on the field required a Chain of Custody (COC) and field-data sheet. These documents should detail the following information:

- exact location of the sampling site;
- information relating to measurement on site and every observation that could have further influence on the study;
- samples collected during sampling period; and,
- date and time of collection.

The field-data sheet must be filled in while sampling and the COC once the sampling has been completed. Once the COC has been filled in, it must be placed in the box containing the samples. The samples must be delivered to the laboratory as soon as possible. The COC should be maintained unbroken during the whole procedure. The samples should be registered as soon as they arrive at the laboratory. Sample log-in is important for legal purposes and tracing the sample. The following information should be required in the log-in:

- sample-number code;
- name of the client;
- name of sampler;
- sampling method number; and,
- sample-storage location.

Table 2. ISO guidelines for water sampling

Guidance	ISO reference
Water Quality-Sampling- Part 1 Guidance on the Design of Sampling Programme	ISO 5667-1:1980/Cor 1996
Water Quality-Sampling Part 3 Guidance on the preservation and handling of water	ISO 5667-3:2003
Water Quality- Sampling Part 6 Guidance on sampling or river and streams	ISO 5667-6:2005
Water Quality-Sampling Part 19 Guidance on sampling on marine sediments	ISO 5667-19:2004 .
Water Quality- Sampling Part 9 Guidance on sampling from marine waters	ISO 5667-9:1992
Water Quality- Sampling Part 2 Guidance on sampling techniques	ISO 5667-2:1991

Besides the computer log-in, it is mandatory to keep the log-in as hard copy.

Table 2 shows the ISO guidelines for water sampling. In general terms, these guidelines set out the principles to be applied to the design of sampling programmes, sampling techniques and the handling of different samples included in water-monitoring programmes (rivers and streams, marine sediments, sea water and tidal water). These guidelines are based on conventional sampling techniques and are used by most people involved in water-monitoring programmes. Each of these guidelines has been developed for a particular kind of water sample and they cannot be used for others.

5. Limitations of, and alternatives to, conventional water sampling

The currently used conventional sampling approaches suffer from several limitations:

1. spot water samples reflect residue composition only at the moment of sampling and may fail to detect episodic contamination;
2. quality control and physical difficulties are often encountered when large volumes of water must be collected and extracted for quantifying and assessing trace organic contaminants;
3. concentrations of truly dissolved contaminants are not accurately measured by most conventional approaches; and,
4. they are expensive and labor-intensive.

A more representative picture of water quality can be obtained using new approaches and emerging tools in sampling, including [15]:

1. a higher frequency of sampling;
2. automatic sequential sampling to provide composite samples over a period of time;
3. continuous, on-line monitoring systems (e.g., the SAMOS system (for the detection of pesticides)), and (new) sensors;
4. biological early warning systems (BEWSs) that sample if there is a pollution alarm; and,
5. so-called passive samplers, which mimic biological uptake.

Among these methods, passive-sampling technology has the potential to become a reliable, robust and cost-effective tool that could be used in monitoring programmes across Europe. In passive sampling, analyte concentration is integrated over the sampling time. This sampling approach is called time-weighted average (TWA) sampling. Passive sampling is less sensitive to accidental, extreme variations of the pollutant concentration. Most passive-sampling devices comprise a receiving phase and a diffusion-limiting barrier. The receiving phase is usually a sorbent material or organic solvent, which binds the sampled chemicals. Among the most widely-used samplers are semi-permeable membrane devices (SPMDs) for hydrophobic organic pollutants and the diffusion-gradient in thin-films (DGTs) for metal and inorganic compounds [16,17].

Solid-phase microextraction (SPME) has also been used to determine TWA concentration. The device was designed so that the overall mass-transfer was contained within the static water inside the needle as that ensured that mass uptake could be predicted with Fick's law of diffusion and the sampling rate is less affected by water turbulence [18]. This study extended the application of SPME technology to long-term water sampling.

The passive-sampling approaches offer a number of advantages compared to the conventional. Passive samplers provide an average concentration over a deployment period of up to a month, are not dependent on a power or other energy supply and can be deployed in a wide range of environments. However, validation and quality control of passive sampling are more complicated than for traditional bottle sampling.

There are devices that cannot be considered as sampling methods but the information they provide may be used to start sampling and reduce the cost of monitoring. BEWSs are based on the toxicological response of an organism to a contaminant or mixture of contaminants [19]. An acute-toxicity measurement based on physiological or behavioral changes provides a rapid warning in response to a deterioration of the water quality. A number of organisms have been used and include fish species, daphnia, microorganisms (algae and bacteria) or bivalve mollusks (Musselmonitor). These on-line continuous (real-time) systems provide rapid evaluation and detection of temporal variation in water quality that

cannot be achieved through standard approaches to chemical monitoring. Applications of BEWSs include monitoring drinking-water intakes, water-distribution systems, wastewater effluents, effluents from contamination-remediation sites (where rapid sensing of a change in the water quality is needed). However, BEWSs suffer from the influence of environmental pathogens present in water and their validation may difficult [20].

Another set of tools that has become available for water monitoring comprises sensors [21]. Many sensors have been developed as continuous monitoring systems and can provide easy, rapid, on-site or in-situ measurements, reducing problems associated with sampling, sample transportation, sample storage and time taken for analytical measurement. Within the broad range of sensor devices, special reference should be made to biosensors, taking into account recent advances in technology and applications to the environmental field. They can be used for monitoring drinking water, effluent discharges, surface water and groundwater. They may also be useful for mapping of contamination when it is important to obtain rapid in-field results (e.g., after accidental spills or pollution events) [22–24].

The WFD determines which parameters have to be monitored to assess water quality. In most cases, these parameters are determined by existing laboratory analytical methods that are quite often expensive, slow and tedious. This justified the interest in developing methods that allow more realistic monitoring of species at the point of discharge, in the external environment or for real-time, on-line, process control. On-line systems, including sensors and biosensors and other continuous systems, passive samplers and BEWSs, can be considered as alternatives to classical water monitoring based on spot sampling and further chemical analysis.

One of the most important shortcomings is validation of these devices under field conditions. If these devices are not properly validated, they will remain mostly within academia and research.

6. Conclusions

Field sampling is the first step where QA is required and the uncertainties associated with this analytical step are often ignored. A badly designed sampling plan always reaches the wrong conclusions. In water and environmental monitoring, mistakes could lead to identification of unreal hazards or harmful contaminants going undetected. In summary, they could lead to misunderstanding of the natural phenomena and the application of wrong statutory and safety regulations. Moreover, a bad sampling plan makes laboratory results useless and, because the laboratory is at the end that provides the results, the laboratory always tends to get the blame. This could lead to controversy, costly repetition of analyses, loss of confidence and personal penalties.

Unfortunately, in most cases, the sampling plan is outside the control of the analyst. However, it should be remembered that the analytical result may depend on the method used for analysis, but it always depends on the type of sampling plan used. Laboratory personnel should at least be aware of the sampling methods and should have input into the sampling process. Samples that have not been taken properly should not be run.

Until now, monitoring of water quality has generally been based on the collection, at prescribed times, of spot samples. Although this approach is well established and validated, it does not provide a truly representative picture or status of the chemical quality of the water. There are a number of emerging sampling tools that could be used to complement standard spot sampling and provide additional information on the temporal and spatial variability of pollutants, the bioavailability of contaminants, and the early detection of pollution events. However, none has proved sufficiently reliable, robust and cost-effective to be incorporated into legislation either by individual EU Member States or across the EU as a whole. In most cases, a combination of field analysis, laboratory analysis and on-line monitoring is the best choice.

Acknowledgement

The authors acknowledge financial support from EU Sixth Framework Programme SWIFT-WFD (Contract no. SSPI-CT-2003-502492).

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