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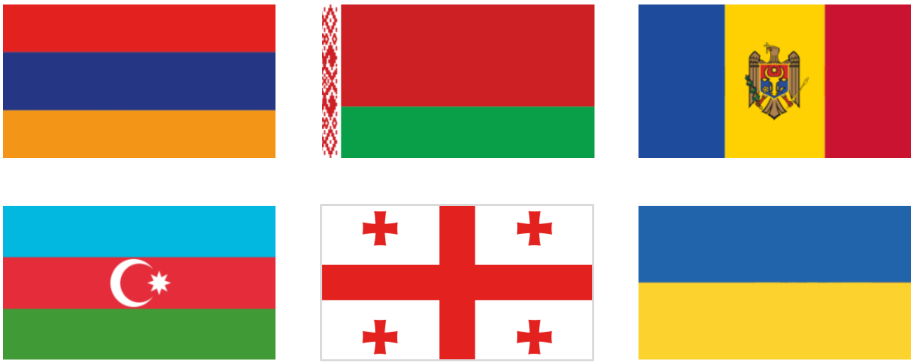
Result 2

GENERAL MANUAL FOR CHEMICAL FRESHWATER SAMPLING

Groundwater, Surface water, Sediments



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Abbreviations

BGBl	Austrian Federal Law Gazette
COD	Chemical Oxygen Demand
DIN	German Standard published by the German Institute for Standardization
DNAPL	dense non aqueous phase liquids
DOC	Dissolved Organic Carbon
EaP	Eastern Partnership
EC	European Commission
EU	European Union
EU-MS	EU-Member States
EUWI+	European Union Water Initiative Plus
GW	Groundwater
GZÜV	Austrian Ordinance on the Monitoring of the Quality of Water Bodies
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LNAPL	light non-aqueous phase liquids
MOW	Method Ordinance Water
NVF	Nitrogen Vapour Freezer
ÖNORM	Austrian Standard published by the Austrian Standards International
RBMP	River Basin Management Plan
SED	Sediments
TOC	Total Organic Carbon
WFD	Water Framework Directive

1 EXECUTIVE SUMMARY

The General Manual for Chemical Freshwater Sampling provides substantial guidance on quality assured sampling of fresh ground and surface waters and of sediments. It serves to raise awareness of the enormous importance of representative and quality assured sampling in the frame of good water governance and management.

Sampling is by far the most significant source of errors in the whole monitoring cycle and hence potential errors are very decisive on the reliability of data which are an important basis for water management decisions.

Within EUWI+ the importance of quality assured sampling has been permanently reiterated and this manual can be used as a backbone or reference document for quality assured sampling and it can be used as training material for sampling trainings.

It covers all aspects of quality assured and safe fresh water sampling covering groundwater, surface water and sediments and it is based on the long-lasting experience of the national freshwater chemical monitoring activities in Austria. It provides an overview of the multitude of standards, guidelines and rules dealing with the sampling of groundwater, surface waters and sediments and it summarizes their essential content and highlights common sources of errors before, during and after sampling.

This document is predominately based on the “Probenahmehandbuch Chemie Wasser. Grundwasser, Oberflächenwasser, Sedimente” (Sampling Handbook Chemistry Water. Groundwater, Surface Water, Sediments) which is owned and edited by the former Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management – BMLFUW (now Austrian Federal Ministry of Agriculture, Regions and Tourism - BMLRT). The original document was published in June 2015.

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All results and documents which were elaborated under this contract are public and accessible at the EUWI+ project website (www.euwipluseast.eu).

2 INTRODUCTION

The “European Union Water Initiative Plus for Eastern Partnership (EaP) Countries (EUWI+)” involves six eastern neighbors of the EU: Armenia, Azerbaijan, Belarus, Georgia, Moldova and Ukraine. The EUWI+ project addresses existing challenges in both development and implementation of efficient management of water resources. It specifically supports the EaP countries to move towards the approximation to EU acquis in the field of water management as identified by the EU Water Framework Directive (WFD).River Basin Management Plans (RBMPs) are the planning tools that give the overall orientation of water management in the River Basin District and the objectives to be reached, and the priorities in the actions to be developed. Monitoring data are an important basis for water management, for risk, status and trend assessment. A strong monitoring system is critical in prioritising investment and creating a cost-effective water management system. Hence, it is crucial that monitoring data are reliable (of high quality) to avoid implementing wrong and potentially costly measures.

As specified under activity 2.3.4 chemical surveys are to be carried out to enable the development and implementation of the RBMPs. The monitoring data gathered under this activity will be used for the validation of the pressure-impact assessment (risk assessment), the validation of the water body delineation, the validation of the monitoring design, for status classification and for trend assessments.

Chemical monitoring of waters plays a key role in water management according to the WFD. Proper, representative sampling is of particular importance for the analytical result of a water sample. Errors that are made during sampling can distort analytical measurements in such a way that comparability and evaluation of data is made considerably more difficult or even impossible.

This General Manual for Chemical Freshwater Sampling is considered as an assisting tool for raising awareness of the enormous importance of representative sampling with regard to water management. Sampling is by far the most significant source of errors in the whole monitoring cycle and hence potential errors are very decisive on the reliability of data which are an important basis for water management decisions.

This manual is predominantly based on the extended experience gathered within Austrian national water monitoring lasting several decades and on the experience gathered within the various sampling trainings and water surveys implemented within EUWI+. It summarises all relevant international standards, guidance, guidelines and rules and it also considers the requirements of the European Water Framework Directive (WFD) and the Austrian legislation.

3 FUNDAMENTALS

3.1 Relevant Standards

This chapter highlights the essential elements which are addressed by the following mandatory international standards dealing with water and sediment sampling.

Table 1: Relevant standards for sampling of groundwater and surface water and of sediments

Standards	GW	SW	SED
ISO 5667-1 Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques	x	x	x
ISO 5667-3 Water quality - Sampling - Part 3: Guidance on the preservation and handling of water samples	x	x	
ISO 5667-4 Water quality - Sampling - Part 4: Guidance on sampling from lakes, natural and man-made		x	
ISO 5667-6 Water quality sampling; Part 6: Guidance on Sampling of rivers and streams		x	
ISO 5667-11 Water quality sampling; Part 11: Guidance on Sampling of Groundwater	x		
ISO 5667-12 Water quality - sampling; Part 12: Guidance on sampling of bottom sediments			x
ISO 5667-14 Water quality - Sampling - Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling	x	x	
ISO 5667-15 Water quality - Sampling - Part 15: Guidance on the preservation and handling of sludge and sediment samples			x
ISO 5667-23 Water quality - Sampling - Part 23: Guidance on passive sampling in surface waters		x	x
ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories	x	x	x

GW ... groundwater; SW ... surface water; SED ... sediments

3.1.1 ISO 5667-1 Water Quality - Sampling - Part 1: Guidance on the Design of Sampling Programmes and Sampling Techniques

- The creation of a sampling programme requires **fundamental considerations** as to the objectives of the sampling and the resulting requirements, such as the selection of suitable **locations and parameters, sampling frequency, sampling duration** and **sampling time** to obtain (statistically) representative samples. For details, reference is made to the relevant ISO standards.
- Basic instructions and references to relevant ISO standards for sampling **specific types of water** (e.g. natural waters, industrial effluents, wastewaters and sludge, water for food processing).

- Parameters for characterizing **flow conditions** (e.g. flow direction, flow velocity, flow rate) as well as adequate measuring methods.
- **Sampling techniques** (random sampling, periodic or continuous sampling) and their adequate application according to the purpose of the sampling and the water body to be sampled (standing water or river).
- **Sampling equipment and sample containers** according to the substances/components to be determined (e.g. photosensitive substances, dissolved gases, organic trace substances, radionuclides) and matrices (water, sediment) as well as references to relevant ISO standards. In addition, the **preparation of the sampling equipment** is described.
- Reference to appropriate quality assurance measures to prevent contamination during sampling.
- Sample transport, sample storage, sample identification and sampling protocols.

3.1.2 ISO 5667-3
Water Quality - Sampling - Part 3: Preservation and Handling of Water Samples

- Explanation of the need for preservation or fixation of samples for physical, chemical, biological and radiochemical investigations.
- The sample **preservation techniques** to be used for a variety of analytes. This includes, among other things, the choice of the appropriate sample container and its preparation, a suitable preservation or fixing agent, the maximum storage time and references to appropriate - international standards.
- The main points about sample labeling and sample transport.
- The reagents (solids and solutions) approved as **preservation agents** and used materials.
- The need for **filtration**.

3.1.3 ISO 5667-4
Water Quality - Sampling - Part 4: Guidance on Sampling from Lakes, Natural and Man-Made

- The standard describes the procedure for the collection, preparation, transport and preservation of water samples from **lakes** (natural and artificial) and is applicable to chemical, physical and biological water analyses.
- Correct use of various **sampling devices** (open dippers, closable bottles or dippers for sampling at defined depths, pumps).
- Correct selection of the **sampling point** to ensure representative sampling. Regarding horizontal placement, the selection should take into account the morphology. Concerning vertical placement, the stratification of the lake needs to be considered. Both dimensions can exhibit considerable heterogeneity and significantly influence the parameters to be sampled. Therefore, preliminary work may be required to establish a suitable sampling point. For large lakes, internal movements must also be taken into account.
- Frequency and timing of sampling, selection of the appropriate sampling method and the correct handling of samples.

3.1.4 ISO 5667-6 Water Quality - Sampling; Part 6: Guidance On Sampling of Rivers and Streams

- Fundamentals of programmes and techniques to be applied in the **sampling of rivers for chemical and physical analysis**. This concerns, for example, aspects such as hydrodynamic and morphological characteristics of the water to be sampled, local conditions (accessibility, vegetation, stratification of the water), water temperature, turbidity, water depth, flow velocity, turbulence, embankment inclination, variable cross sections of the riverbed, etc., which have a long-term effect on the behavior of analytes in the water.
- Correct selection of the sampling point to ensure representative sampling. Major factors include, inter alia, the mixing conditions in the body of water, the flow velocity of water masses with respect to the desired analytes and the homogeneous distribution of the analytes in the water body. In addition, references to relevant ISO norms are provided. Furthermore, the required frequency and timing of the sampling are discussed.
- Sampling at various locations (e.g. upstream or downstream of bridges, embankments, ships) and the associated varying requirements for representative sampling.
- Requirements for sampling from different water depths, sampling of surface films and light phases (light non-aqueous phase liquids, LNAPL) and use of automatic samplers. Additional information on the process of sampling with regard to preparation, preservation, transport, storage, quality assurance, sampling protocols as well as references to more in-depth ISO standards.

3.1.5 ISO 5667-11 Water Quality - Sampling; Part 11: Guidance on Sampling of Groundwaters

- The detailed sequence of representative groundwater sampling starting with the **programme structure** through the **selection of suitable measurement points and parameters**, **sampling** and on to **transport/storage** of the samples taken. In addition, peculiarities of monitoring and sampling of **point sources of contamination** (e.g. in case of presence of **light phases** [LNAPL] or **heavy phases** [dense non aqueous phase liquids, DNAPL]) as well as of **diffuse contamination** are addressed.
- Different types of **groundwater monitoring and sampling methods for the saturated and unsaturated zones**. Unsaturated zone: Procedure for sampling of solid material with subsequent extraction of the pore fluid as well as direct sampling of the pore water (e.g. via lysimeter). Saturated zone: e.g. horizon- or depth-oriented sampling, different pumping methods.
- Overview of the appropriate sampling methods for a variety of groundwater parameters.
- The essential significance of **bailing** before taking a representative groundwater sample as well as the appropriate procedures for different groundwater monitoring types. Suitable criteria for supervising the bailing process.
- The selection of suitable sampling equipment, the preservation of samples, prevention of contamination and safety instructions with references to the more in-depth ISO standards.

3.1.6 ISO 5667-12 Water Quality - Sampling; Part 12: Guidance on Sampling of Bottom Sediments

- The standard applies exclusively to the **sediment sampling of inland rivers and standing water bodies** (lakes, etc.). Sludges of industrial origin and sewage sludge explicitly excluded from its scope.
- Selection of suitable **sample containers** as well as suitable sampling equipment depending on the purpose of the planned investigation (chemical, physical, biological). A large number of different sampling devices (sediment grabbers, core samplers, manually operated devices) as well as methods for sediment sampling are presented. , The appropriate devices for different sediments are listed.
- Requirements for the selection of suitable **sampling location, sampling method** as well as frequency and timing of the sampling. Differences in the sampling of lakes and rivers are addressed.
- Storage, transport and preservation of samples as well as safety instructions. Reference to more in-depth ISO standards.

3.1.7 ISO 5667-14 Water Quality - Sampling; Part 14: Guidance on Quality Assurance and Quality Control of Environmental Water Sampling and Handling

- Quality control measures for water sampling for checking the applied procedures and achieved results.
- **Typical sources of error**, such as sample container contamination, wrong handling of unstable analytes, faulty sample preservation, and errors during sampling.
- **Quality control measures.** Working with replicas allows an estimation after sampling of the statistical error during committed during its various steps. Blank testing can be used to detect contamination of sample containers as well as contamination during sample preparation. Other measures include, among others, rinsing the containers, and checking filtrations with regard to the re-detection and the use of impurity-doped samples.
- **Transport, preservation and storage** of samples, as well as **analysis and interpretation** of the determined quality control data.

3.1.8 ISO 5667-15 Water Quality - Sampling - Part 15: Guidance on Preservation and Handling of Sludge and Sediment Samples

- This standard covers samples of sewage sludge, sludge from water works, suspended solids and sediments, from the time of sampling to the completion of chemical, physical, radiochemical and / or biological analyses in the laboratory. The presented procedures are only suitable for **wet samples of sludge, sediment and suspended solids**.
- List of permitted **reagents**, various **techniques of sample preservation**, depending on purpose of sampling (chemical, physical, biological or radiochemical investigations). **Requirements for container types, preservation and storage conditions** in table form.

- **Sampling, sample transport, container preparation and long-term storage of wet sediment samples** (application of a Nitrogen Vapour Freezer - NVF).

3.1.9 ISO 5667-23
Water Quality - Sampling - Part 23: Guidance on Passive Sampling in Surface Waters

- Fundamentals of the **functionality, use and structure of passive samplers**, supplemented by an overview of existing **passive sampler classes** for different pollutant classes (polar or non-polar organic and non-organic compounds) and the respective **calibration procedure**.
- Proper **handling** of passive samplers, estimation of the **application time** and **advance preparation** and assembly of passive samplers. For **quality assurance**, for example, the use of replicas and control samplers is described.
- Correct **selection of sampling points** as well as criteria and workflows regarding **inserting and removing** the passive samplers.
- Information on the **extraction** of the analytes from the passive samplers, subsequent **analysis** and **concentration calculations**.

3.1.10 ISO/IEC 17025
General Requirements for the Competence of Testing and Calibration Laboratories

- This standard formulates **quality standards** for testing and calibration laboratories and forms the basis for their accreditation.
- It defines general requirements for performing tests and/or calibrations, including sampling. The objective is to establish a laboratory quality system, which generates consistently reproducible or traceable results.
- The standard covers two major topics. The **management requirements** relate to the implementation and effectiveness of the quality management system in the laboratory. The **technical requirements** include aspects such as staff qualifications, testing methodology and equipment. Further technical specifications concern **sampling**, quality inspections and the preparation of test reports and calibration certificates.
- ISO 17025 contains a multitude of references to ISO 9001 ("Quality management Systems - Requirements").

3.2 Qualification and responsibility of a sampler

The responsibility for proper and quality-compliant performance of sampling lies with the sampler.

3.2.1 Qualification of a sampler

- Minimum training as a chemical laboratory technician or adequate technical training;
- Continuous training;
- Quality awareness;
- Special knowledge: analysis of trace substances, preparation of the measurement point, sampling techniques, hydrogeology etc.

Figure 1: Sample filling, © H. Heim - Umweltinstitut Land Vorarlberg.

3.2.2 Scope of responsibility of the sampler

The scope of responsibilities of a sampler goes far beyond the actual activity of sampling on site. The responsibility of the sampler ranges **from receiving the transport containers**, **the sample containers and the reagents** (which are provided by the analysing laboratory), to correct sampling (as specified by the analysing laboratory) including filtration, stabilization, clear and smear-proof labelling and transport of the samples (cooled if necessary), to the **confirmed delivery and handover of the transport containers with the collected samples** and the **delivery and handover of the sampling protocol and the recorded on-site parameters** to the client. With the signature under the sampling protocol, the sampler confirms responsibility for proper sampling.

The activities covered by the sampler include, for example:

- Coordination with the laboratory:

  - Organise preparation of suitable sample containers;
  - Arrange handover of the taken samples upon completion of the sampling;
  - Taking over prepared sample containers from the laboratory;
- Planning and preparation of the sampling tour:
  - Organise appointments with the owners of measurement points or properties; if applicable organise of preparatory measures;
  - Estimate the time required per measurement point;
  - Define the number and sequence of the measurement points to be sampled (in case of contaminated measurement points start with less contaminated ones and move on to more contaminated ones);
  - Take into account the accessibility of the measurement points;
  - When sampling contaminated water, clarify in advance the pumped, where contaminated water will be disposed of;
  - Preparation and verification of materials and measuring equipment (e.g. filters, sample stabilization reagents, sample containers, calibrated measuring instruments, pumps, hoses, sampling site passport, cooling containers, standards or standard instructions);
- On site:
  - Check the information in the sampling site passport, record deviations and, if necessary, report back to the client;
  - Proper sampling on the basis of the standard operating procedure (including, if relevant, filtration and stabilization);
  - Determine the on-site parameters;
  - Documentation of sampling with photos;
  - Verification of the sample container labelling (sample name, name of the sampling point, sampling date and possibly time, parameters, performed preservation or stabilization, possibly numbering of samples in case of identical samples, etc.);
  - Complete and sign the sampling protocol;
- Adequate storage and transport of samples;
- Delivery and handover to client/laboratory:
  - Sample containers;
  - Sampling protocol and other documentation; and
  - Determined on-site parameters.

3.3 Quality assurance

Quality assurance is an accompanying process that covers all stages of sampling. The quality assurance measures start with the awarding of the assignment, accompany sampling and analysis and extend to the plausibility check of the generated data. An essential element is the written documentation of all activities and observations before, during and after the actual sampling for the purpose of comprehensive traceability. This includes, among others:

- Maintenance of sampling equipment;
- Organisational measures prior to sampling; as well as
- The documentation of sampling on site.

The most important provisions for quality assurance in the sampling of groundwater and surface waters can be found in:

- **ISO 5667-14:** Guidance on quality assurance and quality control of environmental water sampling and handling.
- **ISO 5667-11:** Guidance on sampling of groundwater.
- **ISO 5667-4 and ISO 5667-6:** Guidance on sampling from lakes, natural and man-made, and guidance on sampling of rivers and streams.
- **Austrian Water Status Monitoring Ordinance (GZÜV):** Accordingly, the sampling of surface waters as well as groundwater and the analysis of chemical parameters including the relevant methods and the associated quality assurance measures are to be carried out in accordance with the requirements of ISO/IEC 17025.
- **ISO/IEC 17025** - General requirements for the competence of testing and calibration laboratories.

The basic requirements of the GZÜV with regard to quality assurance during sampling and the requirements of ISO/IEC 17025 are summarized in the two following chapters.

3.3.1 GZÜV - Quality Assurance: Applicable methods of sampling surface waters and groundwater – for chemistry

The GZÜV in the latest version stipulates in Annex 3 (Section III) for surface waters and in Annex 15 (Section IV) for groundwater a set of quality assurance measures for sampling and sample preparation, as part of an established quality assurance system.

Referring to sampling, it includes:

- Sampling (including preservation), container preparation and transport must be carried out using a standard operating procedure.
- Sampling must be carried out by qualified personnel only.
- The required sample volumes must be determined by the analytical laboratory.
- A complete on-site survey must be available.
- Sampling and sample run including detailed information on receipt of samples, all disruptions that may have occurred and other procedural information shall be documented in writing.
- The completeness of the samples to be processed must be checked continuously.

3.3.2 ISO/IEC 17025: General Requirements for the Competence of Testing and Calibration Laboratories

ISO/IEC 17025 sets quality standards for laboratories, which are taken as a proof of their capability and performance. With regard to the **taking of representative samples**, the following requirements apply:

- The laboratory must have a sampling plan and procedures for sampling; both have to be available at the sampling point. Deviations or additions to the specified procedure must be documented in detail in all relevant documents.
- The laboratory shall have procedures for recording the essential data and activities of the sampling. The following points have to be documented:
    - method of sampling used;
    - identification of the sampler;
    - environmental conditions;
    - description of the sampling point;
    - where appropriate, a description of the statistical procedure underlying the sampling.

3.4 Occupational safety

3.4.1 General safety precautions

- As a basic principle, existing **legal requirements** (e.g. an Employee Protection Act) with regard to health and safety must be observed.
- **ISO 5667-1** sets general requirements for occupational safety.
- **Weather and terrain conditions** must be taken into account and the method of operation must be adapted accordingly. In the alpine area, there is a risk of rock falls, avalanches and rapid weather changes.
- Once the safety of the executing person(s) is no longer provided, **additional safety measures** must be taken or sampling must be **discontinued**.
- Sampling in **contaminated areas** poses a considerable hazard potential. An advance risk assessment on the basis of available information and special preparatory measures are indispensable.
- When using **electrically operated devices** near water, caution is required.
- When handling **chemicals**, the warning and safety information on the packaging of these chemicals must be observed and obeyed.
- **Hazardous materials** (e.g. bottles with concentrated acid) must be clearly labelled and handled with care.
- Special care must be taken when handling **radioactive samples**.
- If the **air quality is dangerous**, a gas protection device and a breathing apparatus etc. must be carried along. Prior to sampling, the concentrations of oxygen, toxic or suffocating gases and vapors shall be determined. Toxic gases shall not be absorbed through the nose, mouth or skin.

Figure 2: Sampling at Lake Constance, © H. Heim - Umweltinstitut Land Vorarlberg.

3.4.2 Particularities for sampling surface waters

- **ISO 5667-6** sets special requirements for sampling surface waters.
- When taking samples from large waters, **life-jackets, safety ropes**, etc. must be carried. Backup support shall be provided by a second person outside the dangerous zone.
- If **boats** or platforms are used, they must be stable. Nautical rules must be observed (e.g. correct flagging during sampling).
- Sampling from **bridges** is to be preferred. Sampling from **unsafe places** (e.g. unstable embankments) should be avoided. If such sampling locations are unavoidable, this requires additional safeguard by other persons.
- Any equipment left on site must be protected against flooding and vandalism.
- Take care when sampling **special wastewater**: Industrial wastewater may be toxic, corrosive or develop explosive vapors. Municipal sewage can present considerable microbiological pollution or gaseous hazards.

3.4.3 Particularities for sampling at groundwater measurement points

- The **ISO 5667-11** sets special requirements for the sampling groundwater.
- The **surface** around manholes, boreholes etc. can be **unstable** and can collapse.
- Ladders and other **boarding aids in manholes** and similar objects can be unstable. Safety straps and helmet are required when going down. **Another person** has to monitor the activities from the surface.
- Before **entering closed objects** (e.g. manholes) an analysis of the air for oxygen content, flammable or suffocating gases, toxic vapors, etc. must be performed. If necessary, such tests also need to be performed above ground, if there is a significant contamination.

Figure 3: Well ‚Kaindorf‘, © H. Stadlbauer.

3.4.4 Particularities for sediment sampling

- **ISO 5667-12** sets special requirements for the sampling of sediments.
- In swampy terrain and in shallow waters, **frozen ground** may facilitate sampling. Prior to this, however, the stability of the soil has to be checked carefully.
- If the sampling is carried out while **wading** through a body of water, then unstable sediments, holes at the bottom or strong currents need to be taken account of. Adequate security measures are essential. Breast-high waders are to be avoided, as they make it very difficult to rescue the affected person in case of complete submersion.

4 PREPARATION OF SAMPLING

Before starting sampling, the sampler must obtain essential information and prepare the entire sampling. These activities include clarifications regarding the objective of sampling, organizational and technical preparation of the necessary tools and material.

4.1 Objectives – trigger for sampling

The sampler must get himself familiar with the technical background of the sampling and be aware of its purpose in order to be able to select the option corresponding to the respective task in the case any decision must be taken on the site. The following questions should be answered:

- **What is the trigger for the sampling?**
    - For example, regular statutory monitoring in accordance with a law.
- **What is the purpose of the sampling?**
    - For example, the water quality at the respective measurement points should be examined at regular intervals under the same conditions. Time series of the measurement results should allow conclusions to be drawn on changes (+/-) and eventually suggest possible causes of the changes.

1.1.1 Planning

As part of the planning of a sampling, the exact implementation procedure must be determined. Taking into account the background of the sampling, this concerns the temporal and the spatial aspect as well as the exact technical execution of the sampling. The following questions must be clarified:

- **Why** should the **sampling** be carried out?
    - see chapter above
- **Who** carries out the sampling?
    - Are there any requirements regarding qualification and number of samplers? For example, in manholes and potentially dangerous streams there should be two persons.
- **What** should be sampled?
    - Which matrix is to be sampled (groundwater, surface water or sediment) and which parameters are to be investigated? This results in the list of sample containers to be filled and any stabilization or other preservation measures, if relevant.
- **When** should the sampling be carried out?
    - Are there specifications regarding the period and timing of sampling? E.g. season, frequency, 3 months after last sampling, every 14 days, time of the day (daily temperature variation), event-dependent (after precipitation) etc.?
- **Where** should the samples be taken?
    - Precise location of the measurement point and the sampling point; e.g. list of measurement points to be sampled, before water treatment etc.

- **How** should the sampling be carried out?
    - Which specifications are to be followed in line with the background of the sampling and any normative requirements? E.g. volume to be pumped before sampling, random samples, aggregate samples, daily samples, duplicate samples, probe or well sampling, sampling at the tap?

As part of sampling preparation, **contact the client**, the analyzing laboratory and the measurement point operators well in time.

The following has to be requested from the client:

- The measurement points to be sampled;
- the sampling site passports; and
- a list of the parameters to be examined at each measurement point.

The analyzing laboratory thereafter has to request/clarify:

- Sampling and transport containers;
- Freezer packs;
- Required reagents for sample stabilization;
- Dates for sample delivery and handover, and requirements related to parameters.

The basis for **planning a sampling tour** is the overview of the measurement points to be sampled:

- Taking into account the access route, the required effort per measurement point and the order of sampling, a **sampling plan** must be prepared.
- The sampling plan must be transmitted to the client digitally.
- The **measurement point operators** have to be contacted concerning the arrangement of precise appointments and relevant information on the measurement points such as access restrictions, gate keys, entry permits, contact persons, etc.
- Depending on the accessibility of the measurement points, a suitable and functional **sampling vehicle** shall be arranged.

Figure 4: Sampling vehicle, © H. Heim - Umweltinstitut Land Vorarlberg.

- For multi-days sampling, an intermediate storage facility for samples might be necessary (perhaps with cooling!) or other sample transporting options (train, post) could be considered. It is also important to take into consideration potential deadlines regarding sample delivery and handover to the laboratory.

4.1.1 Preparation of sampling equipment, containers and necessary tools and material

Depending on the type and background of sampling, the required sampling equipment, containers and necessary tools and material have to be prepared. They must be checked on their completeness and suitability for the planned sampling and whether they are fully functional prior to sampling at the sampling site, so that potential emerging defects can be remedied in time.

- **Which sampling devices** are required depending on the type of sampling (sampling method):
    - pumps, rods and hoses;
    - measuring devices: various measuring probes, groundwater level meter;
    - power generators including necessary tools and materials (fuel etc.);
    - dippers for surface waters
    - scoops, grabbers for sediments
- **Functioning of the sampling devices and whether they are fully functional**: It must be checked whether the sampling devices are fully functional according to the device-specific requirements. The measuring instruments are to be calibrated according to the respective requirements. Depending on the sampling to be performed, the suitability of the devices must be checked. For example: is the pump capacity sufficient? Are the hoses and the groundwater level meter long enough? Do the devices comply with the qualitative requirements (purity, cleanliness) of the sampling (even between individual sampling sites or events!)?
- **Completeness and condition of the sample containers**: In coordination with the analyzing laboratory, the appropriate sampling and transport containers, together with, if necessary, any stabilization agents and freezer packs in sufficient numbers must be provided. These containers must be checked for completeness and condition (use of a protocol for documentation of the container delivery and handover is recommended).
- **Labelling of sample containers**: clear and smear-proof labelling in accordance with standard procedures;
- **Whether the necessary tools and materials are fully functional**: Necessary tools and materials also have to be checked for their condition and any defects must be remedied. Sampling site passport and sampling protocols are to be checked for completeness. Necessary tools and materials are mainly the following equipment and documents:
    - Filtration equipment and filters: do they comply with the normative requirements?
    - Hoses and connection units
    - Reagents
    - Tools
    - Water and paper towels for cleaning
    - Flashlight
    - Camera

  - GPS
  - Passports of sampling sites
  - Sampling protocols / forms

4.1.2 Sampling of contaminated waters

Special requirements apply to the sampling of contaminated groundwater and surface waters. This concerns, for example, the cleaning of the sampling equipment, the sequence in which measurement points are sampled, occupational and health safety protection as well as special features during transport and storage. The physical and chemical properties of the pollutants (e.g. light or heavy phases, volatility, sorption behavior) and their quantities are to be considered.

For example, sampling courses for contaminated sites and standards and leaflets on contaminated sites provide pertinent instructions.

5 ON-SITE SURVEY

5.1 Purpose

The on-site survey serves to find and register new influences/pressures and changes (on the sampling site and its surroundings) compared to the previously documented condition or the documentation of any notable peculiarities. The on-site survey is a prerequisite for the subsequent interpretation of the measurement and analysis results and basis for assessing the representativeness of the measurement results. It is necessary to regularly check and update the conditions as recorded during the on-site survey.

5.2 Procedure

- Observing and capturing the sensory impressions with regard to the sampling site and its surroundings, especially concerning any abnormal or striking observations
- Comparison with the information in the sampling site passport.
- Documentation of deviations from the sampling site passport or previous sampling in the sampling protocol (in writing, photos, site plan)
- Transmission of the on-site survey to the client.

1.1.2 Groundwater

Important considerations for groundwater are listed below:

- Observations at the sampling point:
    - Checking the information in the sampling site passport (completeness, is it up to date)
    - Condition of the sampling point and whether it is fully functional: examination for visible damages, safety (whether it can be closed), cleanliness, corrosion of metal parts, other changes;
    - Deposition of material and incrustations: e.g. precipitation/deposits, biota (algae, molds, animals), sediments etc.;
    - Mixed water: mixture of waters of different origin, inflow of water, overflows.

In general, operators should be informed if serious deficiencies are detected at drinking water supply systems (including individual household wells used to supply drinking water). The information sheet on household wells developed by the regional government of the Austrian province of Styria can serve as best-practice example.

- Observations in the surroundings of a measurement point:
    - Changes since the last sampling: e.g. agricultural activities, earthworks or construction works, deposition of material, unusual land use, visible sources of contamination;
    - Other abnormal or striking observations
- Weather conditions during sampling:

  - E.g. air temperature, precipitation, degree of cloudiness or sun exposure.
  - Dust being transported through the air.

Figure 5: Household well in good condition, © H. Stadlbauer.

Figure 6: Household well in bad condition, © H. Stadlbauer.

5.2.1 Rivers and lakes

Important considerations for rivers and lakes are listed below:

- Observations at the sampling point:
  - Control of the information in the sampling site passport (completeness, timeliness)
  - Visible spots of chemical reduction: Darkening of the underside of stones as an indication of oxygen deprivation and therefore reduction processes
  - Oil film (visual control), foaming
  - Water level, discharge conditions, impoundment
  - Ice
- Observations in the surroundings of a measurement point:
  - Changes since the last sampling: e.g. agricultural activities, earthworks or construction work, deposition of materials, unusual land use, visible contamination, changes of the river banks, foreign materials, sewage, foam, discharges, withdrawals;
  - Other abnormal or striking observations;
  - River development (e.g. hydraulic engineering works), substrate, sediment,
  - Biocenose (e.g. waterfowl)
- Weather conditions during sampling: e.g. air temperature, precipitation, degree of cloudiness or sun exposition.

1.1.3 Sediment

Important considerations for sediments are listed below:

- Observations at the sampling point:
  - Control of information in the sampling site passport (completeness, timeliness)
  - Visual appearance: chemically reducing (black) or oxidizing
  - Material: gravel, sand, sand to silt, silt to clay
  - Development of gas: yes / no
  - Fouling
- Observations in the surroundings of a measurement point:
  - Changes since the last sampling: e.g. agricultural activities, earthworks or construction works, deposition of materials, unusual land use, visible contamination, changes of the river banks, foreign materials, sewage, foam;
  - Other abnormal or striking observations
- Weather conditions during sampling: e.g. air temperature, precipitation, degree of cloudiness or sun exposition.

6 ON-SITE INVESTIGATIONS

6.1 Purpose

Subsequent to the on-site survey and preparatory measures for sampling, a number of **on-site parameters** are examined. This covers all the information and parameters that cannot be determined correctly later in the laboratory. These include:

- Groundwater level before sampling (at groundwater measurement points) or discharge (e.g. at springs);
- Gauge height/water level (at surface water measurement points), possibly discharge
- Secchi depth (at lakes),
- Organoleptic parameters: odour, colour, turbidity;
- Physical or physico-chemical parameters: temperature, pH, electrical conductivity, dissolved oxygen.

6.2 Special features depending on the nature of the sampling site

6.2.1 Groundwater

The following sequence of actions must be observed when sampling groundwater:

- Groundwater level before sampling (at groundwater measurement points) or discharge (at springs or in artesian groundwater), control of the total depth of the well
- Purging (pumping out stagnant water) of the measurement point until measured values are constant (see chapter 6.3.2.1), as the sampling must be carried out with "fresh" groundwater. For springs, it is possible to determine on-site parameters immediately.
- Measurement of the on-site parameters after constancy of the measured values.

Besides the immersion of the electrodes in the measurement point or in a container filled with groundwater, **flow cells** are often used for measuring the physico-chemical on-site parameters. In this case, water flows through the flow cells under airtight conditions without creating bubbles. To avoid long flow paths, the flow cell should be located directly next to the sampling site. Otherwise, the measured values can be influenced and distorted (temperature, oxygen content).

The flow cell has to be installed in a **bypass** pipe through which only a small part of the pumped water is discharged.

6.2.2 Rivers, lakes, sediments

When sampling of rivers, lakes and sediments is performed, a suitable timing must be chosen: The conditions should be representative, i.e. extreme situations should as much as possible be avoided, as they may distort multi-year time series of data.

The sampling point must be representative for the river or lake.

Sampling of rivers should be done at a location with sufficient mixing and where flow velocity is highest, because it can be assumed that at this point the largest amount of material is transported. When sampling from the embankment, the flow velocity should be around 1 m/s.

Sampling at mixing zones/pollution plumes at discharge points of point source pollution should be avoided.

6.3 Methods

According to the Austrian Ordinance on the Monitoring of the Quality of Water Bodies (GZÜV), the following units and methods are to be used in the on-site investigation:

Table 2: Overview of applicable methods for the determination of on-site parameters during sampling according to GZÜV

	Parameter	Water type *	Method **	Unit
	Groundwater level before sampling	GW	-	m
	Flow rate at sampling	GW	-	l / s
	Total pumped volume	GW	-	l
	spring discharge	GW	-	l / s
	Gauge height/water level; perhaps discharge	river, lake, sed	-	m; m^3 / s
	Secchi depth	lake	-	m
Organoleptic findings	colour	all	sensory	-
	turbidity	all	sensory	-
	odour	all	sensory	-
Measurements	water temperature	all	ÖN M 6616 (March 1994)	° C
	air temperature	all		° C
	pH value	all	DIN 38404 C5 (July 2009)	-
	elec. conductivity (GW: at 20°C, rivers at 25°C)	all	ÖN EN 27888 (December 1993)	µS / cm
	oxygen content	all	ÖN EN 25814 (June 1993)	Mg O_2 / l

** GW ... groundwater, sed ... sediment*
****** *Unless a method is specified, an internationally recognized method should be used and documented. In case a method other than the listed one is used, then it has to be demonstrated that this method is equivalent to the listed one.*

6.4 Groundwater level before sampling

The measurement of the groundwater level before sampling determines the **static groundwater level**. The reference point (e.g. upper end of the borehole pipe, upper end of the well) for measuring the water level should ideally be calibrated geodetically (or according to the information in the passport of a sampling site). It should be documented in the sampling protocol. Changes or damages to the measurement point can cause measurement errors and must be recorded in the sampling protocol.

The water level is measured with a **groundwater level meter** from a defined measurement point. To determine the exact signal point, the groundwater level meter is moved several centimeters up and down several times before reading the measurement value.

Typical problems of the use of these devices may, for example, be bends or twists in the cable. Contamination of the sampling site by the deposit of external substances when immersing the groundwater level meter should be avoided.

The groundwater level meter is to be checked at least once a year.

At installations for automatic measurement devices of water levels (e.g. data loggers), regular control measurements by groundwater level meters must be made.

Figure 7: Measurement of the groundwater level before sampling by groundwater level meter, © H. Stadlbauer.

In the case of artesian wells, the hydrostatic height is measured with pressure sensors or manometers.

Figure 8: Artesian well, © H. Stadlbauer.

It is recommended to record the total depth of the well (bottom depth of the measurement point) simultaneously with the groundwater level before sampling and to compare it with the information in the passport of the sampling site. Deviations due, for example, to excessive silting are to be recorded in the sampling protocol.

The determination of the groundwater level before sampling and the total depth is also important for the sampling itself, since knowing the height of the water column is crucial (see Sampling at groundwater measurement points).

6.5 Spring discharge (groundwater)

The simplest and most accurate method of measuring spring discharge is **volumetric measurement with a container**. This method consists of measuring the time determined which is required for filling a container (e.g. measuring cylinder, bucket) with a known volume. The container size depends on how high the discharge is. The time required for filling should be at least 10 seconds. It should be recorded with an accuracy of 0.1 seconds. The recommendation is to measure the time until the container is full and overflows. The exact volume of the vessel can be determined by calibration. Typical error sources are the use of measuring containers which are inaccurate or too small and reading errors. In case it takes more than 10 seconds to fill the container, at least three separate measurements must be carried out. Subsequently, the average value and standard deviation of these three measurements are calculated. In case it takes only a few seconds to fill the container, the measuring error increases considerably.

In some cases measuring weirs may be in place. In such cases, spring flow can be determined by measuring the water level with a gauge and a mathematical function (relation between water level and discharge). The mathematical function for the measuring weir has to be up to date.

Figure 9: Rothkogel Spring (note the gauge on the right), © H. Stadlbauer.

Other methods include flow measurements with **hydrometric flow meters** (note that the cross section of the channel must be known), **Venturi channels** or with the **salt dilution method.** In this last method, a certain amount of a salt is added to the water and changes in electrical conductivity are measured over time at an adequate distance downstream of where the salt was added (to ensure complete mixing over the entire cross section). Electrical conductivity should be measured until the values have returned to their original level as before salt had been added. Discharge can be calculated as a function of the development of conductivity values over time and the amount of added salt. In addition to these methods, **ultrasound measurements** are increasingly used to measure discharge.

Parts of the discharge which are not covered by the measurement itself (e.g. flow diversions for power plants, drinking water abstraction, etc.) must be taken into account when estimating the spring discharge.

6.6 GAUGE HEIGHT/WATER LEVEL AND DISCHARGE (RIVERS)

For determining discharge of rivers measurements with hydrometric flow meters or ultrasound flowmeters are recommended (as also described in the chapter "Spring discharge" above). The stretch of the river which is selected for applying these methods should be morphologically stable in the long term.

In open channels and basins with measuring weirs and gauges the discharge can be determined through the relation between water level and discharge.

In terms of a rough estimate, the discharge can also be determined by **multiplying the flow velocity by the approximate cross section of the channel/river bed**. In this case, a floating item (e.g. a branch, an apple, ...) is put into the river at its flow line and at a known distance in order to determine the flow velocity (m/sec). The approximate cross section of the channel/river (m^2) is calculated by multiplying its width by the average water depth. Finally, flow velocity and the cross section are multiplied, and are further multiplied by a factor of 0.6. This factor represents an empirical value aimed at reducing the error that results from the fact that the actual cross section usually does not have a rectangular shape, and that the flow velocities across the cross section are also different.

Approximate discharge (m^3 / sec) = flow velocity (m/ sec) * cross section (m^2) * factor 0.6

Experience has shown that this method can lead to large deviations or errors. Therefore, the above-mentioned methods for discharge determination are preferable. Nonetheless, an approximation of the discharge without much effort for the sampler is possible with this method.

In any case, the method used to determine the discharge must be documented in the sampling protocol.

6.7 SECCHI DEPTH (LAKES)

The measurement of the Secchi depth in line with ISO 7027 is used to determine the turbidity of a water body and is carried out by means of a round white disc (so-called Secchi disc) with a diameter of 25 cm. This disc is used to measure the maximum depth at which it is no longer visible in the water with the naked eye.

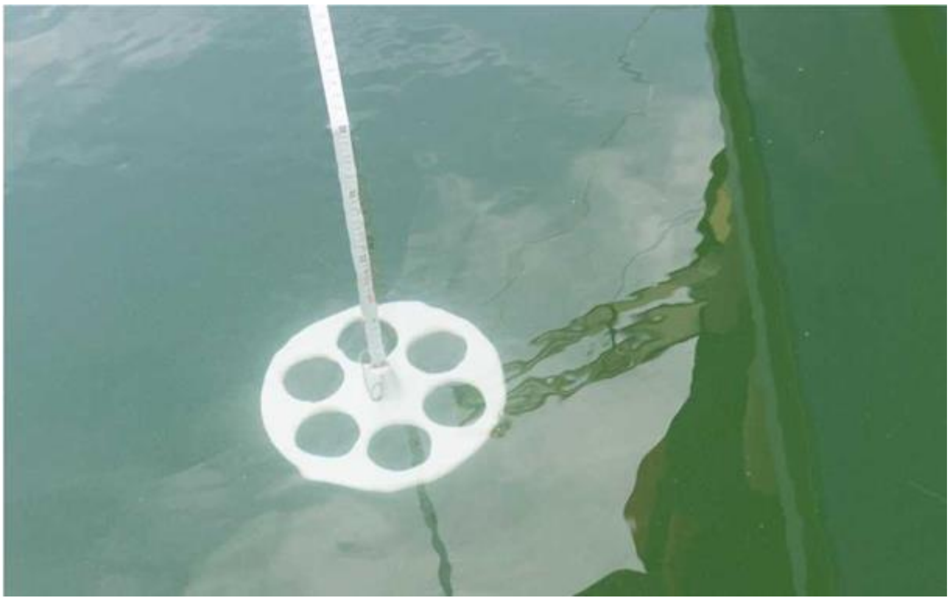


Figure 10: Secchi disc, © H. Heim - Umweltinstitut Land Vorarlberg.

The Secchi disc is attached to a cord with length markers. It is lowered into the water until the contrast of the reference pattern can no longer be discernible. The depth is determined by reading the length markers, and this first reading is recorded. The process is then repeated, but in the opposite direction. The string is lowered a bit deeper than where the first measurement was recorded (about 40-50 cm), and slowly brought up again. Once the reference pattern becomes discernible, the corresponding depth is again determined by reading the length markers, and is recorded. The arithmetic mean of the two measured values is calculated to obtain the mean value of the Secchi depth.

6.7.1 HINTS, ERROR PREVENTION, TROUBLESHOOTING

The measured values depend on the eye-sight of the sampler, as well as on the weather and light conditions and on water currents. This means that all measurements should at least be taken at the same time of the day - around noon - and in calm water.

The accuracy of the measured values can be determined by repeating measurements, by having different samplers conduct several measurement runs, and by wearing polarized sunglasses.

6.8 FLOW RATE AND TOTAL PUMPED VOLUME (GW)

If a mobile pump is used for sampling, a continuous measurement of the abstracted volume must be carried out. The flow rate as well as the total pumped volume water from switching on the pump to the start of sampling must be recorded. Changes in the flow rate during pumping must be documented. When using permanently installed pumps and when sampling at a tap, both parameters must be recorded, as well.

Modern flow measurement devices use magnetic-inductive methods or ultrasound. The method of indirect volume determination from flow rate and duration of the pumping, which is used frequently, is often inaccurate and should be avoided if possible. Its inaccuracies result from adjusting the flow rate - during pumping, from changes in the sampling system, such as when bypasses are opened, and from inaccurate filling of sample containers. Using appropriately sized water meters is also possible.

Essential details on purging a well and pumping can be found in chapter 6.3.2.

6.9 ORGANOLEPTIC PARAMETERS

The organoleptic analysis of water involves the qualitative testing of color, clarity or turbidity, odour and deposited solids or sediments. The analysis takes place when the parameters are no longer changing (constant) and is carried out in a transparent container with a minimum volume of one liter in front of black and white background. Any abnormalities in relation to the water or the measurement point can thus be determined in advance.

- **Coloring**: Determination of color tone, intensity and possibly development of the color over time. Drinking water must be colorless.
- **Turbidity:** caused by very fine, suspended mineral or organic material. Documentation of color and intensity of the turbidity. The test is carried out by means of a light source.
- **Odour:** determination of the type and intensity of the smell (e.g. earthy, foul, certain chemicals). Drinking water should be free from any smell.
- **Water surface:** e.g. oil film, floating solids, foaming

The findings must be documented in the sampling protocol.

6.10 WATER TEMPERATURE

6.10.1 FUNDAMENTALS

Temperature measurements can, for example, allow conclusions about the origin of the water, any pollution or human impacts. Toxic effects of certain substances contained in water are also dependent on temperature (and pH). Temperature is also considered a decisive factor for the growth of aquatic organisms.

The water temperature is sensitive to environmental influences (e.g. sunshine, soil frost or snow), which should be minimized accordingly. In addition, temperature measurements in groundwater can be distorted due to the following conditions:

- low flow rate
  - at low flow rate (<5 l / min) groundwater near the pump can be heated by the pump itself.
- low well volume
- long pipes
  - also to be taken into account when sampling at taps inside buildings

6.10.2 CALIBRATION

The measuring instruments must be checked regularly with reference thermometers. The correction factor must be noted on the instrument or in the recording book belonging to the instrument.

6.10.3 MEASUREMENT

The temperature measurement of the water is carried out at:

- for **groundwater,** usually electronically by handheld measuring device either directly in the discharged water or in a flow cell.
- For **springs**, at source or at the intake of spring tapping or in a small measuring cup under the intake has to be performed.
- In **rivers**, it may be necessary to record vertical or horizontal temperature profiles to determine a mean water temperature.
- In **lakes**, the temperature is usually measured in the vertical profile.

6.10.4 HINTS, ERROR PREVENTION, TROUBLESHOOTING

- IMPORTANT! Before reading values, it is necessary to let the electrodes reach the same temperature as the sampled water. This is the case when the temperature is constant (see chapter 6.3.2.1). The reading accuracy for water temperature is 0.1° C. Wrong measurements often happen because samplers do not wait for sufficiently long time.

6.11 PH VALUE

6.11.1 FUNDAMENTALS

Figure 11: pH measurement, © H. Heim - Umweltinstitut Land Vorarlberg.

The pH value characterizes the acid or base content of an aqueous solution. Accordingly, it reacts very sensitively, to temperature changes, degasification, oxidation or precipitation of insoluble compounds, among others. For this reason, it is crucial that pH value is measured directly on site, because later measurements in the laboratory can no longer be representative.

Normally the measurement is done with electrodes. These glass electrodes are very sensitive and must be maintained regularly. A number of factors can cause a significant impairment of the measurement accuracy and may lead to a situation where it becomes necessary to replace the electrodes:

- Coatings (e.g. mud, lime, gypsum)
- Chemicals (e.g. concentrated acids or bases, acetone, alcohols)
- Mechanical stresses (e.g. hairline cracks, particles, vibrations)
- Aging (e.g. greatly prolonged stabilization time)

6.11.2 CALIBRATION

The pH value is exclusively measured with devices that are recalibrated before each day of use. Regarding calibration and handling, the instruction manual of the devices needs to be considered. The calibration of the pH meter is carried out with two buffer solutions. These solutions must be selected depending on the expected range of the expected pH values of the waters to be sampled (e.g. buffers with pH 7.0 and pH 10.0 for rather alkaline waters, buffers with pH 4.0 and pH 7.0 for rather acidic waters). The measurement accuracy must be within ± 0.05 pH units.

6.11.3 MEASUREMENT

Because of sensitivity to environmental influences described above it must be carried out immediately.

If the measurement is not carried out in streaming water, but at a tap or by pump, then a sufficiently sized container with a volume of at least 250 ml should be used to rinse the electrode and reach the state of equilibrium for the measurement. The following containers are suitable:

- airtight flow cells with low, bubble-free flow,
- Measuring cups which are filled via a hose placed on their bottom (this minimizes gas exchange with the ambient air).

If **spings** are sampled using a small submersed pump, pH value can be measured directly in the pond/pool at the sampling point or in the flow of the pumped water.

In **rivers**, the measurement takes place in an unfiltered bailed sample or ideally directly in the river; where appropriate, a vertical and horizontal profile may need to be taken to determine the mean pH value.

In **lakes**, a depth profile is usually recorded.

While measuring, the electrode is slowly moved in the water. The pH value is only read when it is stable. The stabilization of the value usually takes a few minutes. Due to the fact that the pH value depends on temperature, the temperature of the sampled water should be recorded at the time of reading. During the measurement, the temperature should remain as stable as possible.

The electrode is usually stored in three-molar potassium chloride solution (see manufacturer's instructions).

6.11.4 HINTS, ERROR PREVENTION, TROUBLESHOOTING

- Calibrate the measuring instrument in the expected pH range before each day of use.
- Check the quality of the calibration buffer regularly. If necessary check it with an additional buffer (possibly from a different manufacturer).
- After completion of the calibration (before the first sampling), the measured values of the calibration buffer must be recorded. After completion of the last sampling, the measured values of the same buffer must be measured again. This way, a possible drift of the measuring electrodes can be traced throughout the day.
- Measuring the pH value of very low mineralized waters may be problematic. If the quality criterion according to chapter 6.3.2.1 cannot be achieved, then this must be documented in the sampling protocol.

6.12 ELECTRIC CONDUCTIVITY

6.12.1 FUNDAMENTALS

The electrical conductivity [µS/ cm] in the water is a measure of the content of freely mobile carriers of electrical charge (ions), which can conduct the electric current. The electrical conductivity of waters is a measure of the salinity (total mineralization) and must always be corrected to a reference temperature due to its temperature dependence. **The reference temperature according to GZÜV is 20° C for groundwater and 25° C for surface waters.**

The on-site determination of electrical conductivity provides information about the representativeness of the sample. If the electrical conductivity differs significantly from other measurement points in the area, then this can, for example, be an indication of different origin of the water or of contamination. From an economic point of view, it makes more sense to immediately review these measurements or to go into further detail, than weeks and months later within the framework of the next sampling tours. The electrical conductivity of a sample may change over time due to precipitation processes. Pre-treatment of samples (e.g. acidification) will change the electrical conductivity, too.

The following table provides an overview of the range of electrical conductivity of selected waters.

Table 3: Electrical conductivity of selected waters

Water type	Electrical conductivity [µS/ cm]
"Purest" water	0,055
Distilled water	< 3
Rainwater	5 - 100
Groundwater	100 - 1900 (in Austria on average: 696)
Tap water	150 - 800
Mineral water	150 - 2,000
Seawater	about 50,000

6.12.2 CALIBRATION

Unlike pH and oxygen measurement, the conductivity cell does not wear down and exhaust itself. Calibration of the conductivity cell is therefore to be understood as a verification or control measurement. This control measurement must be carried out according to the manufacturer's instructions. (A 0.01-molar potassium chloride solution has a conductivity of 1.278 µS/ cm at 20° C and of 1.413 µS/ cm at 25° C. If the deviation is more than 1.5% of the set value, the electrode must be thoroughly cleaned). If necessary, the cell constant needs to be adjusted.

6.12.3 MEASUREMENT

- Set reference temperature
    - Groundwater: 20° C (as specified in GZÜV).
    - Surface waters: 25° C (as specified in GZÜV)
- **Determine water temperature.** (Modern measuring instruments usually allow automatic temperature compensation to the selected reference temperature).
- The **smallest possible reading range** for the most accurate determination of the measurement results.
- **Measurement** (to be done quickly)
    - **Complete** immersion of the probe.
    - Rinse and wait for the **temperature** of the probe to **adjust** to the water in the container.
    - **Discard** the first sample.
    - **Definitive** measurement in another sample.
    - **Control measurement** in another sample.

- Documentation in the sampling protocol (mind the units! mS/ cm, µS/ cm).
- Rinse the probe with distilled water.
- If necessary, manual calculation of the temperature compensation to the desired reference temperature for measuring devices without automatic temperature correction.

During **groundwater sampling**, the measurement of electrical conductivity usually takes place either in the flow cell or in a suitable container.

For **springs**, the electrical conductivity can be measured directly at source, free discharge outlet or at the intake of spring tapping.or in a small measuring cup under the intake has to be performed.

In **rivers**, the measurement should ideally be made approximately 10 cm below the water surface. The probe should be moved up and down a bit through the water column. If necessary (depending on the size of the water course), the recording of horizontal or vertical profiles is necessary to determine a mean value.

In **lakes**, measurements are taken along depth levels.

6.12.4 HINTS, ERROR PREVENTION AND TROUBLESHOOTING

- Mind the temperature compensation (reference temperature for groundwater: 20° C or for surface waters 25° C)
- If water with an oil film is sampled, auxiliary means must be used to take oil-free water from below the surface film in order to avoid contamination of the probe.
- Badly connected probes and oxidized connections (moisture!) lead to malfunctioning of the measuring instrument.
- Air bubbles or incomplete immersion of the probes can lead to errors.
- Depending on the hydrochemistry of the examined waters, precipitation may occur on the probe. Calcium carbonate can be removed with diluted hydrochloric acid.

6.13 DISSOLVED OXYGEN

6.13.1 FUNDAMENTALS

The amount of oxygen dissolved in water is proportional to the local atmospheric pressure and is inversely related to temperature and salinity. Since oxygen regulates the solubility of many trace metals and the bacterial conversions of organic compounds in the groundwater (reducing/ oxidizing conditions), measuring dissolved oxygen allows conclusions to be drawn regarding the decomposition of organic substances, the origin of the water or the mobilization of metals. The oxygen concentration in a water sample changes with time. Enrichment of the sample with oxygen by air contact or draining out of gases of the sample, for example by shaking, leads to erroneous measurements.

The measurement of dissolved oxygen in water is to be carried out according to ISO 5814 or ISO 17289. Methods for measuring dissolved oxygen on-site usually include amperometric (oxygen electrode) or spectrometric methods (color change after addition of chemicals). For some time now, optical electrodes have also been used. The measurement of the oxygen content is usually carried out with oxygen electrodes, which are suitable for oxygen contents > 0.01mg/l. For some probes, a minimum water flow is to be ensured.

Commercially available devices allow measuring of the following parameters:

- Concentration of dissolved oxygen (mg/l)
- relative saturation of dissolved oxygen (%, dependent on pressure and temperature)
- temperature

Oxygen saturation refers to the percentage of measured oxygen content to the maximum oxygen content which water can absorb at the same temperature (referred to as the saturation value). Modern measuring devices automatically calculate the measured oxygen concentration into the oxigen saturation. For manual conversion via an oxygen saturation table, the air pressure needs be measured.

Table 4: Water solubility of oxygen depending on temperature

Temperature [° C]	Oxygen content [mg / l]
0	14.64
10	11.25
20	9.08
30	7.55

Different oxygen contents of the water can be defined as follows:

- aerobic: oxygen present in molecular form
- anoxic: oxygen not "free" but in a bound form (e.g. NO3- , SO42-)
- anaerobic: oxygen neither present in molecular nor bound form

6.13.2 CALIBRATION

The calibration is carried out according to the manufacturer's instructions at the beginning of a series of measurements or when pressure conditions (altitude, air pressure) have changed. This is done either by an air calibration or by determining the zero point (0 mg/ l in a sodium sulfite solution) and the inclination (oxygen concentration in oxygen saturated water depending on water temperature and air pressure).

6.13.3 MEASUREMENT

- **Put the oxygen electrode** into the flow cell, the source intake, or directly into the river, lake or well. A minimum flow according to the manufacturer's instructions must be ensured. Avoid turbulence (in order to avoid the input into or discharge of oxygen from the sample).
- **Determine water temperature.** (Modern measuring instruments usually allow automatic temperature compensation to the selected reference temperature).
- **Documentation** in the sampling protocol (in particular also the type of measurement, e.g. directly in the discharging water or in a container).
- **Rinse** the probe with distilled water and store it according to manufacturer's instructions. (This usually means that the membrane at the tip of the electrode must be kept moist.)
- If necessary, manual calculation of temperature and air pressure compensation for measuring devices without automatic **correction**.

If the **measured in a container** at a tap or after pumping or bailing, at least 1 liter of water must be taken and the measurement must be taken immediately. In case of insufficient flow conditions in the container, move the electrode at the appropriate speed to ensure renewal of the dissolved oxygen near the permeable electrode membrane. The stabilization time for a measurement is about one minute. The reading of the measurement result only takes place when the dissolved oxygen content shown on the display of the measuring device is stable.

In **rivers**, the measurement should ideally be made approximately 10 cm below the water surface. The probe should carefully be moved vertically through the water column. It might be necessary (depending on the size of the body of water) to record horizontal or vertical profiles of dissolved oxygen to determine an average value.

In **lakes**, measurements are taken along depth levels.

6.13.4 NOTES, ERROR PREVENTION AND TROUBLESHOOTING

- Check batteries and connections
- Avoid air bubbles and turbulence, minimum flow according to manufacturer's instructions.
- The probe must be calibrated at the beginning of a series of measurements as defined in the manufacturer's instructions.

6.14 PREPARATION AT THE MEASUREMENT POINT

Preparation of devices:

- The air thermometer should be placed at a suitable location (shady, unaffected by heat) about 1 m above the ground.
- The measuring instruments need to be switched on in time, depending on the respective stabilization time, and may need to be calibrated.
- When using a mobile pump, the corresponding power generator should be positioned on the side facing away from the wind and sufficiently far away from the sampling point so that an influence on the sampling can be ruled out.

Preparation of the surroundings:

- In order to rule out any influence on the sampling by exhaust gases, power generators and vehicles should be positioned accordingly. The engine of the vehicle should be switched off.
- Eating, drinking and smoking should be omitted before and during sampling. Products that can lead to distortions or falsifications of the samples to be taken may not be used (depending on the purpose of the sampling, these could, for example, be insect repellents, sunscreens etc. ...).
- Place all equipment and tools on a clean surface. It is preferable to leave them in the vehicle.

Preparation of sampling vessels:

The labeling of the sampling vessels prepared by the laboratory must be checked and complemented if necessary.

The minimum required information is:

- Sample name,
- Name (incl. code) of the sampling or measurement point
- Sampling date and time,

- Performed preservation or stabilization,
- If known, project number, project name,
- Possibly the parameters to be analysed
- Possibly numbering of the sample containers in case of identical samples.

7 SAMPLING OF GROUNDWATER

7.1 SAMPLING AT THE TAP

For cased wells and spring, sampling is often done at the tap. It is crucial to sample raw water. Upstream pumps, air chambers, tanks, treatment plants (thermal, chemical, physical) etc. change the nature of the water.

Any hoses and sieves or strainers need to be removed from the tap.

The pipe system must be sufficiently flushed before the actual sampling. This process may be, for example, tracked via the continuous measurement of electrical conductivity. Flushing is complete when the electrical conductivity is constant over an extended period of time. When sampling at a tap, it should only be turned on to such a degree that the resulting flow is moderate. Let the water flow until the electrical conductivity stabilises, or let it flow for approximately 10 minutes. Water samples should always be taken under exclusion of air and free of turbulence in order to avoid changes in the carbonate balance, precipitation of iron and manganese or incorrect values of oxygen, volatile chlorinated hydrocarbons, etc.

When filling the sample containers, direct contact with the tap should be avoided.

Figure 12: Tap, © H. Stadlbauer.

7.2 BAILING SAMPLE

Especially at springs or in case of special tasks (e.g. concerning mineral oils) the sampling can be done by **bailing**.

The following aspects should be considered:

- Upon entering the spring the sediments may not be swirled up.
- The sampler takes the bailing sample upstream of herself or himself.
- The measuring cup for taking the bailing sample needs to be rinsed several times before use, and the watered used for rinsing must be emptied downstream of the sampling point.

7.3 PUMP SAMPLING

7.3.1 INSTALLATION OF THE PUMP

Depending on the type of measurement point (e.g. dug well, borehole, piezometer...) there are different requirements for the installation of the sampling pump and for the sampling itself.

At **dug wells** (household wells, field wells), it can generally assumed that the water mainly enters the well through the bottom of the well. Accordingly, a mobile sampling pump should be positioned as close as possible to the bottom.

Currently, mostly very light submersible pumps are used for sampling, which means that due to their low discharge capacity full purging of the water in a dug well cannot reasonably be ensured. Therefore, using the much more powerful fixed pumps which are usually installed in dug wells is preferable.

At **groundwater measurement points with filter screens**, the mobile pump should be installed at least 1 m below the water level (or, if known, at least 1 m below the expected maximum drawdown). In any case, however, care must be taken that the distance to the final depth (bottom of the measurement point) is at least 1 m, as swirled-up sediments or turbidity should be avoided.

If the water level in a groundwater measurement point is below the upper edge of the filter screen, then the pump must be installed approx. 0.5 m above the lower edge of the screen and the measurement point must be purged fully. If the water level in the measurement point is still below the lower edge of the filter screen 24 hours later, then the measurement point is considered dry and will not be sampled. Under no circumstances should the water in the sump pipe be sampled.

7.3.2 Well purging

Stagnant water in a groundwater measurement point can be significantly changed in its nature due to contact with the atmosphere and the materials used in the well itself, as well as due to biological processes., Therefore, it must be pumped out completely prior to sampling (IMPORTANT: **do not fully pump out the measurement point until it is dry**, except in case the water level is in the screened part of the well casing). For a representative sampling, ’fresh’ groundwater from the vicinity of the measurement point must be sampled. The physical and chemical parameters of this ‘fresh’ water are the same as those of the groundwater in the inflow of the measurement point.

When purging the well, the **drawdown of the water level is to be kept as low as possible** because a cone of depression which might develop can change flow and mixing conditions in the vicinity of the measurement point. Usual flow rates range from 0.1 to 1 liter per second. At lower flow rate, it must be assumed that the groundwater is heated by the sampling devices.

Both during purging and during sampling it is important to operate the pump continuously. In the event of interruptions, the water from the pumping system flows back into the measurement point, causing swirled-up mixed water from the measurement point to infiltrate back into the gravel filter around the well casing. In case of an interruption of the pumping, it is therefore necessary to start the pumping (and possibly the sampling) again.

CRITERION OF WATER QUALITY EQUILIBRIUM

The water in a groundwater measuring point is purged (pumped out) until it is representative, that is when the pumped water has a constant quality. Constant **electric conductivity** and constant **turbidity** or clarity of the pumped water can be used as proxies for this constant quality. In this case, the pumped water corresponds to the surrounding groundwater and is no longer influenced by the measurement point. The oxygen concentration as well as temperature and pH need to be observed in addition to electrical conductivity and turbidity. Temperature and pH are considered less sensitive parameters.

The changes during purging of the abovementioned parameters are continuously recorded (automatically or manually) in the sampling protocol to determine the appropriate timing for sampling. In addition, the development of these parameters during purging may be important for the interpretation of the data. Intervals of one to five minutes between readings are feasible and useful. The total discharged volumes also must be recorded.

The timing for representative sampling is reached, when the values of the measured parameters are constant at the following values within a purged volume of 50 l:

Table 5: Well purging: target values for the timing of representative sampling

Parameter	Permissible fluctuation range
electric conductivity	± 0.5% or 1% of the final value
temperature	± 0.1K
pH value	± 0.05
oxygen concentration	± 0.1 mg / l

Stronger fluctuations of the parameters even after longer purging are an indication of unusual changes in water quality at the measurement point. The cause thereof may be short-circuit currents either between parts of aquifers with differing water quality through the gravel filter of the measurement point or through faulty seals of the annular space between the standpipe and the well casing.

HYDRAULIC CRITERION

Another method of ensuring that representative ‘fresh’ water from the catchment area of the measurement point is sampled is the hydraulic criterion. This criterion depends on the properties of the measurement point and is based on information on the well casing and screen and the gravel filter.

In general, the hydraulic criterion is equal to 1.5 times the volume of the circular cylinder, which is calculated by multiplying the length of the casing with its diameter.

$V = n \frac{\pi}{4} d_{BL}^{2} l_{F}$ Where V… Volume (m^{3})

l_{f}…Length of the filter filled with water (m)

d_{BL}.. Borehole diameter (m)

n…Factor (recommendation: $n > 1.5$)

To ensure that the sample is representative according to the quality criterion and the hydraulic criteria, the pumping time should be at least 10 minutes.

7.3.3 DISPOSAL OF PUMPED WATER

Non-contaminated pumped water from groundwater sampling can be infiltrated at a distance of at least 5 meters downstream, taking into account the surface terrain. It may also be discharged into a river or may be disposed differently if this does not cause any damages. The infiltration must not have any detrimental consequences (e.g. impoundment), and may not influence the sampling.

The infiltration of polluted pumped water at contaminated sites/brownfield sites and the infiltration of pumped water in case of soil or groundwater pollution are subject to special regulations. These special regulations need to be checked before the sampling. They may, for example, concern permits, containers for collecting the water and possibilities for disposal.

8 SAMPLING OF SURFACE WATERS

When sampling surface waters, the right choice of sampling location and timing are crucial. The samples should be representative with regard to time and place.

The weather and runoff conditions immediately before and during sampling must therefore be documented. A method for the approximate determination of the discharged volume is described in chapter 5.6.

Concerning spatial representativeness, it is important to take care that the sampling is not carried out at sewage plumes, in dead water zones or in areas of re-turbulence. Rather, the sample should be taken where the largest solute transport is to be expected or where the flow velocity during sampling from the embankment is approximately 1 m/s (see Chapter 5.2.2).

Entering the water body should be avoided as much as possible both for safety reasons and in order to prevent that sediment is swirled up

Taking water samples from **rivers** is done in the form of individual samples by means of dippers. Before sampling, the used equipment must be thoroughly rinsed several times with the water to be sampled. When sampling from bridges or similar structures, care should be taken that no contaminants get into the dipper, for example by touching the bridge with the sampling equipment. The dipper should not be placed on the floor between sampling.

Figure 13: Water sampling in a river, © H. Heim - Umweltinstitut Land Vorarlberg.

When sampling the bottom of the water should not be touched with the dipper in order to prevent the sediment being swirled up. Likewise, the sampling of floating solids should be avoided.

The dipper must be put into the upper third of the total depth of the water body (approximately 10-20 cm below the surface of the water is generally a useful depth). The opening of the dipper or sampling container should be oriented downstream.

If several rounds of bailing are required to fill the sample containers, then the homogeneity of the sample must be ensured.

When sampling **lakes**, individual samples from several depth levels are used to analyze the chemical parameters at the measurement point. The following minimum number of individual samples must be observed:

- During the stagnation phases:
    - Epilimnion: 3 depth levels
    - Metalimnion: up to 20 meters: 2 depth levels
    - Hypolimnion: 1 depth level per 20 meters, the last sample 1 meter above ground
- During the circulation phases:
    - Epilimnion: 1 depth level
    - Metalimnion: up to 20 meters: 1 depth level
    - Hypolimnion: 1 depth level per 30 meters, the last sample 1 meter above ground

In Lake Neusiedl (a very flat lake in Austria), sampling is done at one depth level, and in the Old Danube (a major back water of the Danube in Austria) two depth levels (surface, above ground) are sampled. In the case of stratified lakes, the mean concentration is calculated as the arithmetic mean of the samples from the individual depth levels weighed by volume.

9 SAMPLING OF SEDIMENTS

Sediment examinations are part of the Austrian trend monitoring programme, which is conducted every third year to record long-term developments of pollution levels. The sampling points should be selected so that the samples at the measurement point are representative.

In general, the finest sediments (silt, clay) are of particular interest in the sampling of sediment, since they are usually deposited during low and mean water conditions and also because the finest part of the sediment always has the highest sorption capacity. These uppermost fine sediments are usually several weeks to several months old. It is also very likely that they were only deposited after the last flooding.

Sampling must be prepared and performed by persons with adequate expertise in sedimentology, geochemistry and hydrology.

The sediment needs to be taken from several sampling points, that is at least six sampling points which are representative of the measurement point. The entire sampling area should be homogeneous with regard to sedimentology (uniform sedimentological conditions). If possible, it should also be large enough to allow long-term sampling of comparable sediments.

The topmost part of the bank sediments (upper 3 cm) has to be sampled with a small hand shovel/dustpan made from an inert material such as teflon. The sampled material needs to be put in precleaned sample containers until enough material is sampled (gross sample) (minimum sample quantity: 1.5 kg of fine material, if possible without water on top). It is especially important to ensure that the fine sediment is not washed out because of the flow or because the sample is removed too rapidly and carelessly, thereby causing a distorting relative accumulation of coarser sand.

To ensure that samples are comparable between years, the sampling should be carried out at the most similar conditions (discharges) possible, preferably at the end of the low water period during winter and prior to the onset of the snowmelt and its increased discharges. Sampling during extreme conditions or prolonged periods of low water should be avoided.

The sediment sampling should preferably take place at the same time as the regular chemical sampling. Contrary to previous practice, today from the samples are no longer sieved on site, because this practice had repeatedly caused contamination and granulometric fractionation (splitting into different grain sizes) of the sample. Weighing and screening (after freeze-drying) is usually done in the laboratory.

For special tasks/issues, sampling the uppermost sediment layer in a body of water may be necessary. To ensures comparability, the sediment layers of 0-10 cm should be sampled using a core sampler. The sediment needs to be sampled at least at six points. The samples taken in this way should be combined into aggregate samples.

If no core sampler is available, it is also possible to use a PE pipe (diameter max 2 inches or 50 mm, transparent if possible)and to pierce or press it into the sediment to obtain a comparable sample of 0-10 cm. Larger pipe diameters may not be suitable. The high water content of fluvial sediments may lead to the loss of the sample when the pipe is pulled out. If such a commercially available PE pipe is used, it needs to be rinsed or cleaned with water in advance.

In order to ensure as uniform and reproducible sampling conditions as possible, the samples should not be taken with sediment grabbers, since the penetration depth of the grippers differs depending its size and weight, the associated sinking speed and, above all, the sediment density.

If sampling with a core sampler is not possible, a gripper can be used as a last resort if the sample can be taken out with the grippers closed, that is via a sampling flap. When sampling with a gripper, particular care must be taken to ensure that it is pulled out very slowly and carefully, in order to limit the amount of the fine sediment which will be washed out.

For each sampling, a sampling protocol is to created. This protocol needs to include the sampling site, if applicable the individual sampling points (geographical coordinates, GPS), the external influences at the time of sampling (e.g. water temperature, weather conditions, other peculiarities), the used sampling device and a macroscopic description of the sediment.

10 FILLING, FILTRATION, PRESERVATION

10.1 FILLING A SAMPLING CONTAINER AND PRESERVATION

The material of the sample containers depends on the parameters to be analyzed. It should be taken into account already during the preparation of the sample containers by the laboratory, that the sampling team, among other things, is to be informed about the extent of the sampling. The stabilization of the samples on site by the sampler according to the specifications of the laboratory is a further step. The preservation should be done as quickly as possible.

Figure 14: Filling, © H. Heim - Umweltinstitut Land Vorarlberg.

Some of the ISO standards presented at the beginning of this handbook contain the requirements on permissible preservation agents and suitable sample containers. With regard to suitable containers, the following principles apply:

Table 6: Materials of sampling containers depending on parameters (selection)

Parameter	Material of the sample vessel
Metals	High density polyethylene
Volatile organic pollutant	gas-tight, closable glass containers
Organic compounds (e.g. pesticides, trace substances)	brown glass
Organic sum parameters (e.g. DOC, TOC, COD)	brown glass
Anions, cations	preferably high density polyethylene

To avoid carryover, the sampling tools must not get into contact with the preservation agents. Any risk of cross-contamination needs to be ruled out.

The preservation of the samples is specified by the analyzing laboratory. The nature of the preservation agent determines the order in which the sample containers are filled:

- First, those sample containers should be filled which had **not** been prefilled by the laboratory with a preservation agent.
- Subsequently, those sample containers should be filled, which had been prefilled by the laboratory with a **powdered** preservative.
- Finally, all other sample containers are filled.

10.2 FILTRATION OF WATER SAMPLES

For most parameters, the analysis is done with the unfiltered sample. However, some parameters require filtration of the water sample. These parameters include **DOC and metals**.

The filters which need to be used, as well as the filtration methods, are specified by the analyzing laboratory. Usually, 0.45 µm pore size filters are used to remove particulate matter from dissolved substances. The laboratory regularly needs to check the used filters for contamination. The product specifications and the blank value check of the filters must be documented.

The filter material must not retain the substances to be determined and the filtration device must not contaminate the sample.

The filtration is always done before preservation (cooling, adding preservation agents).

11 DOCUMENTATION

11.1 SAMPLING PROTOCOL

- Name (incl. code) and description of the sampling points (location and well description)
- Groundwater level before sampling and lowered water level (in m above sea level; required accuracy: centimeters; type of measuring device used, e.g. groundwater level meter)
- Time of sampling (date, time)
- Name of the sample (unique labeling)
- Description of the sampling process (pumped, bailed; flow rate, pumping duration, total pumped volume until sampling)
- On-site parameters (organoleptic, physicochemical parameters, dissolved gases)
- Type of sample treatment and preservation, as well as material of the sample container
- Are the groundwater measurement points fully functional (e.g. damage to the pipe)
- Any observed peculiarities! (e.g. any strange/conspicuous deposits)
- Name and organization of the sampler
- Protocol of delivery and handover to the laboratory of the samples in the prepared containers
- Delivery and handover of the sample(s) to the laboratory; example: Sampling protocol DIN 38402-13

11.2 DELIVERY AND HANDOVER PROTOCOL

- Sample number
- Sample size
- Sample container
- Condition of the samples
- Cooling and transport

12 AFTER SAMPLING

12.1 LEAVING THE SAMPLING POINT

Before leaving the measurement point and the sampling site, it must be restored to its original condition. The following activities will therefore have to be carried out:

- Closing taps, wells, probe pipes, etc.
- Closing any locking devices, including any barriers or gates
- Returning keys, checking out at the reception if applicable
- Reporting any damages or other impairments that may have occurred or that may have been noted

Sampling equipment, containers and necessary tools and material must be stowed away and transported properly and completely.

12.2 SAMPLE TRANSPORTATION

In addition to cooling, the requirements for the transport of the filled sample containers include protecting the containers against leaking and spoilage of the samples, protecting them from contamination, and from severe vibration and breaking. For a number of parameters, the time between sampling and analysis must not exceed 24 hours, even if the samples stored properly. Detailed regulations on this topic can be found in ISO 5667-3 Water quality - Sampling Part 3: Preservation and handling of water samples. In general, the shorter the time interval between sampling and analysis is, the more reliable the result of the analysis will be.

The filled sample containers must be labeled in a correct and unique manner. During transport and storage in appropriate transportation containers, the sample containers must be kept **cool** (5 ± 3 °C) with sufficient freezer packs and **in a dark place**. However, because of possible precipitation reactions in the sample and danger of glass containers breaking, the samples must not freeze. Special care must be taken when transporting at negative temperatures.

12.3 DELIVERY AND HANDOVER OF SAMPLES

Arrangements on the delivery and handover of samples should already be made during preparations together with the analyzing laboratory. It is necessary to prepare a protocol for sample delivery and handover, and to hand this protocol over to the analyzing laboratory. The following points should be considered during sample delivery and handover:

- Creating the protocol of delivery and handover with at least the following information: date and time of sampling, name of sampler, sample number, number and type of containers per sample number
- Checking for completeness: Both the number of samples and the associated containers must be checked for completeness

- Delivery and handover together with the protocol: When handing over, the date and any possible damages or other peculiarities (e.g. that sample containers are only half-full) should be noted and the delivery and handover has to be confirmed.

12.4 DOCUMENTATION

12.4.1 SAMPLING SITE PASSPORT

The sampling site passport of the respective measurement points need to be updated at each sampling. When carrying out the sampling, any possible changes or peculiarities at the measurement point need to be recorded with a note of the date and the name. This information needs to be transmitted to the client. Depending on the requirements, the sampling site passport must be stored or sent to the client.

12.4.2 ON-SITE SURVEY

Details on the on-site survey can be found in chapter 4. After taking the samples, the on-site surveys must be checked for completeness and must be supplemented if necessary. Depending on the requirements, they must be stored or sent to the client.

12.4.3 SAMPLING PROTOCOLS

Details of the sampling protocols can be found in chapter 10.1. After sampling, the protocols must be checked for completeness (clear name of the measurement point, full recording of the on-site survey, other peculiarities) and supplemented if necessary. Depending on the requirements, the sampling protocols must be stored or sent to the client.

12.4.4 PHOTO DOCUMENTATION

Any photographic documentation must be provided with clear name and date. Depending on the requirements, this photo documentation must be stored or sent to the client.

12.5 Cleaning and maintenance of the sampling devices and any necessary tools and materials

After the end of a sampling day, the sampling equipment and the necessary tools and materials must be cleaned and maintained in accordance with the device-specific and qualitative requirements. Possible contamination must be ruled out or checked with blank samples. Thereafter, the sampling devices and the necessary tools and materials, including the required measuring equipment records, must be stored properly. Any damages must be remedied or, if the equipment is no longer fully functional, the sampling devices and the necessary tools and materials must be sent for repair or taken out of operation.

Sampling equipment and necessary tools and materials include the following (see also chapter 3.1.2 under preparation):

- Pumps, rods, hoses,
- Measuring instruments: groundwater level meter, measuring probes,
- Power generators including necessary tools and materials
- Measuring cup
- Dipper, scoop, core sampler, sediment grabber, ...

Verification of the sample container labelling (sample name, name of the sampling point, sampling date and possibly time, parameters to be analysed, performed preservation or stabilization, possibly numbering of samples in case of identical samples, etc.).

13 SOURCES OF ERROR

Sampling is the basis for all further procedures in the monitoring of bodies of water. Figure 15 illustrates that, in terms of the final result, sampling is the basis for all subsequent steps. It can also be by far the most significant source of error. Analytical errors are far smaller and merely the tip of the iceberg in terms of potential sources of error. Consequently, sampling must be done with utmost care and in compliance with applicable quality assurance measures.

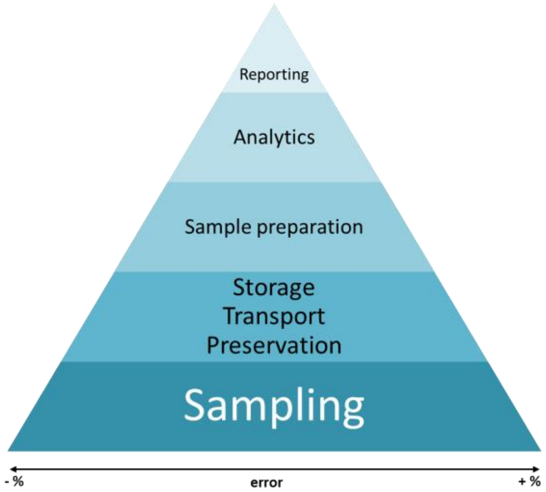


Figure 15: potential sources of error and their extent in sampling and analytics.

13.1 TYPICAL SOURCES OF ERROR IN SAMPLING

13.1.1 GENERAL ERRORS

- Taking the wrong sample because the measurement point was mixed up with a different one
- Measurement point incorrectly shown in the map or wrong coordinates given
- sampling point not described precisely (for example, is it located before or after an air chamber)
- Mixing up samples due to incorrect labeling
- Incorrect selection of parameters
- Ignoring the variability of characteristics with time

13.1.2 CONTAMINATION BY INTRODUCING SUBSTANCES

- Contamination by carryover of substances due to insufficient cleaning of equipment and containers
- Contamination by using equipment and containers made of unsuitable materials
- Cross-contamination by preservation reagents
- Mixing up of caps/lids/seals of sample containers
- Contamination from ambient air (e.g. exhaust gases from combustion engines, solvents)

13.1.3 LOSSES DUE TO DISCHARGE OF SUBSTANCES

- Discharge of volatile components when filling the sample container because of incorrect sampling technique
- Discharge of volatile components due to caps/lids/seals of the sample containers which are not gastight
- Diffusion through, into and out of the container material (in both directions)
- Sorption of substances on the sampling device
- Chemical and biochemical reactions with precipitation of substances

13.1.4 OTHER METHODOLOGICAL AND LOGISTIC ERRORS

- Sampling protocol incomplete or created at all
- Sample not preserved or wrong methods used
- Storage and transport of the samples
- Data collection and transmission done in a faulty manner
- Impermissible interpolations between the measurement points during analysis of the created data

13.1.5 TYPICAL ERRORS FOR GROUNDWATER MEASUREMENT POINTS

- Water level not measured, thus incorrect positioning of the pump
- Stagnant water sampled, because the well was not purged sufficiently long time
- Contamination or damaging of the measurement point
- Depth-dependent variability of groundwater quality
- Faulty construction of the measurement point with the screen at the wrong depth and with insufficient sealing of the annular space
- Vertical flows in the measurement point
- Material used in the measurement point
- Material used in the annular space
- Aging of measurement points
- Error due to incorrect design and construction of the measurement point

13.1.6 TYPICAL ERRORS FOR SURFACE WATER MEASUREMENT POINTS

- Non-representative sampling time (flow conditions)
- Non-representative sampling point (sewage plume, dead water zone, ...)
- Contamination by the sampling device
- Sediment swirled up
- Floating solids included in the sample

13.1.7 TYPICAL ERRORS IN SEDIMENT SAMPLING

- Non-representative sampling time, no fine sediment (e.g., after flooding)
- Non-representative sampling point (flood sediment)
- Contamination by the sampling device
- Non-representative sampling by sampling of only one site
- Fine sediment washed out during sampling

14 CHECKLISTS

General minimum requirements:

- Qualified sampling staff who regularly undergo training and who are conscious of the importance of high quality sampling;
- Knowledge of the measures for quality assurance
- Knowledge and understanding of the task at hand
- Adapting the sampling to local conditions (including weather and terrain conditions) and to the parameters to be investigated;
- Knowledge of occupational health and safety requirements;

The quality management requirements presented here can only be minimum requirements. In each individual case, it must be checked whether these are adequate and appropriate to the task. In addition to the requirements described in the previous chapter, further general minimum requirements concerning quality assurance during sampling are specified in this chapter.

Planning and preparation of the sampling:

- Coordination with the laboratory/ client:
    - Technical background and purpose of the sampling. Number and sequence of the measurement points to be sampled is determined.(in case of contaminated water, first sample at less polluted measurement points and then move on the more polluted ones; accessibility of measurement points);
    - requirements regarding qualification and number of samplers;
    - requirements regarding period and exact timing of sampling;
    - Comprehensive information on the measurement point (sampling site passport) with exact details on the sampling site;
    - special requirements concerning the type of sampling (e.g. volume to be purged before sampling, random samples, aggregate samples, daily samples, duplicate samples, probe or well sampling, sampling at a tap, bailed samples);
    - Scope of sampling (list of the parameters to be examined per measurement point, measuring devices, filtration, stabilization, etc.);
    - Preparation of suitable sample containers (taking into account the required sample volumes);
    - Handover of prepared sample containers, freezer packs and required stabilization agents from the laboratory;
    - Arrange timing for the delivery and handover of the samples after the end of sampling;

- Planning the sampling tour
    - estimating the time required per measurement point;
    - Fix an appointment with the owner of the measurement point or the property and arrange preparatory measures if applicable. For probes with automatic data loggers, the owners/operators of the measurement point need to be contacted beforehand to arrange the removal of the device, if necessary.

  - Decide on the sampling plan including the itinerary and send it to the client;
  - organize a suitable and functional sampling vehicle;
  - In case of sampling over multiple days, organize interim storage for samples or means to transport the samples (train, post), as well as accommodation for the sampler(s);
  - When contaminated water is sampled, arrange the disposal of the pumped contaminated water in advance;

- Equipment (depending on the type of sampling)
  - Sampling plan and sampling procedures must be available at the sampling site;
  - Preparation and verification of materials, sampling and measuring equipment. Checking whether they are fully functional, suitable and compliant with the quality requirements (purity, cleanness);
    - Pumps, hoses and connectors;
    - Power generators including necessary tools and material
    - Sampling devices (e.g. dippers)
    - Tools
    - flashlight
    - camera
    - GPS
    - Filtration units and filters
    - stabilization agents
    - sample containers
    - calibrated measuring devices
    - Cooling container (and freezer packs)
    - groundwater level meter
    - tape measure
  - Check the containers for completeness, condition and labelling;
  - Information on the measurement points (sampling site passport);
  - Sufficient number of sampling protocols, pencils/pens;
  - standard operating procedures;

On site

- On-site survey – Determining any changes to the situation on site as documented in the sampling site passport
  - Documenting the sensory impressions in relation to the sampling site and its surroundings;
  - checking the condition of the measurement points and indicating possible impairments

  - checking the information in the sampling site passport (e.g. land use in the surroundings, earthworks), recording any deviations from the previously documented situation (in writing, photos, site plan) and, if necessary, giving feedback to the client;
  - weather conditions during sampling.
  - oil film (visual inspection)
  - ice
- Equipment
  - set up and, if necessary, calibrate measuring instruments;
  - rinse the clean sampling system at regular intervals and in case of suspicion rinse it with ultrapure water. Check the water used for rinsing for special control parameters. If the defined limit values are exceeded: targeted cleaning, replacement of individual parts, use only in highly polluted waters or dispose of the sampling system;
  - set up the disposal of the purged water.
- Observations / measurements / investigations
  - Measuring the water level, the drawdown or the spring discharge and flow
  - Organoleptic parameters: smell, colour, turbidity;
  - Purge (pump out) the standing water at the groundwater measurement point until the measured values are constant (except at springs and at wells which are used continuously)
  - Measuring the physicochemical parameters temperature, pH, electrical conductivity, dissolved oxygen (preferably with a flow cell).
- Sampling
  - sampling according to the standard operating procedure;
  - follow the correct sequence of filling the sample containers;
  - Set the pump flow rate correctly
  - wait until the measured values are constant;
  - filter and stabilize the sample if necessary
  - verify the labelling of the sample container (sample name, name of the sampling point, sampling date and possibly time, parameters, preservation or stabilization performed, possibly numbering of samples for identical samples, etc.);
  - continuously check the completeness of the samples .
- Documentation (in writing)
  - identification of the sampler;
  - environmental conditions;
  - description of the sampling site;
  - description of whether the groundwater measurement points is fully functional (e.g. damage to the pipe)
  - Description of the sampling process (pumped, bailed; flow rate, pumping duration, total pumped volume until sampling);
  - If necessary, description of the statistical procedure used to determine the sampling;

  - Any incidents that may have occurred and further specific information on the process;
  - deviations or additions to the required procedure as defined in the sampling plan and the sampling procedure;
  - documentation of the sampling with photos;
  - sampling method used;
  - On-site parameters (organoleptic, physicochemical parameters, dissolved gases)
  - Type of sample treatment and preservation, as well as material of the sample containers
  - Add any pertinent comments to the sampling protocol, including on peculiarities during sampling, and sign the protocol;

Leaving the measurement point and the sampling site

- Closing taps, wells, probe pipes, etc.
- Closing any locking devices, including any barriers or gates
- Returning keys, checking out at the reception if applicable
- Reporting of any damage or other impairments that may have occurred or that may have been noted

Storage and transport of samples and equipment

- Sampling equipment, containers and necessary tools and material must be stowed away and transported properly and completely;
- The filled sample containers must be labeled in a correct and unique manner. During transport and storage in appropriate transportation containers, the sample containers must be kept **cool** (5 ± 3)°C with sufficient freezer packs and in a **dark** place
- Samples must not freeze (due to air temperatures near the freezing point).

Delivery and handover to the client/laboratory:

- Sample containers;
- Signed sampling protocols including recorded on-site parameters;
- Sample delivery and handover protocol of the prepared containers to the laboratory (including sample number, sample quantity, containers, condition of the samples, cooling devices and means of transport)
- Delivery and handover of the sample(s) to the laboratory - Example: Sampling protocol DIN 38402-13
- Other documentation with regard to changed master data of the sampling site passport, impairments of measurement points etc. and possibly photo documentation.

15 TEMPLATES

15.1 SAMPLING PROTOCOL GROUNDWATER

15.2 SAMPLING PROTOCOL SURFACE WATERS

15.3 SAMPLING PROTOCOL SEDIMENTS

15.4 PROTOCOL FOR SAMPLE DELIVERY AND HANDOVER

SAMPLING FIELD PROTOCOL – GROUNDWATER

Project:

General

Sampling Date:

Time (hh:mm):

Sample ID:

Sampling person:

Institute:

Sampling site

Sampling site ID:

Type of sampling site: ☐ Well ☐ Spring ☐ …………………

Inner diameter of well (mm):

Distance between land surface and well head (m):

Calm water level (m below well head):

Final depth of well (m below well head):

Further information of the sampling site (e.g. coordinates):

Sampling

Type of sampling: ☐ with bailer ☐ with pump ☐ at a tap

Abstraction device:

Pumping duration (min):

Abstraction rate / discharge (l/sec):

Field parameters (at the sampling)

Weather:	Colour:	Turbidity:	Sediment:	Smell:
☐ sunny	☐ colourless	☐ no	☐ no	☐ odorless
☐ cloudy	☐ slight	☐ low	☐ low	☐ putrid
☐ changing	☐ strong	☐ moderate	☐ moderate	☐ fishy
☐ rain	☐ brown	☐ strong	☐ strong	☐ chemical
☐ heat	☐ grey	☐ ……………..	☐ ……………..	☐ chlor
☐ frost	☐ yellow			☐ gasoline/oil
☐ ……………..	☐ ……………..			☐ ……………..

Measuring device:

pH-value:

Water temperature (°C):

Dissolved oxygen (mg/l):

Electrical conductivity incl. reference temperature (µS/cm): ☐ at 25 °C ☐ at 20 °C

Sample treatment: ☐ chilled ☐ filtrated ☐ stabilised with acid ☐ ……………….

Remarks:

Execution of the sampling and of the above works according to the sampling manual and the requirements of the laboratory.

Signature of sampler: ____Date:___________________

Name of sampler:____

SAMPLING FIELD PROTOCOL – SURFACE WATER

General aspects

River Basin / River Name					
Site Name					
Site Number		Surveyor (name)			
Site Number coordinates	N	E	GPS Waypoint:		
Sample number		GPS Photo Number			
Sampling date and time	Date (DD-MM-YYYY)	Time (HH.MM)			
Stream order		River Type		Est. Discharge	
Air temperature °C					
Weather conditions (mark with „X“)	**Light conditions** 0…Not available 1…Sunny 2…Covered 3…Gloomy 4…Cloudy 5…Foggy	**Precipitation** 0…Not available 1…Dry 2…Drizzle 3…Rain 4…Hail 5…Snow 6…Thunderstorm	**Air temperature** 0…Not available 1…Cold 2…Mild 3…Warm 4…Hot 5…Sticky	**Wind** 0…Not available 1…Calm 2…Slightly windy 3…Wind 4…Strong wind 5…Storm 6…Hurricane	

Water quality parameters – field measurements

Water temperature	°C			
pH-value				
Electrical conductivity at 20°C	µS/cm			
Dissolved oxygen concentration	mg/l			
Oxygen saturation	%			
Colour (Please describe)				
Turbidity of water (mark with “X”)	1…no turbidity	2…low	3…moderate	4…strong
Smell (Please describe)				

☐	Preservation measures for chemical / biological samples carried out according to the specifications of the laboratory
☐	Deviating preservation measures (see remarks)
☐	No changes in the condition of the sampling site or its surroundings compared to the situation as documented in master data sheet
☐	Changes detected (see remarks)

Execution of the sampling according to Standard Operating Procedure No.:

Name of Surveyor: Signature:

SAMPLING FIELD PROTOCOL – SEDIMENTS

River Basin / River Name					
Site Name					
Site Number		Surveyor (name)			
Site Number coordinates	N	E	GPS Waypoint:		
Sample number		GPS Photo Number			
Sampling date and time	Date (DD-MM-YYYY)	Time (HH.MM)			
Stream order		River Type		Est. Discharge	
Air temperature °C					
Weather conditions (mark with „X“)	**Light conditions** ☐…Not available ☐…Sunny ☐…Covered ☐…Gloomy ☐…Cloudy ☐…Foggy	**Precipitation** ☐…Not available ☐…Dry ☐…Drizzle ☐…Rain ☐…Hail ☐…Snow ☐…Thunderstorm	**Colour of sediment:** ☐ reducing (black) ☐ oxydizing ☐ ☐ brown ☐ grey ☐ yellow ☐ …………….	**Smell of sed.** ☐ odorless ☐ putrid ☐ fishy ☐ chemical ☐ chlor ☐ gasoline/oil ☐ …………….	
Sample	☐ Single sample	☐ composite sample (min. 5 single samples)			
Sampling depth	☐ 0–3 cm	☐ > 3 cm			
Collection device	☐ Scoop	☐ dredge	☐ Corer	☐ other_____________	
Material	☐ Gravel	☐ Sand	☐ Ssand-silt	☐ Silt-clay	
Gassing	☐ yes	☐ no			

Field measurements	**unit**	**Water**	**Sediment**
Temperature	°C		
pH-value			
Electrical conductivity at 20°C	µS/cm		
Dissolved oxygen concentration	mg/l		
Oxygen saturation	%		

Remarks

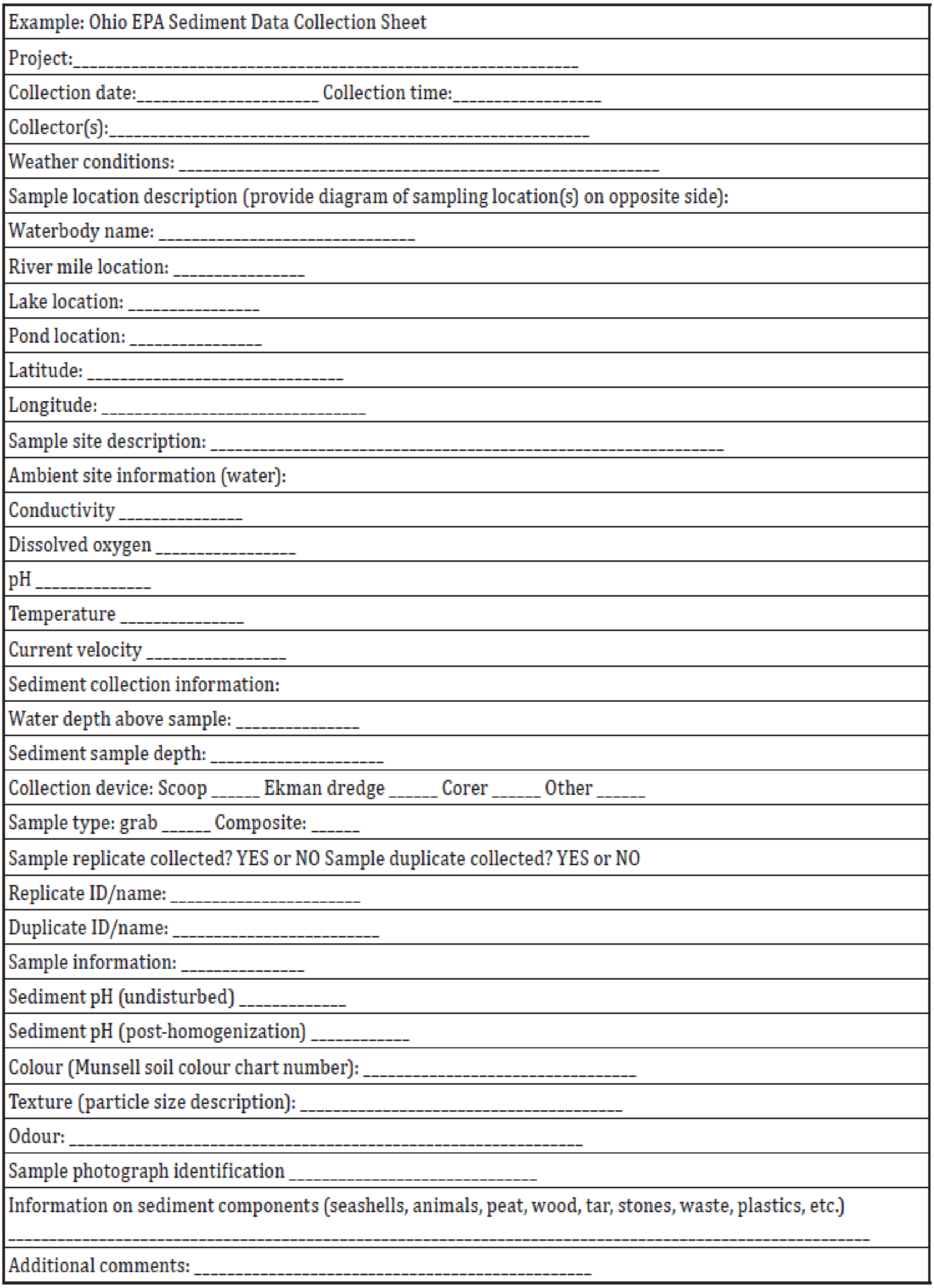
Execution of the sampling according to Standard Operating Procedure No.: ________from_________

by (Name of Surveyor) __________________ Signature_________________________________

Sample preparation

Sample sieving	☐ in the laboratory	☐ on site	**Mesh size**	µm
Sample container	☐ Aluminium	☐ Glass	☐ other_____________	
Cooling	☐ yes ☐ no	**Keep dark**	☐ yes ☐ no	

Further example for a sampling protocol for sediment sampling



Example: Ohio EPA Sediment Data Collection Sheet

Project:____

Collection date:_____________________ Collection time:_________________

Collector(s):____

Weather conditions: ____

Sample location description (provide diagram of sampling location(s) on opposite side):

Waterbody name: ______________________________

River mile location: _______________

Lake location: _______________

Pond location: _______________

Latitude: ______________________________

Longitude: ______________________________

Sample site description: ____

Ambient site information (water):

Conductivity ______________

Dissolved oxygen ________________

pH _____________

Temperature ______________

Current velocity ________________

Sediment collection information:

Water depth above sample: ______________

Sediment sample depth: ____________________

Collection device: Scoop _____ Ekman dredge _____ Corer _____ Other _____

Sample type: grab _____ Composite: _____

Sample replicate collected? YES or NO Sample duplicate collected? YES or NO

Replicate ID/name: ______________________

Duplicate ID/name: ________________________

Sample information: ______________

Sediment pH (undisturbed) ____________

Sediment pH (post-homogenization) ___________

Colour (Munsell soil colour chart number): ________________________________

Texture (particle size description): ______________________________________

Odour: ____

Sample photograph identification ____________________________

Information on sediment components (seashells, animals, peat, wood, tar, stones, waste, plastics, etc.)

____

Additional comments: ____

Example: Protocol for sample delivery and handover – general

RECEIPT OF HAND-OVER OF SAMPLES AT THE LABORATORY	
Project:	
Client:	

Date and time of hand-over:	
Number of samples received:	
Matrix (e.g. groundwater):	
Parameter groups to be analysed:	
Samples stabilised [yes/no]:	
The submitted samples are according to the announcements / expectations (matrix, bottles, number of samples,…):	
Remarks:	

Confirmation of the laboratory of hand-over of samples

Date: ________________________________

____ ____

Received by (name in capitals): Signature

Example: Protocol for sample delivery and handover – Surface water

River basin			
River			
Sampling site			
Sample type			
Sample number			
Sample date			
Sample time			
Number of samples/bottles			
Handed over on (Date):		Handed over on (Time):	
Handed over by: Signature:		Received by: Signature:	

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