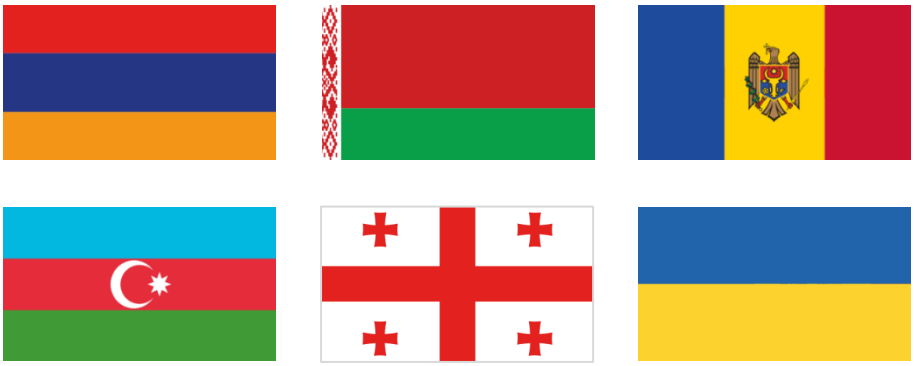
Action funded by the EUROPEAN UNION

EUWI+ EU WATER INITIATIVE FOR EASTERN PARTNERSHIP

European Union Water Initiative Plus for the Eastern Partnership Countries (EUWI+)

Result 2

SPECIFIC MANUAL FOR CHEMICAL SURVEYS IN GROUNDWATER



Final version; December 2020

umweltbundesamt ENVIRONMENT AGENCY AUSTRIA

OiEau International Office for Water

Responsible EU member state consortium project leader

Alexander Zinke, Umweltbundesamt GmbH (AT)

Responsible international thematic lead experts

Andreas Scheidleder, Christoph Leitner, Umweltbundesamt GmbH (AT)

Authors

Franko Humer, Andreas Scheidleder and Christoph Leitner, all Umweltbundesamt GmbH (AT)

Imprint

Owner and Editor: EU Member State Consortium

Umweltbundesamt GmbH	Office International de l'Eau (IOW)
Spittelauer Lände 5	21/23 rue de Madrid
1090 Vienna, Austria	75008 Paris, France

Responsible IOW Communication officer:

Ms Chloé Déchelette c.dechelette@oieau.fr

December 2020

CONTENTS

List of Tables

List of figures

Abbreviations

DG NEAR ..... Directorate-General for Neighbourhood and Enlargement Negotiations of the European Commission

EaP ..... Eastern Partnership

EC ..... European Commission

EPIRB ..... Environmental Protection of International River Basins

EU ..... European Union

EU-MS ..... EU-Member States

EUWI+ ..... European Union Water Initiative Plus

IOWater/OIEau .... International Office for Water, France

ISO ..... International Organization for Standardization

IWRM ..... Integrated Water Resources Management

LOQ ..... Limit of Quantification

NGOs ..... Non-Governmental Organisations

OECD ..... Organisation for Economic Cooperation and Development

QA ..... Quality Assurance

RBD ..... River Basin District

RBMP ..... River Basin Management Plan

ToR ..... Terms of References

UNECE ..... United Nations Economic Commission for Europe

WISE ..... Water Information System for Europe

WFD ..... Water Framework Directive

1 EXECUTIVE SUMMARY

This Specific Groundwater Survey Manual is focused at and provides guidance on groundwater sampling and is considered as an assisting tool for the tailored preparation and planning of sampling campaigns for gathering data on groundwater quantity and quality.

The manual tackles sampling, logistics and documentation (reporting) and covers all elements of a successful groundwater sampling campaign, including the clarification of the scope of the survey, the timing and logistics, all responsibilities, the extent of sampling and chemical analyses, the sampling equipment and tools and the general principles and procedures of groundwater sampling. Many of these aspects are assisted by respective tables and templates which are partly prefilled and which need to be amended and completed during the preparation process.

This Specific Groundwater Survey Manual has already been applied and tested within all groundwater surveys under EUWI+ and refined according to the gathered experiences.

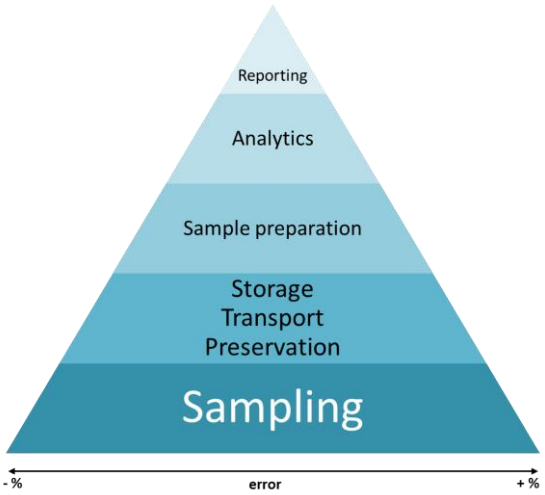
2 INTRODUCTION

The “European Union Water Initiative Plus for Eastern Partnership (EaP) Countries (EUWI+)” involves six eastern neighbours 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 the 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 several steps in water management, in particular for the risk, status and trend assessments. A strong monitoring system is critical in prioritising investment and in creating a cost effective management system. Hence, it is crucial that monitoring data are available and reliable (of high quality) to avoid implementing wrong and potentially costly measures.

As specified under the EUWI+ 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 newly delineated groundwater bodies, of the monitoring design and of the pressure and impact assessment. Furthermore, the gathered data build a basis for the upcoming risk, status and trend assessments as well as for the overall reporting.

When gathering monitoring data, sampling is of utmost importance, as mistakes and errors in sampling cannot be ‘repaired’. This specific groundwater survey manual is aiming at summarising all aspects and elements needed in order to avoid as many errors as possible, and to guarantee that the upcoming groundwater survey delivers monitoring data of high confidence.



Each groundwater sampling campaign needs the tailored preparation of an individual and detailed Survey Manual and this Specific Groundwater Survey Manual acts as a template. It needs to be completed before each individual survey by involving all relevant players and by specifying all details.
A smooth and quality-assured implementation of a groundwater survey is guaranteed when all the aspects and steps in this Specific Groundwater Survey Manual are clarified beforehand, and when all the provided tables and templates are carefully completed.

Finally, the completed Groundwater Survey Manual serves as a basis for the preparation of the technical Groundwater Survey Report.

3 GENERAL ASPECTS

Date of survey	<____>
Location	The survey is performed in the <___>
Sampled monitoring sites	The sampling covers in total <___> monitoring sites. The list of the monitoring sites and the passports of the sites are attached as Annex.
Objective, reason for sampling	- to validate the newly delineated groundwater bodies; - to validate the monitoring design; - to validate the pressure and impact assessment; - to gather data as a basis for the upcoming risk, status and trend assessment. - <___>

3.1 Contact persons and responsibilities

Responsibilities	Institution, contact person, email-address
Overall responsible for groundwater chemical monitoring	Institute: Address: Contact person: E-Mail:
Responsible for organising groundwater sampling	Institute: Address: Contact person: E-Mail:
Groundwater sampling team	Institute: Address: Contact person: E-Mail:
Responsible for functional check of sampling equipment	Institution: Address: Person: Email / phone:
Responsible for calibration of field measuring equipment	Institution: Address: Person: Email / phone:
Analysing laboratory and contact person.	Institute: Address: Contact person: E-Mail:

3.2 Analysed substances and preservation method

Table 1: Parameters for field measurement *(list to be amended, in close consultation with the laboratory)*

Field parameters	Unit	Type of measurement < field device / test strip / …>
Water temperature	°C	
Electrical conductivity	µS/cm	
Dissolved oxygen	mg/l	
pH value		
Ammonium NH4	mg NH4/l	
Total hardness	°dH	
Nitrite NO2 / Nitrate NO3	Mg/l	

Table 2: Parameters for laboratory analyses *(list to be amended, in close consultation with the laboratory)*

Parameters	Unit	Treatment of samples	Bottles
Major ions			
Calcium Ca	mg/l		
Magnesium Mg	mg/l		
Sodium Na	mg/l		
Potassium K	mg/l		
Chloride Cl	mg/l		
Fluor F	mg/l		
Nitrite NO2	mg NO2/l		
Nitrate NO3	mg NO3/l		
Sulphate SO4	mg SO4/l		
Metals			
Mercury Hg	mg/l		
Arsenic As	mg/l		
Lead Pb	mg/l		
Iron Fe	mg/l		
Chromium Cr	mg/l		
Copper Cu	mg/l		
Nickel Ni	mg/l		
< >			

The bottles need to be stored in a **dark and cool place**

4 PREPARATION FOR FIELD TRIP

Careful planning and preparation for groundwater sampling campaigns is a matter of quality assurance. It safes time, helps reducing the number of problems - which commonly occur during fieldwork - and significantly contributes to raising the quality and reliability of the analysed data.

Thorough preparation in the office and laboratory prior to sample collection is important. The contracted laboratory will provide field measuring devices, sampling containers, required filtration units and acids for stabilisation. It is important to agree on the timing of handing over the sampling equipment at the beginning and to agree on a schedule for handing over the filled bottles for laboratory analyses.

4.1 Checklist of logistics

General

- Organise official papers from the beneficiary in national language to facilitate access to wells.
- Prepare and take along sufficient business cards.

Monitoring sites

- Inform the well owners of the planned sampling activity, acquire permission for sampling and arrange access to the sites.
- Study the well locations (maps, plans) and define sampling route.
- Check the passports of the sites.
- Study past analysis of water quality.
- Analyse the technical characteristics of each sampling site (e.g. type and diameter of the casing, well yield, depth of well and water level) to select the correct sampling equipment (pump type, length of tubes, size of bucket, length of rope for sampling bailer, safety equipment).

Laboratory logistics / timing

- Contact the laboratory well in advance for preparing bottles, chemicals and equipment for field measurements. Submit the list of indicators and substances which are going to be analysed.
- Agree on logistics and timing for handover of bottles, chemicals and equipment before the sampling campaign, during the sampling and after the sampling. Identify contact person.
- Prepare a protocol for delivery and handover of samples (including: date and time of sampling, name of sampler, sample number, number and type of containers per each sample number).
- Pick-up bottles and chemicals and equipment for field measurements from the laboratory well in advance of the sampling and check completeness and functioning.

Transport / Logistics / Sampling and measuring equipment

- Organise transport for sampling campaign, check functionality and ensure sufficient gasoline.
- Pick-up and collect all necessary equipment and devices and check completeness (e.g. power supply, pumps, tubes, field measuring devices etc.).
- Functional check of the sampling equipment and check on cleanliness.
- Calibrate field measuring equipment and check on cleanliness. Replace batteries.
- Prepare / copy sufficient sampling protocols.

- Prepare self-adhesive sample labels.
- Cool the cooling elements.
- Pack bottles in such a way that they do not break during transport.
- Check first aid equipment.

4.2 Check list of material to be prepared

The following material has to be prepared prior to the sampling trip *(list to be amended and completed well before the field trip)*:

Transport		
Unit	Item	Specification
	Car	

General / Logistics		
Units	Item	Specification
	Clean plastic **sheets** for protecting field equipment from pollution with soil.	size 2x2 m
	Paper towels	2 packs
	Clean plastic **bucket** for measuring well yield, purge volume of groundwater and measure field parameters.	10 l in volume
	Clean plastic **bucket** for filling the sampling containers.	3,5 l in volume
	Clean plastic **bucket** for cleaning the pump and the tubes	20 l in volume
X pairs	Disposable **rubber gloves** for sampling (L size)	
X pairs	Work gloves	
	Self-adhesive sample **labels**	2x5 cm
	Groundwater sampling **field data sheets**	
	Handover protocol with laboratory (for confirming delivery of samples)	
	Spare **batteries** for on-site measuring equipment	Size AA or AAA
	Digital **camera** and storage card for documenting the status and the surrounding of the monitoring site.	
	Dropper	
	Marker	

Pump / Water abstraction		
Units	Item	Specification
	Pump	
	Bailer	
	Cable ties	
X m	Plastic **tube** for pump	
	Batteries for pump	

Material for sample preparation / stabilisation		
Units	Item	Specification
X ml	Concentrated **nitric acid** (HNO_3) for preserving groundwater samples for the analysis of metals	
X ml	HCl (10%)	
X ml	Kaliumdichromate 10%	

Field equipment		
Units	Item	Specification
	Groundwater **level meter**	
	Test stripes	
	pH meter	
	Laboratory thermometer	
	Conductometer	
	Cooling box	
	Cooling elements	

Bottles from laboratory			
Units	Item	Size (ml, L)	Labelling of bottle
	PET		
	Brown glass		
	Borosilicate glass		
	Borosilicate glass		
	Borosilicate glass		

4.3 Contact and timing with laboratory

Responsibilities	Institution, contact person, email-address
Overall contact person at the laboratory for the sampling crew	Laboratory: Address: Person: Email / phone:;
Before sampling Pick up bottles, chemicals and equipment for field measurements	Laboratory: Address: Person: Email / phone:; Date:
During sampling Handover of filled bottles	Laboratory: Address: Person: Email / phone:;
After sampling Handover of filled bottles, remaining chemicals and equipment	Laboratory: Address: Person: Email / phone:; Date:

5 LIST OF SAMPLING SITES

Table 3: Groundwater sampling sites *(table header to be amended as necessary)*

№	Sampling Site Code	district	location	Type of regime [phreatic / under pressure]	Approx. depth of groundwater level [m]	Groundwater body Code	Groundwater body Name
1							
2							
3							
4							
5							

6 LOCATION OF SAMPLING POINTS AND PROPOSED SAMPLING ROUTE

Table 4: Travel plan

Day	Visited sampling sites	Total travelled distance per day [km]	Place for staying overnight
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			

Figure 1: Sampling route and location of sampling sites

7 SAMPLING

7.1 Well purging

The stagnant water in a well is quite different (physically and chemically) to the water in the surrounding aquifer. Therefore it is necessary to purge each well before sampling of representative water samples can be done. The purging of a well abstracts the stagnant water and allows the groundwater from the surrounding aquifer to flow into the well casing. The amount of the water that needs to be abstracted before must guarantee that the sampled water is representative of the water in the surrounding aquifer. This depends on the height of the water column in the well and on the diameter of the well casing. The pumping rate is very much depending on the hydraulic properties of the aquifer.

There are two options to assess the amount of groundwater that should be purged before taking samples:

- **Option 1:** Purge the well until the measurements of pH, electrical conductivity, dissolved oxygen and temperature for the abstracted water stabilize. Permissible fluctuation ranges are: pH-value (±0.05), electrical conductivity (± 0.1 or 1% of the final value), oxygen concentration (± 0.1 mg/l) and temperature (±0.1K)
- **Option 2:** Purge a minimum of 1.5 times of the volume of the circular cylinder in the well. The volume of the purged water can be roughly calculated by the following formula:

  $V = n \frac{\pi}{4} d_{BL}^2 l_F$, where:

  V – volume (m^3)

  d_{BL} – diameter of the borehole (m)

  l_F – Length of the filter filled with water (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 last at least 10 minutes.

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 the flow and mixing conditions in the vicinity of the measurement point. Usual flow rates range from 0.1 to 1 liter per second. At a lower flow rate, it must be assumed that the groundwater is heated by the sampling devices.

7.2 Using a pump

When using a pump for abstracting water, please take regard of the following steps and remarks:

1. Prior to inserting the pump into the well, connect the pump to the required length of tubing. A low-density polyethylene (LDPE) tube is recommended, as it is softer and easier to connect to the pump.
2. Lower the pump into the well, so that pump intake is submerged. Avoid placing the pump too close to the bottom of the well to avoid ingress of silt or other sediments.
3. Connect the pump's negative alligator clamp securely to the negative terminal on your power supply, and then connect the positive pump clamp to the positive terminal.
4. The pump will start immediately. The pump can run continuously when submerged.

5. When pumping is complete, remove the pump from the well. When removed, hold the pump in upright position to drain all water from the unit.
6. After you are finished with collecting groundwater samples, clean the pump with clean water.

Remarks:

If a vehicle battery is used, it is important that the vehicle is started and runs for 2 minutes every 30 minutes in order to maintain the charge in the vehicle's battery. Failure to do this may result in damage to the battery and in an inability to restart the vehicle. Running the vehicle while the pump is running does not damage the pump.

Do not run dry the pump! This will damage its motor.

Do not allow water to freeze inside the pump! Frozen water will expand and damage the unit.

7.3 Using field measurement equipment

At the beginning of a sampling campaign, the on-site field measurement devices should be **calibrated**. The calibration of measuring devices for electrical conductivity (EC), pH, temperature (T), and total dissolved solids (TDS) is done by using standard solutions provided in instrument field kits.

Every day, measure your standard solutions with your field measurement devices and write down the measured values. This helps you to see if there is a drift in the measurements and whether calibration is needed or not.

The on-site field measurement parameters should be measured following the proper purging of wells and prior to collecting samples to be shipped to the laboratory

All on-site field data and observations have to be entered into the Groundwater Sampling Protocol and also recorded in a field book.

7.4 Taking samples

The purpose for groundwater sampling is to obtain data that most accurately reflect the water quality conditions within the aquifer. Sampling takes place after purging the well and after field measurements were taken.

Samples can be taken with a stainless steel bailer or by pump sampling.

The material of the sample container, any necessary treatment of samples (e.g. filtration and stabilisation) depends on the parameters that are going to be analysed in the laboratory. The appropriate sampling containers are provided by the laboratory as well as the filtration units and the preservation substances.

7.5 Sample labelling

Samples shall be labelled in such a way that they are readily identifiable at all times.

Labels must be durable and need to resist moisture. The ink has to be non-water soluble. Most samples are preserved in ice and a wet surrounding. Careful packaging of samples is important, as vibration of sample containers during transport may cause container labelling to rub off or become illegible.

Labelling on samples should contain as much information as practical. Labels may contain:

- unique identifying code
- date and time of sampling
- location and name of sampling site (including GPS coordinates if available)
- project number
- name of sample collector
- information about container pre-treatment, filtration and added sample preservatives
- observations on other factors, which may affect the analysis method or results.

Sample labels must specify a clear and unique identifying code, which can be used to cross-reference to the location of monitoring and time of sampling.

7.6 Transport and storage

Samples should be transported to the laboratory every day. In practice, the remote location of some sampling points from laboratories may make this difficult. Therefore, samples should be kept in coolers and transported to the lab every two days. Samples, which require low temperatures of storage, should be placed on ice immediately.

It is vital that all procedures regarding sample transportation and storage are followed. This will ensure that sample condition remains mostly unaltered and suitable for laboratory analysis. During transportation, contamination of samples can easily occur due to container cross-contamination, packaging material, chilling products or reserve gasoline cans. During storage, sample degradation can occur due to lack of appropriate preservation, inappropriate storage conditions, excessive storage time, and sample cross-contamination.

7.7 Health and safety

Fieldwork should be conducted in such a way as to protect the health and safety of field personnel. Each team member has the authority and responsibility to stop operations, should any unsafe conditions exist or develop. All groundwater monitoring personnel should perform their field activities in a safe manner and undertake actions to remove, reduce or control any risk.

Field personnel should carry a safety kit as well as information on emergency procedure and the location of the nearest medical facility. Using the appropriate safety equipment will reduce such risk during the sampling process. Safety equipment can increase prevention or provide assistance in case of an incident.

A number of risks should be considered during fieldwork. The fieldwork team should study the potential risks and be prepared to control them, to ensure work safety in all field conditions. During sampling, typical risks include:

- vehicle breakdown or accident, bogging in wet conditions;
- exposure to hazardous substances, such as decontamination chemicals, toxic products formed during sample preparation or stabilisation (e.g. acidification), toxic gases (e.g. hydrogen sulphide), bacteria in the wellhead or groundwater;
- risks, related to temperature exposure, e.g. sunburn and heatstroke;
- risks, related to working in, over, or close to water;
- poisonous animals (spiders, snakes) and plants.

When receiving containers and preservatives from the laboratory, they should be checked for leaks. Many preservatives can burn the eyes and skin, so they must be handled carefully. Sample container labels should include information on the type of preservative used, if any.

8 FINISHING THE SURVEY

8.1 Hand-over of samples

At the end of the survey, the sampling team has to hand the samples over to the responsible laboratory or laboratories. The exact date and time of the hand-over of samples needs to be agreed with the laboratory and the hand-over needs to be duly confirmed by the laboratory with the hand-over protocol included in this manual.

8.2 Cleaning of equipment

The responsibilities of the groundwater sampling team include the thorough cleaning and maintenance of the measuring and sampling equipment. This is necessary to ensure that there is no cross-contamination between sampling tours, and to ensure that all required equipment will be available and functional at the time of the next sampling tour.

8.3 Reporting

The groundwater sampling team needs to write a survey report. This report serves to bring all information about the sampling tour together in written form; this will enable the necessary analyses and is important to make sure that no collected information is lost.

The survey report will be an expanded version of the present survey manual. It needs to include detailed information about the survey, such as:

- Information on the sampling team, particularly if there were any changes from the initial plans (see chapter 9.1);
- A summary protocol of the survey which should list the activities, the persons involved, the travel and the overnight stays during the survey. Please also keep the receipts for the overnight stays (see chapter 9.2).
- Remarks to the sampled sites and updates of the monitoring site passports needed according to changes observed during the survey;
- All completed sampling protocols for each groundwater sample (template included in this manual);
- All completed hand-over protocols for each groundwater sample (template included in this manual);
- A photo documentation of each sampling site (it would be good if the sampling team could take several photos from each site, also with the surroundings and with the sampling experts themselves. This would be important for the identification of refurbishment needs of the well and for the future analyses of anthropogenic pressures);
- An overview of the sampling results, including both field parameters and the results of the laboratory analysis for each groundwater sample;
- The completed metadata forms in English and Russian language are attached separately for the newly produced datasets, e.g.;
    - E4E_metadata_form_<country>-EN.pdf
    - E4E_metadata_form_<country>-UA.pdf

The survey report needs to be provided in English and national language.

9 SURVEY/SAMPLING PROTOCOLS

Summary protocol of the survey which lists the persons involved, the activities, the travel and the overnight stays during the survey.

9.1 Sampling team of this survey

Date	Name	Organisation

9.2 Log book / Journal

Field sampling route in the Dnipro River Basin Districts for collecting groundwater samples.

Date	Time (from – to)	Location	Activity

SAMPLING 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 □ cloudy □ changing □ rain □ heat □ frost □ ……..	□ colourless □ slight □ strong □ brown □ grey □ yellow □ ……..	□ no □ low □ moderate □ strong □ ……..	□ no □ low □ moderate □ strong □ ……..	□ odorless □ putrid □ fishy □ chemical □ chlor □ 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:_____

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

Action funded by the
EUROPEAN UNION

EUWI+
EU WATER INITIATIVE
FOR EASTERN PARTNERSHIP

UNECE

OECD
BETTER POLICIES FOR BETTER LIVES

umweltbundesamt
ENVIRONMENT AGENCY AUSTRIA

OiEau
International Office for Water

www.euwipluseast.eu