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technical bulletin

CL:AIRE technical bulletins describe specific techniques, practices and methodologies currently being employed on sites in the UK within the scope of CL:AIRE technology demonstration and research projects. This Bulletin outlines the principles and practice governing the collection of representative groundwater samples.

Principles and Practice for the Collection of Representative Groundwater Samples

1. INTRODUCTION

Groundwater sampling is a fundamental part of most site characterisation programmes. In the context of contaminated land and groundwater assessment, groundwater samples are usually collected for chemical and microbiological analysis upon which future decisions or judgements may be made regarding the suitability of the groundwater for a specific use (e.g. potable or industrial), source and assessment of contamination, design and performance assessment of remediation programmes, asset value, liability and long-term monitoring needs. More broadly, groundwater samples are also required for water resource evaluation and development. The groundwater chemistry can also provide important information on the groundwater flow system (e.g. relationships between different aquifers), recharge mechanisms, and interactions between groundwater and surface water bodies (Brassington, 2007). Developing and implementing an effective groundwater sampling programme for such uses requires consideration of the various factors that can affect the collection of representative groundwater samples and the quality of data obtained from the analysis of these. This is important, given that the achievement of data quality objectives (DQO) underpinning decisions on site management can be affected by bias introduced at any stage of the sampling process, from initial collection through to ultimate analysis (Environment Agency, 2002). It is prudent to note that most errors introduced in groundwater quality data arise from practices and procedures implemented during sample collection at the field site, rather than analysis in the laboratory. These errors are related to formation and monitoring well hydraulics, monitoring well placement, design, installation and maintenance, purging methods, purging and sampling device selection and operation, and sample collection, pre-treatment and handling (Nielsen and Nielsen, 2006; Nielsen and Schalla, 2006). While errors from these sources vary in magnitude and may not apply in all cases, they can be significant in certain circumstances. The aim of this bulletin is to outline the principles and practice governing the collection of representative groundwater samples, by understanding the source and mitigating the effects of, potential errors occurring during the sampling process.

2. DEFINING A "REPRESENTATIVE" GROUNDWATER SAMPLE

The collection of "representative" samples which reflect *in situ* groundwater conditions at the time and location of sampling is a key objective of groundwater quality monitoring. This implies that the chemical and microbiological properties of the groundwater sample reflect those in the aquifer adjacent to the sampling point. However, the precise definition of "representative" varies, depending on the focus of the investigation and parameters of interest. It may differ, for example, in groundwater pollution assessments compared with water resource quality evaluation and in single event versus repetitive sampling. Two typical examples illustrate this concept. Groundwater sampling for regulatory compliance is usually done to confirm that a particular site complies with regulatory standards, based on the measured groundwater quality. In this case, the sample will be used to determine any impact on groundwater quality (e.g. type and form of contamination), the spatial and temporal distribution of contaminants, their rate and direction of transport with respect to concentration limits and compliance points (e.g. property boundaries or abstraction boreholes), the selection, design and performance of remediation measures and long-term monitoring to evaluate post-remediation site management, use or closure. This objective will often require highly targeted depth-discrete sampling using a monitoring well design with short screens that allows relatively precise location of contaminant distribution and peak concentrations in the aquifer, for risk assessment and remediation design. This may be necessary to evaluate a "worst-case" scenario. Conversely, groundwater sampling for non-regulatory objectives, such as water resource evaluation or characterisation of risk to a receptor, where knowledge of the volume-averaged groundwater chemistry is more relevant, will usually require monitoring wells with long screens to obtain a composite sample in the target water-bearing zone (Nielsen and Nielsen, 2006). Both groundwater samples are conceptually "representative" for their contexts. However, obtaining groundwater samples which represent the *in situ* groundwater quality in such situations (and therefore providing data quality appropriate for the intended purpose) depends significantly on how the samples are collected, as outlined below.

3. PHYSICO-CHEMICAL AND MICROBIOLOGICAL STATUS OF GROUNDWATER SAMPLES

It is necessary to understand the physico-chemical and microbiological status of groundwater, as a basis to developing good practice in procedures used to collect representative samples. Figure 1 is a typical organic contaminant plume in an aquifer, considering the relevant compartments that influence groundwater quality during the sampling process. Although volatile organic compounds (VOCs), are used as an example for the contaminant plume, this conceptual model applies to any plume containing biodegradable organic compounds. Microbiological degradation of organic contaminants linked to consumption of aqueous and solid phase electron acceptors in the aquifer will change the groundwater chemistry in the plume. Relative to the unaffected aquifer, groundwater in the plume will typically have decreased dissolved O_2, NO_3, SO_4 and Eh (redox potential), but increased dissolved Mn^{2+}, Fe^{2+}, HS^-, CO_2, CH_4 and organic metabolites, arising from biodegradation by aerobic respiration, denitrification, Mn/Fe-reduction, SO_4-reduction and methanogenesis. Microorganisms responsible for contaminant biodegradation will also be typically elevated in the plume. The groundwater samples will be at a higher pressure and different temperature than the atmosphere at the ground surface. Consequently, the groundwater under *in situ* conditions is in disequilibrium with the atmosphere, but re-equilibration will occur during sampling that may lead to irreversible changes in sample quality, producing either negative bias (underestimation) or positive bias (overestimation) for measured analytes by direct and indirect mechanisms.

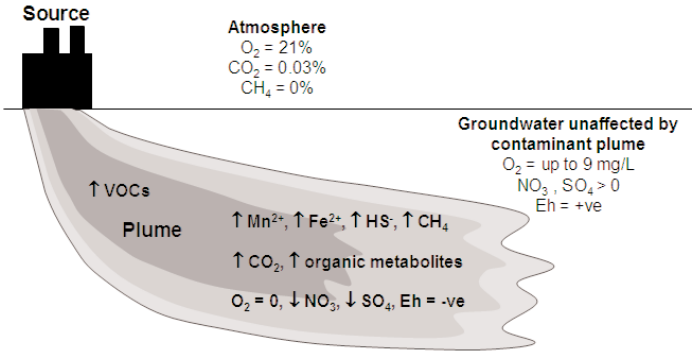


Figure 1. Biogeochemical conditions in different environmental compartments which affect the quality of groundwater samples (↑/↓ = increased / decreased value relative to adjacent compartments)

Degassing of groundwater will occur when a sample is brought to the surface and collected at atmospheric pressure. The solubility of dissolved gases is proportional to the height of the water column (10 m depth = 1 atmosphere) above the sampling point and so concentrations of gases (e.g. CO_2 and CH_4) having a high partial pressure in the groundwater sample will re-equilibrate with the lower concentration (partial pressure) in the atmosphere. The loss of these dissolved gases will directly underestimate their concentration in samples and indirectly affect the concentration of other species influenced by them. For example, loss of CO_2 will induce a rise in sample pH (Eq. 1, reaction shifts to the right) and potential loss of dissolved metals (e.g. Ca^{2+} Fe^{2+}, Mn^{2+} and other trace heavy metals) by chemical precipitation (Eq. 2, reaction shifts to the right), leading to negative bias in their subsequent analysis.

Direct effects of sample degassing

$$H^+ + HCO_3^- \longleftrightarrow H_2O + CO_2\,(gas)\uparrow \qquad \text{(Eq. 1)}$$

Indirect effects of sample degassing

$$Ca^{2+} + 2HCO_3^- \longleftrightarrow CaCO_3\,(ppt) + H_2O + CO_2\,(gas)\uparrow \qquad \text{(Eq. 2)}$$

Loss of volatile organic compounds (VOC) such as contaminants from the sample will also occur by degassing, as these components volatilise either directly into the atmosphere or into the headspace created by exsolution of the dissolved gases. Conversely, re-equilibration with the atmospheric pO_2 can increase the sample dissolved oxygen concentration (positive bias) and result in underestimation (negative bias) of many redox-sensitive species (e.g. organic contaminants, Mn^{2+}, Fe^{2+}, HS^-, heavy metals) as these are oxidised by exposure to the atmosphere (Eq. 3 and Eq. 4).

Indirect effects of sample aeration

$$\downarrow O_2\,(gas) + 4Fe^{2+} + 10H_2O \longrightarrow 4Fe(OH)_3\,(ppt) + 8H^+ \qquad \text{(Eq. 3)}$$

$$\downarrow 2O_2\,(gas) + HS^- + \longrightarrow SO_4^{2-} + H^+ \qquad \text{(Eq. 4)}$$

Changes in sample temperature may also occur during collection, since year-round groundwater temperatures tend to be 10-12°C, whereas temperature at the ground surface may vary daily or seasonally outside this range. The solubility of dissolved gases is decreased at higher temperatures and samples will degass as they rise in temperature. Consequently, samples should be kept close to *in situ* temperature during collection and storage to minimise the attendant effects related to degassing (Eq 1 and Eq. 2).

An often overlooked issue in groundwater sampling is ensuring the microbiological status of samples. There may be a need to sample microbiological determinands (e.g. type, number and activity of microorganisms) in samples directly, but the concentration of chemical species may also be indirectly influenced by the activity of microorganisms in samples after collection. Exposing anaerobic groundwater samples to the atmosphere may kill or suppress the activity of specific bacteria which are sensitive to oxygen concentration, negatively biasing sample analyses. Also, microbiological activity is proportional to temperature and so appropriate sample handling after collection is needed to ensure that concentrations of analytes affected by microbiological activity (e.g. organic contaminants and most redox-sensitive species) are maintained. Further review of these issues can be found in Nielsen and Nielsen (2006). Such changes must be minimised during the sampling process (selection and operation of equipment for well purging and sampling) onsite sample processing (manipulation and filtration of samples) and sample transportation (preservation and storage) to the laboratory for analysis.

4. EFFECT OF AQUIFER HYDROGEOLOGY AND WELL HYDRAULICS ON SAMPLE QUALITY

Understanding factors which affect the collection of representative groundwater samples should begin by considering how aquifer hydrogeology and well hydraulics can influence sample quality. Formation hydrogeology affects the design, installation and 3-D placement of monitoring wells, relative to known or suspected contaminant source zones in an aquifer (Nielsen and Nielsen, 2006; Nielsen and Schalla, 2006). For this reason, it is necessary to have an accurate 3-D understanding of the groundwater flow regime at a site, based on an initial conceptual site model (CSM) which considers potential geological and structural controls on groundwater flow (e.g. spatial variation in high- and low-flow zones due to sedimentary architecture and fracture network geometry) and temporal variations in vertical and horizontal flow direction arising from pumping (e.g. existing abstraction or remediation boreholes) or recharge, amongst other factors. This information enables monitoring wells to be installed in locations which target either uncontaminated or contaminated groundwater, and to develop a monitoring well network that links preferential flow paths in the aquifer to deduce the spatial and temporal distribution of contaminants, plume geometry and processes controlling contaminant fate and transport at the appropriate scale (Wealthall et al., 2002; Thornton et al., 2006). Without this knowledge, non-representative data can be generated on the distribution of contaminated zones and peak contaminant concentrations, potentially leading to erroneous interpretation of remediation performance and costly management decisions, regardless of how well the sample is subsequently collected and analysed (Wilson et al., 2004).

Aquifer hydrogeology also influences groundwater flow within monitoring wells, and therefore sample quality. Groundwater flow in aquifers occurs in response to variation in horizontal and vertical hydraulic head, which creates hydraulic gradients. Where groundwater flow is predominantly horizontal, flow through the well screen will also be horizontal, such that this groundwater will not mix significantly with stagnant groundwater trapped in the well casing above the screen. Therefore, groundwater within the well screen should be representative of the adjacent formation and provided the overlying stagnant water column is not disturbed, representative groundwater samples can be collected from the well screen using appropriate well purging and sampling methods (Nielsen and Nielsen, 2006), described below. However, this is not necessarily the case where differences in aquifer hydraulic head result in vertical groundwater flow across a zone screened by a monitoring well. Under this condition, the well screen short-circuits groundwater flow, which moves from zones of highest to lowest hydraulic head within the well bore. This mixes groundwater within the well screen, producing a composite sample that then reflects the weighted contribution of groundwater chemistry from the high- and low-flow zones, rather than the adjacent formation. Collecting representative groundwater samples in these situations requires particular attention to monitoring well design (see below).

5. EFFECT OF MONITORING WELL INSTALLATION, CONSTRUCTION, DESIGN AND MAINTENANCE

Groundwater samples will often be collected for the analysis of microbiological, organic and inorganic parameters in most monitoring programmes. These parameters will have different physico-chemical properties, be present at different concentration and require analysis to different levels of detection in groundwater samples. Consideration must therefore be given to procedures and practice used to install, construct, design and maintain the performance of monitoring wells to minimise bias that may be introduced into subsequent sampling (Nielsen and Schalla, 2006).

When monitoring wells are installed by drilling methods using drilling fluids, the latter should be selected to minimise potential contamination of groundwater samples. Air and water are commonly used as drilling fluids, but these may invade the formation, inducing oxygenation of anaerobic groundwater and mix with the ambient groundwater chemistry. Both can result in the chemical alteration of groundwater adjacent to the borehole, potentially biasing groundwater sampling. It will usually be necessary to mitigate these effects by removing a volume of groundwater equivalent to the drilling fluid used (and possibly lost to the formation) during well development, in addition to allowing a period of hydraulic and hydrochemical stabilisation of the monitoring well prior to groundwater sampling (Thornton et al., 2006). Materials used to construct monitoring well components (e.g. casing, screen, filter pack and annular seals) can chemically interact with groundwater in the well, changing the sample chemistry (Parker et al., 1990). This occurs by sorption of target analytes to, or desorption/leaching from, the construction materials. It can result in false positive or negative detection of analytes in samples and is particularly important for species at a level upon which a critical site management decision will be made. Usually, trace organic contaminants (e.g. priority pollutants) and the use of plastic materials in monitoring well construction are of key concern in this respect, but interactions between heavy metals and sand filter packs, bentonite seals and stainless steel well construction materials are also important (Nielsen and Schalla, 2006). The compatibility between proposed well construction materials and the known or expected sample matrix should be reviewed prior to monitoring well installation.

Due to spatial variability in aquifer properties contaminant plumes are heterogeneous in structure, with contaminant migration occurring along high permeability zones which form preferential flow paths for solute transport, particularly in multilayered or fractured aquifers (Thornton et al., 2001; 2006). Consequently, the 3-D distribution of contaminants, transport paths and relevant biodegradation processes must be deduced for the correct assessment of contaminant fate in aquifers. Unfortunately, monitoring well designs which use single screens of several metres length may provide non-representative groundwater samples and incorrect interpretation of plume geometry and behaviour (Wilson et al., 2004). This arises because long well screens may intersect and connect zones with different groundwater chemistry in an aquifer, resulting in the potential mixing of uncontaminated and contaminated groundwater in the borehole, dilution of *in situ* contaminant concentrations and re-distribution of dissolved and free-phase contaminants (e.g. dense non-aqueous phase liquids, DNAPLs) to zones which would otherwise not be impacted by the plume (Martin-Hayden and Robbins, 1997; Varljen et al., 2006). Sampling data obtained from such installations may lead to underestimation of peak contaminant concentration, under- or overestimation of natural attenuation, poor resolution of contaminant distribution, concentration gradients and plume geochemical conditions and misleading understanding of plume development (Martin-Hayden and Robbins, 1997; Wilson et al., 2004). However, this bias can be minimised by installing multilevel samplers (MLS) or multiple monitoring wells fitted with small screens (e.g. <1 m), which enable level-discrete sampling of specific zones to provide significantly improved resolution of contaminant distribution, plume geometry and transport paths (Thornton et al., 2001; 2006; Wealthall et al., 2002). Other potential problems related to monitoring well design (e.g. selection of screen and filter pack size, improper installation of annular materials) are described in Nielsen and Schalla (2006). In some circumstances, monitoring wells may be designed with a dual or multiple purpose of sampling groundwater and the gas phase overlying the groundwater at the same location. Example applications include contaminated sites where there is a need to sample the groundwater chemistry and organic vapours or gases related to the contamination, and landfill sites, where combined sampling of leachate chemistry, gas composition and the capability for gas and leachate extraction is desired. Such monitoring installations will often be designed to sample both the saturated and unsaturated zone, with the need to ensure that the intended multiple uses do not conflict with the monitoring objectives in each case (Environment agency, 2002).

Development and long-term maintenance of monitoring wells is required after their installation to ensure continued function for the duration of the monitoring programme. Well development is necessary to rectify the effects of drilling (e.g. contamination by fluids), remove fine particulate material that has entered the well screen, stabilise the filter pack adjacent to the well screen and improve the hydraulic connection between the well screen and adjacent formation (Nielsen and Nielsen, 2006). This is essential to reduce turbidity in samples, which can significantly bias certain chemical analyses. Long-term maintenance involves the repair of damaged surface seals (minimising surface contamination and infiltration) and re-development of monitoring wells in which siltation has occurred to increase sample turbidity.

6. WELL PURGING

Purging of monitoring wells is undertaken to remove stagnant groundwater in the casing and introduce fresh groundwater into the well for sampling. Figure 2 shows the basis for purging according to the processes that may affect groundwater chemistry inside a monitoring well. These arise because groundwater stored inside the well casing is physically isolated from the well intake and chemical disequilibrium can occur between the casing water and formation groundwater, biasing sample quality.

Research over the last two decades shows that the method used to purge monitoring wells can significantly affect sample quality and may itself lead to non-representative groundwater samples (Barcelona et al., 1994; Nielsen and Nielsen, 2006). The purging methods and their potential impact on groundwater sampling are outlined below. They generally differ according to the purge volumes required, effect of purging rate on sample quality, purging low permeability formations and waste disposal costs. Purging strategies, considering different monitoring well designs and hydraulic properties, are described in Environment Agency (2002). These have been developed for situations in which a composite groundwater sample (comprising a mixed composition representative of the entire screen section/open borehole) or depth-discrete groundwater sample (collected from a specific depth in the well screen) is desired.

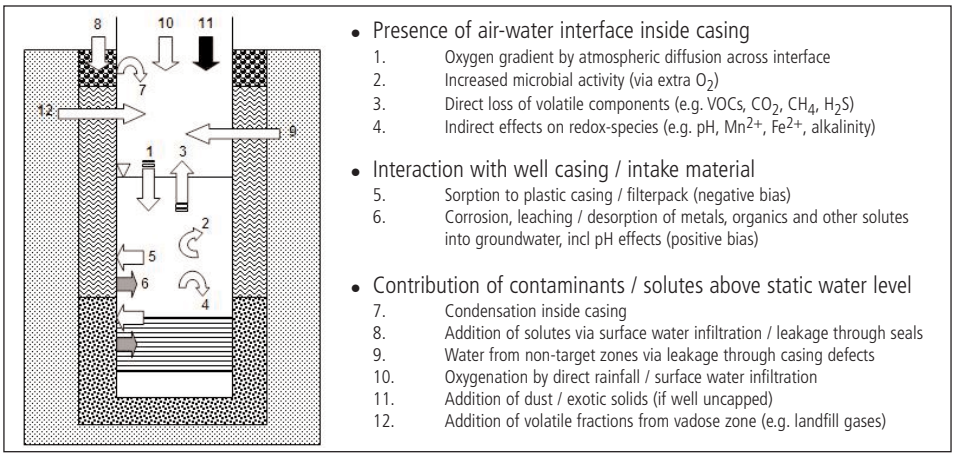


Figure 2. Processes affecting groundwater quality inside a typical monitoring well

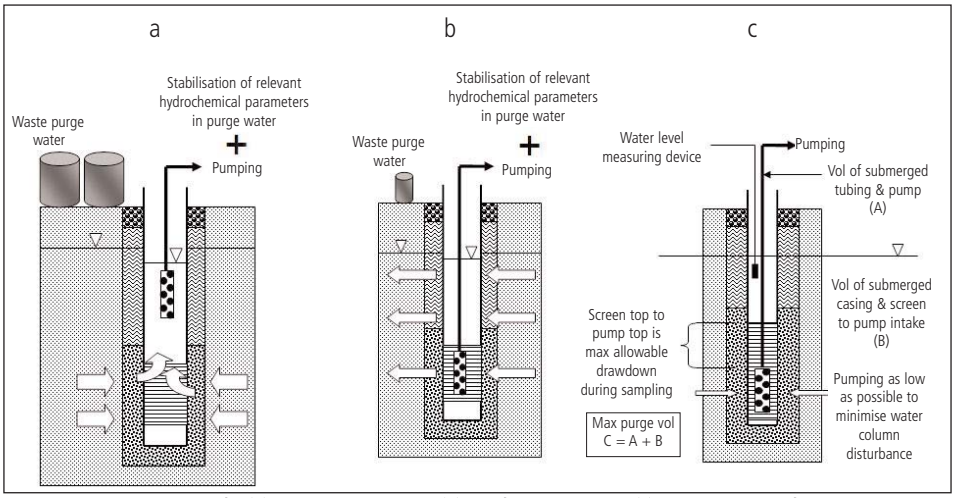


Figure 3. Purging strategies for (a) variable well volume; (b) low-flow micropurge; (c) low permeability formations

Purging fixed or variable well volumes

A traditional purging strategy is the removal of a fixed, but arbitrarily defined, number of well volumes from the casing, by placing the pump intake above the well screen and drawing stagnant groundwater upwards. This "rule of thumb" approach may typically involve purging 3-5 well volumes but has no technically defensible basis, since it does not account for variation in site-specific hydrogeology, well response, purging rate or provide independent chemically-based confirmation of when a "representative" groundwater sample enters the well (Barcelona et al., 1994; Nielsen and Nielsen, 2006). Because no purging rate is specified, or related to well-specific response, the well may be hydraulically over-purged and dewatered, causing aeration of the formation and increased sample turbidity (see below). This method also creates large volumes of potentially contaminated waste groundwater requiring disposal and has higher overall monitoring costs than other, more appropriate, methods (Schilling, 1995).

A scientifically more rigorous alternative to this method is to use the stabilisation of pre-determined groundwater hydrochemical parameters, which are continuously monitored during pumping, to define the purging time (Figure 3a). The purge volume removed by this method is then variable and related to the hydraulic and hydrochemical characteristics of each monitoring well. This approach requires a "purging trial" for each monitoring well, to establish the well-specific purging time, based on stabilisation of the hydrochemical parameters, usually pH, temperature, dissolved oxygen, oxidation-reduction potential (ORP) and electrical conductivity

(Barcelona et al., 1994; Environment Agency, 2002). However, the time required for these parameters to stabilise during purging can vary significantly for monitoring wells located on the same site (Figure 4). According to the examples in Figure 4 and the relevant criteria, purging would be completed only after stabilisation of groundwater pH (Well A) or ORP (Well B), which requires several hours of pumping before a representative sample can be collected. Hence, this method can also generate a variable but potentially large volume of waste groundwater for disposal.

Low-flow micropurging

Low-flow micropurging and sampling (also known as minimum-purge sampling) offers significant technical and practical advantages over other well purging methods. The technique relies on sampling groundwater moving through the well screen under laminar flow conditions from the adjacent formation (Figure 3b). Provided mixing between groundwater in the well screen and overlying stagnant water in the casing is minimised during entry and operation of the pump, groundwater samples taken from the well screen should be representative of the adjacent formation. This condition is achieved by placing the pump intake within the well screen and purging at a low flow rate (e.g. 0.1-0.5 L/min) comparable to the natural flow through the screen, which avoids significant drawdown of the water level in the well (Puls and Barcelona, 1996; Nielsen and Nielsen, 2006). Continuous monitoring of the water level and purge water chemistry is required to satisfy this criterion and deduce when a representative groundwater sample can be collected, from stabilisation of the hydrochemical parameters (usually much less than one well volume). Operationally, this purging (and sampling) method significantly improves sampling precision and reduces sample turbidity, loss of volatile constituents, waste water volume and overall monitoring costs (Schilling, 1995). A well-specific purging trial is usually required to establish stabilisation times for hydrochemical parameters (Environment Agency, 2002). This method is not suited to purging of low-yield formations or NAPL sampling (Nielsen and Nielsen, 2006).

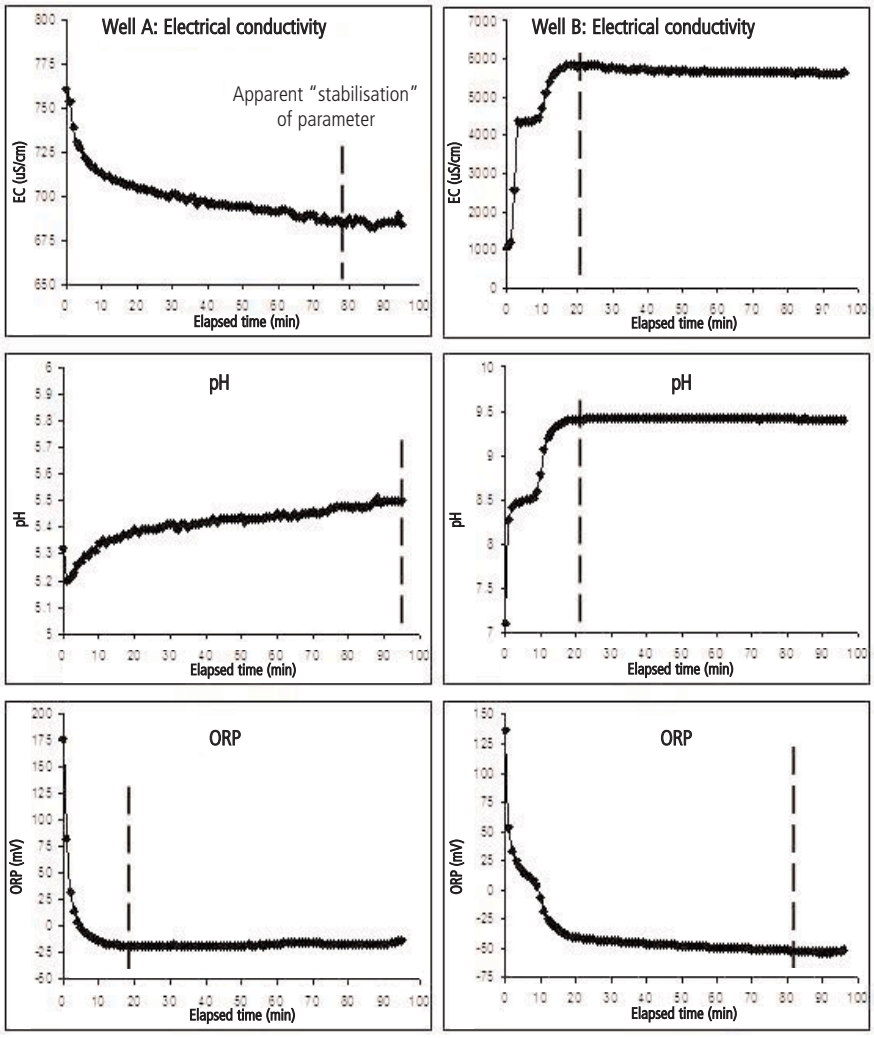


Figure 4. Stabilisation of groundwater hydrochemical parameters during purging of two monitoring wells on the same site (dashed vertical line denotes time for value of parameter to stabilise)

Purging low-yield monitoring wells

Low-yield formations are those that cannot be pumped at low rates (e.g. 0.1 L/min) without continuous drawdown of the water level. In very low yield formations (e.g. clay-rich strata), purging to remove stagnant groundwater can dewater the well, with attendant bias on sample quality (see below). There are two practical techniques which are used to overcome this problem and ensure representative groundwater samples can be obtained. The first approach relies on purging the casing water only and sampling groundwater in the well screen, by pumping from the top of the water column and moving the pump downwards to the well screen. This requires knowledge of the screen depth and length, and measurement of drawdown to minimise agitation. The second approach uses a pump placed within the well screen and removal of water within the sampling system and well to the pump intake only (Figure 3c). No drawdown of water below the top of the pump is permitted and usually measurement of hydrochemical parameters is not possible in this case (Nielsen and Nielsen, 2006).

7. GROUNDWATER SAMPLING DEVICES

Many devices are available for purging and sampling groundwater. The selection and use of these can significantly affect sample quality. Consequently, the selection of purging and sampling devices should be completed on a site- and groundwater matrix-specific basis, considering the following operational criteria (Nielsen and Nielsen, 2006):

- Accuracy and precision of device, considering specific bias or sampling artefacts introduced during use, and reproducibility of performance by different personnel over extended periods of monitoring.
- Materials used to construct components of device in contact with groundwater, considering compatibility with intended sample matrix and possible bias over short and long-term use.
- External diameter of device, considering internal diameter and construction quality (e.g. telescoping casing, internal casing joints) of monitoring well.
- Lift capability of device, considering depth to rest water table and pumping capacity.
- Flow rate control and range of device, considering flexibility for purging and sampling for different conditions and parameters.
- Ease of operation and field maintenance, considering consistency and reliability in performance for use by different personnel, robustness of application in different media (e.g. effects of suspended solids) and effect of sample discharge (e.g. intermittent, cyclic or steady flow) on sampled parameters and onsite measurements (e.g. flowcell use).
- Portable vs dedicated devices, considering risk of cross-contamination through use, ease of decontamination, sampling commitment (e.g. number and frequency of events), accessibility to monitoring wells, capital cost of equipment, contribution to overall monitoring costs (e.g. purging and sampling time).
- Ease of field decontamination, considering robustness and practicality for onsite disassembly and cleaning.
- Reliability and durability, considering sampling commitment, compatibility with sample matrix (e.g. corrosion) and sampling operation (e.g. manual handling and transport).
- Capital and operational costs, considering sampling objectives, required sampling precision and accuracy, reliability and long-term performance, regulatory confidence.

The relative advantages and disadvantages of commonly used groundwater purging and sampling devices, considering the above selection criteria, are summarised in Table 1. Further details can be found in Environment Agency (2002), Nielsen and Nielsen (2006) and references therein.

Table 1. Main features influencing performance of commonly used groundwater purging and sampling devices

Device	Advantages	Disadvantages
Depth samplers Bailers	● Low cost, portable, easy to use & clean ● Sample water from any depth ● Flexible bailers will pass through non-plumb wells ● Will fit any well diameter & length for desired sample volume ● Transparent bailers can provide LNAPL sample from top of water column	● Slow purging in deep wells ● Sample aeration, degassing & turbulence via water column agitation (also via sample transfer) ● Mixing of stagnant & dynamic water via surging ● Avoid for VOCs, redox-sensitive species, trace metals, colloids & dissolved gases ● Cable is source of cross-contamination ● Discontinuous water flow to surface ● Difficult to deduce point of sampling in water column ● Check valve failure when suspended solids high ● Higher operator error – lower sampling precision
Pumps Suction-lift (incl centrifugal & peristaltic)	● Portable & inexpensive relative to other pumps ● Variable & easily controlled flow rate possible ● Dedicated tubing can be left in well & used in plumb / non-plumb wells of any diameter ● Sample only contacts pump tubing in pump head which is easily cleaned (peristaltic pumps)	● Sampling limited to water tables < 8m depth ● Sample degassing / volatile loss (gases & VOCs, pH shift) via pressure drop from suction ● Purging time-consuming / impractical due to low pumping rates, unless small diameter sampling tubes / monitoring wells used ● May require priming to initiate sampling, causing cross-contamination (centrifugal pumps) ● Sample agitation & aeration with centrifugal pumps
Vacuum-lift	● Relatively portable & inexpensive ● Single flow rate limited by pump efficiency ● Dedicated tubing can be left in well & used in plumb / non-plumb wells of any diameter	● Sampling limited to water tables < 9m depth ● Sample degassing / volatile loss more extensive than suction-lift
Inertial lift	● Low-cost, low-maintenance, portable & easy to clean ● Can operate with suspended fines / silt present ● Used for purging & sampling ● Not affected by dry pumping ● No pressure changes during sampling	● Ball-valve & sample tube blocked by particles during storage & operation ● Sample agitation & aeration at surface by oscillation of sample tube during rapid operation – increased turbidity, VOC & dissolved gas loss ● Small diameter (6mm) sample tubes may require lubrication when used in deep (>50m) wells
Gas-lift	● Can be used in wells down to 30mm ID ● Operates at any depth (limited by burst strength of sampler materials & tubing), provide near steady flow of groundwater at surface, up to vol of sampling device ● Can be constructed from inert materials ● Easy disassembly, decontamination, repair ● Discrete depth sampling possible ● Multiple temporary or permanent installations possible in single well (MLS) ● Can pump dry - suitable for low-yield wells ● Use of inert drive gas (N_2) minimises sample oxidation	● Drive gas directly contacts groundwater sample ● Use of air or O_2 as drive gas may oxidise chemically reduced species (e.g. Mn^{2+}, Fe^{2+}, S^{2-}), causing pH & Eh changes & precipitation of metals ● Stripping of dissolved gases (CO_2, CH_4 and VOCs) from sample, causing pH shift & indirect effects on other species (e.g. heavy metals) ● Air compressor, compressed air or N_2 cylinders must be transported to monitoring well, reducing portability ● Permanently installed devices difficult to maintain or repair ● Proper installation in MLS systems may be difficult
Bladder	● Easy disassembly for cleaning & repair ● Can be made of inert materials ● No contact of drive gas with sample, avoiding sample aeration or gas stripping ● Portable, but accessory kit is cumbersome ● High pumping rate relative to other devices allows purging & collection of large vol samples ● Pumping rates precisely controlled for high flow rate purging & low flow rate sampling ● Suitable for low-flow micropurging & sampling	● Expensive relative to alternative devices ● Deep sampling requires large volumes of gas & longer cycles, increasing sampling time & monitoring costs ● Long / inefficient purging for high vol wells ● Non-continuous (cyclic) flow ● Check valve failure in water with high suspended solids ● Minimum sample discharge rate for some models may be higher than ideal for sampling VOCs
Electric submersible (helical rotor and gear-drive)	● Portable, easy to use & clean ● Available for well diameters down to 50mm ● Inert / nearly inert construction & suitable for sampling various groundwater matrixes (provided inert discharge lines also used) ● Continuous sample flow at variable rate for purging & sampling of same well ● Flow rate precisely controlled for low-flow micropurging & sampling	● Accessory kit can be cumbersome, requiring vehicle access ● Reduced capability & mechanical wear (failure) in presence of high suspended solids ● Turbulence & heating (5-7°C) at high flow rates can alter turbidity & sample chemistry (VOCs & dissolved gases) ● Cavitation (pressure changes) possible in gear-drive motors

When designing a purging and sampling programme for groundwater quality monitoring, the potential impact of this on the collection of representative samples should guide the selection and operation of appropriate sampling devices. Figure 5 shows the processes that can affect groundwater sample composition in a monitoring well, due to overpumping and well dewatering during purging or sampling. These processes include increased sedimentation of the well (increasing sample turbidity), aeration of the filter pack (introducing oxygen into the well intake and formation), aeration of groundwater cascading into the well (inducing positive and negative sample bias), loss of dissolved volatile components, vertical redistribution of light non-aqueous phase liquid (LNAPL) through the well intake after well recovery, cross-contamination or dilution of groundwater from different levels via mixing, and increased spreading of the plume towards the monitoring well. Given these potential problems, purging and sampling commitments should be considered in monitoring well design (e.g. purging costs increase significantly with well diameter), the availability and suitability of devices (e.g. compatibility of materials and operation on sample quality) and site-specific monitoring requirements (e.g. relevant parameters which define a "representative" groundwater sample and species potentially affected during sampling).

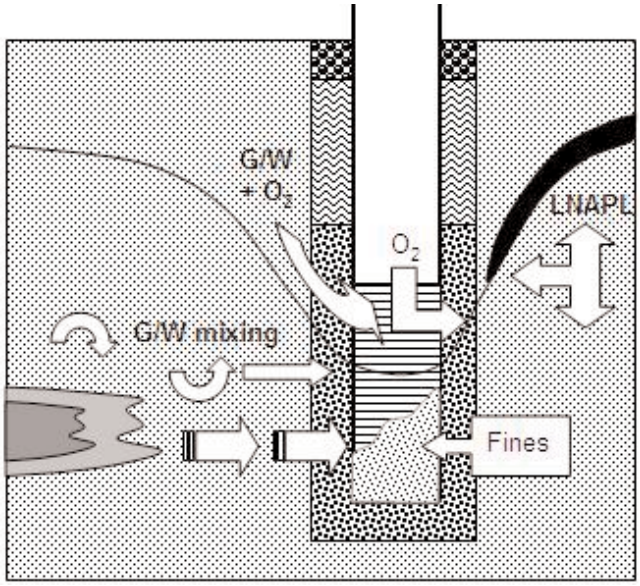


Figure 5. Processes affecting groundwater quality in a monitoring well during purging and sampling (see text for details)

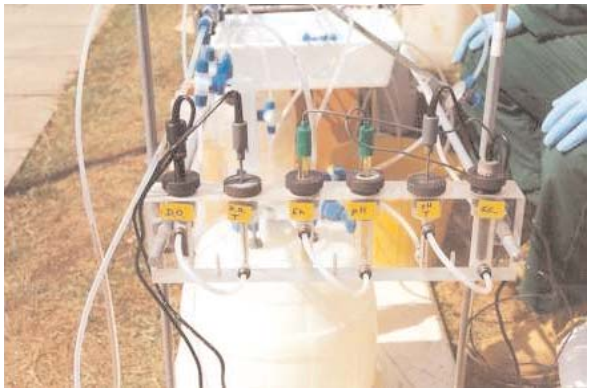
8. SOURCES AND TYPES OF ERROR DURING COLLECTION OF GROUNDWATER SAMPLES

The various activities undertaken to collect groundwater samples can introduce errors in the process, manifest as a positive or negative bias on sample quality. This bias defines the difference between the analysed and true sample composition (that under *in situ* conditions in the aquifer at the time and location of sampling), and results from a combination of *systematic* errors and *random* errors (Environment Agency, 2002). Systematic errors produce consistent and reproducible bias in sampling data and affect the ability to obtain groundwater samples with accurate composition (Keith, 1991). Using inappropriate monitoring well designs, sampling equipment and sample preservation methods are sources of systematic error in groundwater sampling (Nielsen and Nielsen, 2006; Nielsen and Schalla, 2006). Random errors produce inconsistent and non-reproducible bias in sampling data and affect the ability to obtain repetitive samples with the same composition, irrespective of the accuracy (Keith, 1991; Environment Agency, 2002). Random sampling errors include contamination of aqueous samples with solid matter or residues from the field site, sampling equipment and carryover of groundwater in the sampling device between samples. Generally, systematic errors create the greatest source of bias in groundwater sampling. Random error can be significantly reduced by cleaning sampling equipment prior to use, suitable onsite decontamination procedures and processing of groundwater samples to reduce contamination with residues. All groundwater sampling programmes must account for systematic and random errors in the design and implementation of the sampling plan to ensure DQOs are met. In practice, this is done using various field-based quality control samples and procedures (see below). It should be noted that systematic and random errors from the sampling process are separate from the same type of error attributable to laboratory analysis of samples. Separate quality control samples and checks are required to account for bias in data arising from laboratory-based errors. The final sample composition may thus reflect bias from both field and laboratory sources of error.

Systematic errors due to inappropriate selection and operation of sampling equipment can usually be minimised by (i) considering the suitability and compatibility of sampling devices and accessory equipment for the groundwater matrix and parameters of interest; and (ii) adherence to good practice in the collection and processing of samples. For example, errors due to sample degassing can be avoided by not using peristaltic and vacuum pumps, where the chemical species of interest are affected by this bias (Table 1). Similarly, turbidity in samples can be reduced significantly by proper well installation, development, avoidance of bailers as sampling devices and use of low-flow micropurge sampling techniques. Loss of volatile constituents and aeration of samples can be avoided by not using bailers as sampling devices (Table 1), using low pumping rates (to avoid excessive drawdown and sample agitation) and short lengths of thick-walled plastic tubing with low gas diffusion coefficients, when transferring or processing samples at the well head (Kjeldsen, 1993).

9. MEASUREMENTS MADE ONSITE AT THE WELL HEAD DURING GROUNDWATER SAMPLING

Frequently it is necessary to measure some groundwater quality (or field) parameters (e.g. pH, temperature, dissolved oxygen concentration, ORP, electrical conductivity and alkalinity) onsite, at the well head during the collection of groundwater samples. This is required because samples cannot be preserved or stored for later measurement of these parameters, but also because they are often used for operational reasons, to identify purging times for individual monitoring wells and confirm completion of purging for sampling fresh formation water (see above). With the exception of alkalinity, measurements of the other field parameters should be undertaken either downhole, using *in situ* probes, or (more commonly) performed in a flow cell, using a continuous stream of groundwater that flows directly from the sampling device to the measurement probes contained within the flow cell (Figure 6).



Common errors in measurement of field parameters
No instrument-specific definition of stabilisation
No / incorrect instrument calibration
Expired / incorrect calibration standards
Poor equipment cleaning / maintenance
Poorly trained field staff
Failure to understand operating ranges, accuracy, resolution of probes / methods
Failure to recognise measurement errors
Failure to record correct measurement units
Measurement of Eh & D.O. in open containers
Delay in recording values of temperature-sensitive parameters
Interferences from sample in parameter measurement

Example criteria defining stabilisation of water quality parameters	
D.O.	±10% of reading or ±0.2 mg/L, whichever greater
Temp	±0.2°C
pH	±0.2 pH units
Eh or ORP	±20 mV
Conductivity	±3% of reading

Figure 6. (top) Illustration of flow cell and probes used for onsite measurement of field parameters in groundwater at the well head, (middle) sources of error in measurement of field parameters and (bottom) typical criteria used to define parameter stabilisation for measurement.

Various criteria are used to confirm stabilisation of the field parameters for measurement and identify potential errors (Figure 6). Either bespoke or commercially available flow cells can be used, but the flow cell should be protected from direct sunlight to avoid temperature changes that will affect the values of the measured parameters.

Groundwater alkalinity must also be measured immediately after sampling, as degassing and loss of CO_2 from samples can occur during storage, which changes the alkalinity. This analysis can be easily done by chemical titration, using commercially available kits. However, dilution of coloured or turbid samples is necessary to avoid measurement errors (Thornton et al., 2001). Samples containing $CaCO_3$ particles will also require filtration to avoid dissolution of these particles and overestimation of groundwater alkalinity (Thornton et al., 2006). Other parameters may also be commonly measured at the well head. These include rest water level (prior to any purging and sampling) and free product level, at NAPL-contaminated sites.

10. PROCESSING, PRE-TREATMENT AND PRESERVATION OF GROUNDWATER SAMPLES

After collection, groundwater samples must be processed to minimise changes in composition prior to analysis in the laboratory. This requires pre-treatment and preservation procedures which prepare the sample for later analysis and stabilises the sample chemistry during storage. Sample pre-treatment usually only involves filtration to remove suspended solids for the analysis of the "dissolved" fraction, estimating the concentration of suspended solids, separation of solids for chemical analysis and removal of substances which clog laboratory instruments or interfere with chemical analysis. Conventionally, a filter pore size of 0.45 μm is used to separate "dissolved" from "particulate" fractions in samples, but constituents in groundwater have a range of sizes and other operational definitions may apply to determine the "true" dissolved, "colloidal", "mobile load", "sterile" or "non-sterile" fraction (Nielsen and Nielsen, 2006).

Sample filtration should be done immediately after collection in the field, using positive-pressure methods which reduce atmospheric exposure and sample aeration, to minimise possible bias on sample composition by loss of volatile components and oxidation of reduced species (Thornton et al., 2001). Vacuum filtration should **not** be attempted, since this will degas samples, radically altering their chemistry. Filter media which are compatible with the species to be measured should be used, to ensure that target species are not leached from, or absorbed by, the filters. The rationale for filtering samples should be defined by the DQOs, as analyses for risk and remediation assessments may require "whole" (i.e. unfiltered) samples, whereas the true dissolved fraction is needed for geochemical transport modelling.

Groundwater samples may also require preservation to minimise post-sampling changes in the concentration of species, where immediate analysis is not possible. Sample preservation is done after any filtration to prevent or slow biological and chemical processes (e.g. microbiological activity, oxidation, volatilisation, adsorption, precipitation) which cause irreversible changes in the concentration of dissolved organic and inorganic species after collection. It is **parameter-specific** and not required or the same for all sample types. Usually, different chemical reagents are added to sample containers, which are then chilled at 4°C until analysis in the laboratory. This preservation will slow but necessarily prevent compositional changes and individual sample types have different recommended maximum holding times prior to analysis (Nielsen and Nielsen, 2006). Different sample containers (e.g. plastic and glass) are needed for specific sample types. The compatibility between the chemical reagent used as a preservative, sample container and species to be measured should be established to avoid interactions (e.g. leaching or sorption) that bias the sample composition. Figure 7 summarises the sequence of sample handling procedures for different chemical species, considering the onsite analysis of field parameters and subsequent processing of filtered and preserved samples according to sensitivity of handling and risk of cross-contamination. Unless specific sample processing or preservation procedures apply, groundwater samples for microbiological analysis should be collected unfiltered in sterile, nitrogen gas-filled dark glass bottles, using a discharge line connected directly to the sampling pump, kept in the dark and chilled at 4°C. This procedure has been used to ensure the preservation of both aerobic and anaerobic microorganisms in groundwater samples from contaminated sites (Pickup et al, 2001). It should be noted that there is an intrinsic bias in the microbiological analysis of groundwater samples, since planktonic (suspended) rather than sessile (fixed) bacterial cells are collected (and represented) in the sample. Generally, suspended cells contribute only a small fraction of the total cell numbers present in an aquifer and consequently this quantity will be underestimated in the analysis.

11. FIELD-BASED QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

Quality assurance (QA) and quality control (QC) procedures must underpin groundwater sampling since the data will be used to support decisions on site management, remediation, risk assessment, regulatory compliance and liability. Significant costs can be incurred if such decisions are based on flawed data or samples must be retaken. Decision-makers therefore need confidence that the results are technically reliable and defensible within prescribed limits. For this reason, field-based QA and QC procedures are developed for groundwater sampling, which are different from those related to laboratory analysis (Keith, 1991). The collection and analysis of groundwater QC samples enables assessment of the extent to which the sampling or analytical procedures have significantly affected the analytical results. An

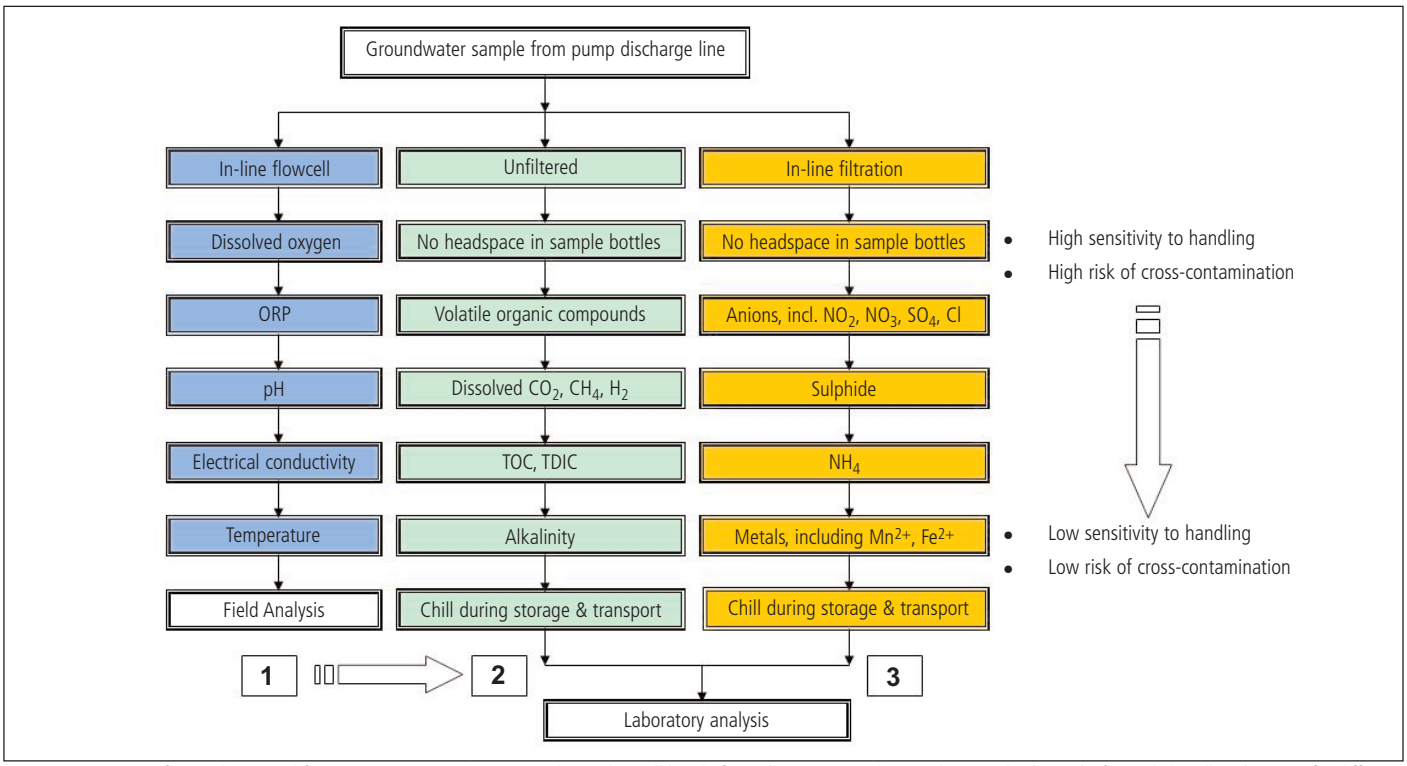


Figure 7. Summary of procedures used for processing groundwater samples at the well head after collection, considering relative order (1 to 3) of sample handling (see text for different pre-treatment and preservation methods)

effective groundwater QC sampling programme is an essential part of QA, as it may otherwise be difficult to identify if the monitoring programme measures real changes in groundwater quality or simply records variations in groundwater composition caused by sampling and analytical procedures (Environment Agency, 2002).

Field-based QA procedures ensure data of a stated quality with stated probability of being true (Nielsen and Nielsen, 2006). In a practical sense, this includes implementing technically sound standard operating procedures, establishing protocols for the operation, calibration and maintenance of sampling equipment and field instruments, the collection of field QC samples (see below), Chain of Custody procedures, following consistent sample pre-treatment and preservation, methods to check the accuracy of field parameter measurements and description of corrective actions following detection of sampling errors (Environment Agency, 2002). Field-based QC procedures are specific actions to identify and minimise errors and bias in the sampling process, ensuring the collection of representative sample quality which meets specified DQOs (Nielsen and Neilsen, 2006). Sampling QC measures assess sampling accuracy and precision, using field QC sample blanks, which are various sample matrices carried through all phases of sample collection and transport to the laboratory (Environment Agency, 2002). These samples typically include trip, temperature, field, equipment and blind duplicate blanks, together with spiked and field-split samples to assess, for example, sample contamination, quality of preservation methods, equipment decontamination procedures and performance of laboratory analyses. These QC checks will usually be required by regulatory authorities and third party interests to verify the reliability of sampling data and relative contribution of sampling error to total error in the monitoring effort.

A convenient and simple QC check on the overall quality of chemical analyses undertaken for groundwater samples can be made by calculating an *ion balance* (IB). This considers the major ions measured by field and laboratory analyses and relies on the fact that aqueous solutions must be electrically neutral, such that the concentration of cations must equal the concentration of anions, when both are expressed as milli-equivalents per litre (meq/L). The percentage error (e.g. difference between analysed cations and anions) in the IB for a sample analysis is calculated in a standardised way using the following expression (Environment Agency, 2002):

$$IB\,(\%) = \frac{\left(\sum \text{meq/L cations} - \sum \text{meq/L anions}\right)}{\left(\sum \text{meq/L cations} + \sum \text{meq/L anions}\right)} \times 100 \qquad \text{(Eq. 5)}$$

A sufficient number of major ions must be measured in a sample to calculate the IB, even if only a few are of interest (Environment Agency, 2002). The IB can confirm the overall quality of chemical analysis by a laboratory, or identify which laboratory is in error when several are used to provide the full analysis. An error of ±5% in the IB is considered acceptable (Nielsen and Nielsen, 2006). It should be noted that an IB is **not** a measure of good sampling practice, since groundwater samples collected (and biased) using poor techniques can be analysed accurately and produce a good IB. Common causes of imbalance in the IB include incomplete chemical analyses, errors in the analysis of individual species (e.g. poor calibration), errors due to the method used (e.g. inappropriate technique), sample contamination during analysis, incomplete reporting of chemical analyses and errors related to the groundwater sampling process (e.g. field measurements and preservation methods). When landfill leachate or landfill leachate-contaminated groundwater samples are analysed, consideration should be given to the possible contribution of negatively charged organic acids (e.g. volatile fatty acids, VFAs) in the estimation of sample alkalinity and IB. This is because VFAs can provide an important component of the negative ion suite and (organic-based) alkalinity (erroneously) attributed to inorganic species, when these organic compounds occur in significant concentrations in aqueous samples (Thornton et al, 1996).

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Further information

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