



**"Cr(VI) Impacted water bodies in the Mediterranean:
Transposing management options for Efficient
water Resources use through an
Interdisciplinary Approach"**

WATER SAMPLING PROTOCOL

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1.0 INTRODUCTION

This document addresses the preparation steps and appropriate methods for collection of water samples in the framework of the Eranetmed project entitled '*Cr(VI) Impacted water bodies in the Mediterranean: Transposing management options for Efficient water Resources use through an Interdisciplinary Approach*' (CrITERIA). The development of a water sampling and analytical programme depends on the purposes of the project. The procedures described in this document for the collection and handling of water samples are designed to be used in conjunction with the analyses for specific chemical constituents that are representative of the overall chemical quality of the Cr(VI) impacted water bodies. The following documents have been taken into consideration to develop the present: a) ISO 5667-3: 2012. Water Quality-Sampling, Part 3: Preservation and handling of water samples, b) ISO 5667-14: 2014. Water Quality - Sampling, Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling, c) ISO 5667-6: 2014. Water Quality - Sampling, Part 6: Guidance on sampling of rivers and streams, d) ISO 5667-11: 2009. Water Quality - Sampling, Part 11: Guidance on sampling of groundwaters.

In order to generate water quality data that are both trustworthy and scientifically credible, adherence to a strict and defined sampling and analytical protocol is necessary. Among the topics covered within the protocol, are procedures and considerations to prevent sample contamination, types of sampling and relevant field equipment, and the implementation of fundamental chemical practices to ensure that valid results are comparable among the participating countries. The guidelines have been developed to assist those involved in water sampling and analysis procedures not only to reduce the potential for error, but also prescribe in detail quality assurance and quality control procedures to be applied during water sampling and analysis. This approach allows the subsequent interpretation of analytical data taking into consideration the relevant stated uncertainties from sampling and analysis, thus providing a realistic basis for water management decisions and improving our knowledge on dynamic water systems affected by Cr(VI).

This document is divided into three chapters. The first chapter provides an overview of the document; the second includes background information and preparation steps that should be undertaken before every sampling event; section three describes each step of the field sampling procedure; and section focuses on the relevant quality control in the field. Given the diverse analytical equipment and instrumentation of the participating countries, this document does not intend to describe in detail the analytical methods and techniques to be used in each laboratory for measuring the selected chemical constituents. Because different techniques may yield different results, the best approach to ensure the analytical quality of the data is to be consistent with the guidelines given by WISE SoE database for reporting chemical data, in order to facilitate comparison of the chemical data among the different countries and over time. The present document emphasizes the determination

of detection limit, repeatability, reproducibility and accuracy for each analyte as a prerequisite for producing results of high and known quality.

It is reasonable that unpredicted circumstances may occur during the sampling events that could result to deviations from the sampling procedures. These site-specific circumstances may require alternative approaches that are not specified. Such deviations, nonetheless, should be approved by the research leader and documented in the water sampling information form.

2.0 PLANNING OF THE WATER SAMPLING SURVEY

2.1. Sampling frequency

For this document, a 'sampling event' represents a single sampling day, whereas the 'sampling campaign' refers to each seasonal sampling period that may stretch over a one to five days period. Specifically, four sampling campaigns, two in the end of the dry seasons (autumn) of 2017 and 2018 and two in the end of the wet seasons (spring) of 2017 and 2018 have been scheduled to take place. The suggested surveillance of seasonal variation of the water chemical composition over two years is considered to be adequate to provide a complete depiction of water quality under different hydrological conditions.

2.2. Selection of analytical parameters

For the purposes of the CrITERIA project, specific analytical parameters have been selected to be determined that provide a good representation of the overall chemical quality of the Cr(VI) affected water bodies. In particular, electrical conductivity, pH, temperature, redox potential and dissolved oxygen shall be measured in the field for all sampling campaigns. Laboratory analyses should ensure the measurements of major and minor ions and compounds including K^+ , Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , NO_3^- , SO_4^{2-} , Cl^- , PO_4^{3-} , as well as trace elements including Cr_{tot} , Cr(VI), Ni, Fe, Mn, Co, Pb, Zn, Cu, As, Al, Si and B. These chemical constituents are not only essential for exploring the geochemical processes responsible for the increased contents of Cr(VI) in the water, but also for investigating the potential for the water bodies to be simultaneously contaminated with other chemical components, as has been reported in the scientific literature.

2.3. Sample containers

The correct sampling containers and preservatives to be used for each parameter group are identified in Appendix 1. Clean **polyethylene** bottles of 500 ml (for anion determinations), 200 ml (for Cr(VI) determinations) and 50 ml (for major cations and trace element analyses) should be used. It is recommended to add the preservative $NH_4OH/(NH_4)_2SO_4$ in the 200 ml bottles used for Cr(VI) analyses in the laboratory, prior to the sampling event. The laboratory steps for the preparation of this preservative are given in Appendix

2. Filtration and acidification of the aliquot for the major cations and trace metal analyses should be performed in the field.

2.4. Decontamination of equipment

It is necessary to realize that contamination of samples can occur not only during sampling, but also prior to fieldwork. Sampling equipment should be protected from cross-contamination and decontaminated after each use. Below are stated some protective measures and practices that should be implemented prior to every sampling event:

- Sampling containers for trace metals and Cr(VI) determinations shall be soaked for at least 24 h in 10 % (v/v) nitric acid solution made from reagent grade acid and deionized water, and rinsed with metal-free water.
- Wash sampling equipment inside and outside where possible, with clean water and a phosphate-free detergent/clean water solution. Rinse three times with clean water. Ensure that contaminants and detergents have been adequately flushed out.
- When transporting or storing equipment after cleaning, protect the equipment in a manner that minimizes the potential for contamination (e.g. use plastic, zip bags).

2.5. Selection of water monitoring points

The selection of water sampling point locations is crucial for the purposes of the CrITERIA project. The target sampling points should include production boreholes and wells used for irrigation, domestic and industrial purposes according to the specific characteristics of studied water bodies and the respective conceptual models. In addition, discharging water at springs can be sampled. Alternately, surface water from stream or rivers could also be monitored in case of exhibiting elevated dissolved Cr(VI) concentrations. Information on the geology, hydrogeology, the anticipated chemical composition and the land use of the investigation sites is of great importance for establishing the appropriate waters to be monitored. All of these factors should be carefully considered during the preliminary stages of the monitoring programme to enable the most appropriate and effective strategy to be implemented. According to the conceptual model of each case study area, the selected water sampling locations should provide at least some representative water samples that are prone to contain elevated Cr(VI) concentrations. Such samples will provide information on interaction processes between water and ophiolite rock or other potential sources of Cr(VI). Such areas have been identified in Greece and Italy and will be further evaluated and monitored. Potentially affected water bodies are also identified in Cyprus, Turkey, Jordan and Oman. Reconnaissance trips at the early stages

of the project may prove beneficial for selecting the appropriate sampling points.

Prior to the selection of the monitoring points in the case of ophiolite related aquifers, it is necessary to gain information for the borehole/well description details and characteristics to ***verify that at least some samples are obtained from water bodies affected by interaction processes with Cr-bearing formations; as a prerequisite, lithologic data from cores or cuttings are needed.*** The ***total depth of the bore/well*** should also be obtained in order to calculate the volume of water within the bore or the well that needs to be removed prior to sampling (see Section 3.4.3). The above information should be obtained from local water managers or other stakeholders that are been identified as potential participants in the planned CrITERIA training workshops. It is advisable that the land use is taken into account by selecting sampling points within agricultural areas, if possible.

Nonetheless, it is necessary to check the sampling point according to the local circumstances. Only on-site is it possible to assess whether a sampling point is suitable to be examined and monitored, and whether the sampling point is easily accessible.

2.6. Field preparations

It is advisable to prepare a workplan before fieldwork that will delineate the study activities and establish the timeframe in which the activities are to be completed. This workplan should include a calendar of planned field trips (sampling dates, members of field team incorporating the local stakeholders, vehicles to be used). Other activities that should be arranged before the fieldwork are the ordering of necessary supplies and the check of expiration dates of reagents. In addition, a check-list for the necessary pre-trip planning preparations is essential (Appendix 3).

3.0 WATER SAMPLING PROCEDURES

3.1. Quality assurance for field procedures

Potential contamination of the water samples during field work can occur by surface soil and vegetation, but could also arise by improper practices from the field crew. Guidance on quality assurance practices that should be implemented in the field by the sampling personnel is outlined below:

- Thoroughly clean the sampling devices between each water sampling point.
- Minimize the amount of water left on washed materials.
- Minimize the time that sampling containers are exposed to airborne dust.
- Place equipment on clean ground-covering materials instead of on the ground. Avoid placing the sampling containers near vehicle exhaust.
- Wear clean gloves during sample collection. The gloves should be kept clean while handling sampling-related materials and should be replaced with a new pair at each sampling site.
- Avoid handling bottles or equipment with dirty hands.
- Prohibit eating, drinking, or smoking near samples.
- Keep excessive heat sources and flames away from samples and sampling locations.
- All sampling staff should be fully trained before being allowed to work unsupervised.

3.2. Sample documentation and identification

The Sampling Forms (Appendix 4) shall be completed at each sampling point in the field. All the samples collected at a given sampling point shall be assigned the same serial number for all the sampling campaigns. If a sampling point coincides with a point that belongs to an established monitoring network (e.g. the National Water Monitoring Network of Greece) that has been ascribed a special identifier code, then this code should be noted in the remarks of the sampling form.

The Sample Code of each water sample will include 4 parts according to the coding system described below, using a waterproof marker or preferably by attaching an appropriately inscribed tag or label:

- ✓ A first alphabet character denoting the country from where the water sample is collected, e.g. *G* for Greece, *I* for Italy etc.
- ✓ A second letter character, either *A*, *B*, *C* or *D* corresponding to each of the planned sampling campaigns, starting with *A* for the Spring 2017 sampling campaign, *B* for the autumn 2017 sampling campaign etc.

- ✓ A serial number (i.e. Identity Number); the Identity Number will not change during the whole project. For example, if fifteen water sampling points have been planned to be collected during the sampling campaign, the third sign will be some number between *01* and *15*.
- ✓ A letter character denoting the specific area from where the sample is collected. For example, in Greece three areas have been selected to be investigated, Assopos, Loutraki and Euboea; the last sign shall be either *A,L* or *E*.
- ✓ Field blank samples (see Section 4.2.2), will be collected for every sampling event at random sampling points. They will be labeled following the coding system described above, same as the normal samples. For instance, a field blank from the third sampling campaign during the second sampling event in Loutraki area from Greece should be coded *GC02L*.
- ✓ Field triplicate samples (see Section 4.2.3), will be marked by adding (*R1*), (*R2*) and (*R3*) after the last symbol in the code. For example a triplicate sample with serial number 07 from Loutraki area in Greece for the autumn 2017 sampling campaign should be coded as *GB07L(R1)*.

3.3. Chain of custody form and field log

In addition to filling in the Sampling Form (Appendix 4) for every sampling point, a Chain of Custody Form (Appendix 5) should be filled in. Also one member of the sampling crew should keep a daily field log of sampling activities. Because sampling situations vary widely, it is imperative to record sufficient information so that one could reconstruct the sampling event without relying on the sampling team's memory. The daily field log shall supplement information entered on the Sampling Information Form containing, at minimum, a record of the following:

- Description of sampling point and sampling method. The exact geographical coordinates for each sampling site should be recorded by a Geographic Positioning System (GPS).
- Fix sampling points by detailed description in the sampling plan, by maps, and or with the aid of signs - landmarks that will permit their identification by other persons without reliance on memory or personal guidance.
- Field conditions. In particular, any relevant information regarding the general physical condition of the well/bore, weather conditions at the time of sampling or immediately prior to sampling (e.g amount of rainfall), the surrounding soil and vegetation, or other objects in the immediate vicinity of the bore/well should be noted. Information about

any unusual field conditions and exceptional anthropogenic sources that may have a significant impact on the integrity of the analytical results should be included.

- In the case of surface water sampling, additional information that should be noted includes the name of the river or stream, the flow condition of the water body, the appearance of the sample (e.g. the color of the water and suspended solids) and anything that could have influenced the sample (e.g. nearby traffic).
- The presence of airborne dust and ambient odor should be evaluated.
- Description of the geological formations outcropping in the immediate and surrounding area should be recorded. Identified minerals contained in the bedrock should be noted.
- A description of the exceptions to this protocol and how they can potentially have impacted the analytical results.
- A list of the quality control samples for the specific sampling event.
- Good quality photographs should supplement the description of the sampling site.

3.4. Groundwater sampling procedures

3.4.1. Water level elevation measurement

Prior to any water sampling, the initial static water levels to the nearest 0.1 m should be recorded. We recommend use of an electronic water-level sensor that indicates with a tone when the sensor contacts water. The water level will be used to calculate the volume of water that should be removed prior to sampling (see Section 3.4.3). The depth of water shall be referenced to the measuring point marked at the top of the bore/well casing.

The water level measurements should be done twice at each sampling site. If there is poor agreement (> 10% difference) between the first and the second water level measurements, a third water level measurement should be obtained to assess the water level and verify non-steady state conditions.

3.4.2. Water-quality measurements in the field

Electrical conductivity, pH, dissolved oxygen, redox potential and temperature should be measured in the field during purging to determine water stabilization. All measurements including the steady-state value for each field water-quality parameter should be recorded in the Sampling Form, Appendix 4. *The on-site measurements should be performed before the actual sampling in a spot sample to be discarded after the measurements. For this purpose, a glassware beaker could be used.* Significant considerations for the measurements of field-related parameters are given:

- Follow general care, maintenance, calibration procedures and operation instructions as specified in the instruction's manual for each measurement device.
- All probes used should be allowed to equilibrate with fresh groundwater before beginning to record measurements.
- The pH equipment must be handled carefully, including all steps from taking the cap off the electrode to keeping the electrode tip moist between sampling points. Take special care to protect the fragile glass bulb on the end of the pH electrode.
- For the pH measuring equipment, we recommend a two-point calibration method prior of the sampling event. Because the pH values of the water samples in the framework of the CrITERIA project are expected to be alkaline, it is suggested to use two fresh buffer solutions with pH values representative of the range of values expected in the field (pH=7 and pH=10 would be ideal), unless otherwise mandated by the specific equipment. If the meter holds its slope well over time, routine calibration later in the day can be done with only one meter. The single buffer calibration shall normally be done using a pH = 7 buffer. A single point calibration should be done in the field every three sampling points. The pH values should be measured and recorded to the nearest 0.1 units.
- Measure and record the electrical conductivity to the nearest 10 $\mu\text{S}/\text{cm}$. Calibration of the conductivity meter shall be performed each day before taking measurements at the first site.
- To ensure that the temperature probe is in good operating condition, immerse the probe and a liquid column thermometer (e.g. mercury etc.) in a water bath, and compare the readings. The temperature should be measured and recorded to the nearest 0.1 degrees Celsius. *This procedure shall be performed before the sampling event and again the day after the return.*
- The redox potential values should be measured and recorded to the nearest millivolt (mV), and the dissolved oxygen values to the nearest mg/L.

3.4.3. Purging

The purpose of groundwater sampling is to acquire a water sample that represents the characteristics of the water below the ground surface. To obtain a representative sample, it is necessary to remove the stagnant water from the bore/well casing before a sample is taken. This is called purging. It is recommended that **three volumes** of bore/well water be removed and left to refill before sampling. This allows the pH, electrical conductivity, redox potential, dissolved oxygen and temperature of the ground water to stabilise,

thereby ensuring that the obtained sample is truly representative of the groundwater residing in the aquifer surrounding the borehole/well. Nonetheless and considering the anticipated time limitations constraints during fieldwork, ***purge volumes can be reduced*** by monitoring for chemical stability during pumping. At minimum, one water column volume should be removed, even if field parameters stabilize first. Such changes to the protocol should be documented in the Sampling Form, Appendix 4. The field water quality parameters should be measured and recorded during purging to determine stabilization. The following target criteria for three consecutive measurements shall be used to define stabilization:

- ✓ temperature ± 0.1 degrees Celcius
- ✓ electrical conductivity $\pm 5\%$
- ✓ pH ± 0.1 units
- ✓ Eh (± 10 mV)

If field parameters do not stabilize after three water column volumes, check operator procedures and equipment for potential problems. After the chemical stabilization of the four parameters, the groundwater is now ready for sampling. The collection of groundwater sample should begin immediately after purging. The direct filling of the sample into the sample container should be favored.

- The volume of water required to be purged before a sample can be taken will depend on the diameter of the bore/well and the depth of the water column.

Calculation of the volume of water in a bore or a well

The volume of the water in the bore or well is calculated using the following formulae:

$V = \pi \times r^2 \times L \times 1000$ (volume in litres), (x 3 = volume to be removed in litres)

V = volume (in litres)

r = radius of the casing in meters

L = length of the water column in meters

π = constant (3.14)

The appropriate purging time in the case of productive bore/wells can be estimated by taking into account the calculated water volume (V) and the pumping rate. Information on pumping rates should be provided by the bore/well managers.

Procedure:

- Measure the radius ($\frac{1}{2}$ diameter) of the bore casing in meters (eg. 50mm casing = $0.025\text{m}^2 = 0.000625$).
- Measure the water level which means the depth from the top of the bore/well to the standing water level.
- Calculate the length of the water column (total depth – water level). The total depth is known beforehand by pre-trip communication with the relevant stakeholders.
- Calculate the volume of water using the formula above.
- Then multiply the final figure by three (x 3) to calculate the total amount of water to be removed from the bore/well.

3.4.4. Sample collection

Because samples are collected from the installed pump of production well, the samples must be collected as close to the well head as possible. Appendix 1 identifies the three types of sample containers that shall be used in the field for every groundwater (and surface water) sampling point. Appendix I also summarizes the preservation method and holding time for each analytical parameter. The 50 ml and 200 ml polyethylene bottles for trace elements, major cations and Cr(VI) determinations shall be filled with sample water that has been filtered in the field using 0.45 μm pore size membrane filters and disposable syringes. *For the 500 ml polyethylene bottles used for the chemical analyses of anions, filtration of the samples with 0.45 μm filters should be performed immediately after the arrival in the laboratory.*

Guidelines and considerations when collecting the groundwater samples are given below:

- Ensure that the quality assurance for field procedures (Section 3.1) is taken into account. Remember also that field blanks and triplicate samples are required for all sampling events, as described in Sections 3.4.5 and 3.4.6.
- The sampling bottles should be labeled according to the procedure described in Section 3.2.
- Do not open the sampling bottles until they are to be filled with the sample water.
- Sampling personnel shall not touch the inside of sampling containers, bottle caps, or rim of sample containers.
- Hold the sample water discharge point as close as possible to the sample container without allowing the discharge point to contact the container.

- Fill the polyethylene bottles with water to be analyzed in the order: anions (500 ml bottles), major cations and trace elements (50 ml bottles) and Cr(VI) (200 ml bottles).
- The sample containers for anion determinations (500 ml) shall be **rinsed twice** with the water sample and **subsequently** filled completely with unfiltered sample water.
- The containers for trace metals and Cr(VI) determinations (50 ml and 200 ml bottles) shall be filled approximately 95 % full with filtrated water.
- Flush the new filters with fresh sample water before the filtration twice. Use each flushing to rinse the containers for trace metals (50 ml bottles).
→ *Do not rinse the containers for Cr(VI) determinations*
- Acidify the bottles for trace element analyses with a few drops of concentrated HNO₃ to bring the pH <2 as soon as the water has been filtrated. If available, use ultrapure HNO₃ preservative to prevent contamination.

3.4.5 Field blanks

The field blanks should reflect all of the potential exposures to background contamination and cross-contamination and are used to identify any errors relating to contamination of sampling containers and the sampling process. Important considerations for the collection of field blanks are the following:

- The blanks should be collected in the field using the same type of container as for the actual samples. The blanks shall be filled with deionized water in the field. This deionized water should be run through all of the sample collection devices.
- The field blanks should be subjected to the same sampling, filtration, storage and transport procedures as the actual samples. Field measurements should be taken in the same manner as for the rest of the samples.
- The field blank shall contact all the equipment surfaces that the sample water contacts.
- The same preservatives to both the field blanks and the actual samples should be added (concentrated HNO₃ for the trace elements blank and NH₄OH/(NH₄)₂SO₄ for the Cr(VI) blank). For the field blank analyzed for Cr(I) content, remember to add the preservative prior to the sampling event.
- Collect one field blank for each group of parameters in every sampling event from a randomly selected sampling point.

3.4.6. Field triplicates

The field triplicates are included in the sampling and analysis procedures to evaluate variability caused by random errors during sampling and analytical procedures. The field triplicates should be collected in one randomly selected sampling point for every sampling campaign, with the aim to determine the reproducibility of the entire sampling and analytical procedure. The reason behind the collection of the triplicates instead of duplicates is that the greater number will produce statistically better results for the standard deviation and calculation of the coefficient of variation. Important aspects for their collection are given below:

- The two replicate samples of actual waters should be collected for each group of parameters.
- Fill the two replicate sample bottles as closely as possible to the time the actual sample is collected. The replicate samples should be collected immediately after the primary sample from each parameter group is collected. This means that after the primary trace element sample is collected, the two replicate trace element samples are collected, then the anion sample, and so on.

3.5. Surface water sampling procedures

For the purpose of the CrITERIA project, surface water shall include contained water within any stream or river suspected to exhibit elevated Cr(VI) concentrations.

3.5.1 Selection of sampling points

Guidelines for the selection of surface water sampling points are given below:

- The choice of surface water sampling sites is relatively straightforward. For example, it may be desirable to sample the main channel of a stream or river along all its length, from upstream to downstream. A convenient bridge could be taken into account when identifying the precise points at the sampling sites. In this case, the site should be located far enough upstream to avoid contamination from road-related material.
- When the effects of a tributary or an effluent on the quality in a particular identified stretch of river of the main stream are of interest, two sampling sites should be chosen; one should be just upstream of the confluence and the other should be sufficiently far downstream to ensure that mixing is complete. Moreover, it might be necessary to sample the tributaries or effluent themselves just before they reach the main river/stream.

- Practical sampling issues, such as accessibility, can make the ideal sampling point impractical. Any change to the designated sampling point should be recorded in the field notes including the new coordinates and directions to the new sampling site.
- Sampling at or near the surface, bottom, bank and stagnant areas should be avoided. Particular care is needed not to disturb sediments of either the bed or the bank of the watercourse. Samples should be collected at a well-mixed and flowing sampling point and not in stagnant or back eddy areas where the flow is not typical of the main water body.
- Where a sample is to be obtained from the bank side, it is essential that sampling only be carried out where the bank is stable. Usually, an extension pole is required, but often a vessel on a rope can be used, allowing sampling up to several meters from the bank side. For streams that are narrower, attempt to sample from approximately the middle.
- Whenever possible, attempt to sample from positions at least 30 cm above the bottom of a stream and at a similar distance below the surface. Otherwise, target to collect water at mid-height between bed and surface.
- For samples collected from a shallow (< 50 cm) river or stream, sample collection is performed by wading.
- When sampling from a boat, care should be taken to avoid contamination from any discharges from the boat. When the sample is collected, the boat engine should be cut, and the samples collected from the prow of the boat or off the sides.
- In regions that have considerable periods without rain, sampling sites should be chosen to ensure that they remain appropriate and practical for sampling during periods of both maximum and minimum flow.
- All surface locations should be designated by an appropriate mark so that samples from subsequent sampling campaigns may be collected from exact the same location. Any departure from collecting a sample at the normal location must be documented in the field notes and recorded with the analytical results, together with the new coordinates where applicable.

3.5.2. Collection of surface water samples

- The sampling point should be approached from downstream. Point the sample container upstream so as not to contaminate the water volume being sampled.
- The sample bottles can be directly immersed in the river or stream. If this is not possible, a clean container (e.g. a bucket or can) is sufficient.
- Allow the bottle to fill right to the top to exclude air. When filled, remove the bottle from the water and place the cap securely. If a vessel is applied, allow the vessel to fill and subsequently, fill each sample bottle.
- Before collecting the sample, the equipment that comes in contact with the water should be rinsed, preferably up to three times.
- Follow the same guidelines for the sample containers and filtering methods as for the groundwater samples (Section 3.4.4. and Appendix 1). Use a vessel for obtaining the appropriate water volumes that need to be filtered and for measuring the field water quality measurements, i.e, pH, Electrical Conductivity, dissolved oxygen, temperature and redox potential.
- Label the bottles as detailed in Section 3.2. ***Add the letter S at the end of the code to denote that the sample represents surface water.***

3.6. Sample preservation, handling and transport

The samples should be kept cool by placing them in an insulated ice chest containing ice packs immediately after sample collection. Exposure to heat and light should be avoided. The temperature just before transporting the samples and upon arrival to the laboratory should be recorded to verify the sample temperature. The samples should be kept to approximately 4°C during transport to the laboratory. The samples should be transported, if possible, to the laboratory on the same day as sampling.

3.7. Summary of sampling protocol

An overall summary of the chain of the most important events in the field is provided below; field procedures should be carried out in accordance with the detailed description of the sampling protocol:

- Upon arrival to the water sampling point, document field conditions (Section 3.3).
- Prepare area around the bore/well for sampling.

- Measure static water level elevation; calculate water column volume (Section 3.4.1.)
- Complete the field conditions in the field log book and other appropriate forms.
- Wear protective gloves.
- Measure field parameters while simultaneously purging the well/bore (Section 3.4.2).
- Suitably label the three different types of sampling containers (500 ml, 200 ml and 50 ml) according to the procedure described in Section 3.2.
- When field parameters have been stabilized, perform the sampling procedure (Section 3.4.4).
- Place the collected samples in the ice chest (Section 3.6).
- Incorporate quality control samples, if specified.
- Complete documentation in the field log book and the sampling form.
- Decontaminate any reusable equipment.
- Transport the water samples to the Laboratory.

In the case of sampling surface waters, the chain of activities should be:

- Document field conditions.
- Carefully inspect the surface water body and select an appropriate sampling point according to the guidelines provided in Section 3.5.1.
- Complete the field conditions in the field log book and the sampling form.
- Wear protective gloves.
- Measure field parameters.
- Suitably label the three different types of sampling containers (500 ml, 200 ml and 50 ml). Do not forget to add the letter 'S' at the end of the code to denote that the sample represents surface water.
- Perform the sampling procedure including filtration and acidification when necessary.
- Place the collected samples in the ice chest.
- Incorporate quality control samples, if specified.
- Complete documentation in the field log book and the sampling form.
- Decontaminate any reusable equipment.
- Transport the water samples to the Laboratory.

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Appendix 1:

Sample containers, preservation method and holding times

Parameter	Bottle volume	Filtration	Preservation	Holding time
HCO ₃ ⁻	500 ml	In lab after sampling	cool	24 hours*
NO ₃ ⁻	500 ml	In lab after sampling	cool	48 hours*
SO ₄ ²⁻	500 ml	In lab after sampling	cool	7 days
Cl ⁻	500 ml	In lab after sampling	cool	1 month
PO ₄ ³⁻	500 ml	In lab after sampling	cool	48 hours*
Si	500 ml	In lab after sampling	cool	48 hours*
Cr(VI)	200 ml	On site	NH ₄ OH/(NH ₄) ₂ SO ₄ (Lab)**, cool	4 days
major cations (K ⁺ , Na ⁺ , Ca ⁺⁺ , Mg ⁺⁺)	50 ml	On site	HNO ₃ / pH < 2 (field)***, cool	1 month
trace metals (Cr _{tot} , Ni, Fe, Mn, Co, Pb, Zn, Cu, As,Al)	50 ml	On site	HNO ₃ / pH < 2 (field)***, cool	1 month

* sample to be split in sub-samples and frozen if not possible to analyse within time (account for extra bottles), the laboratories should try to conclude these analyses at most within two weeks from sampling,

** preservative added to container in laboratory before going to the field,

*** preservative added in the field

Appendix 2:

Preparation of the preservative to be added in the 200 ml sample bottles

NH₄OH/(NH₄)₂SO₄: Preservative for the analysis of Cr(VI)

Reagents:

- Ammonium hydroxide (NH₄OH, CASRN 1336-21-6), e.g. Sigma Aldrich 221228- 1L-A, or equivalent.
- Ammonium sulfate ((NH₄)₂SO₄, CASRN 7783-20-2), e.g. Sigma Aldrich A4915, or equivalent.

Preparation:

Dissolve 3.3 g (NH₄)₂SO₄ in 75 ml of reagent water. Add 6.5 ml NH₄OH and dilute to 100 ml final volume. The stability of the concentrated preservative was verified for one month.

Addition of Preservative

The preservative should be added to sample bottles **prior** to the field trip, at a rate of 1 ml per 100 ml of sample. Thus, for the 200 ml sample, 2 ml of the preservative should be added.

Appendix 3:

Check list for pre-trip planning activities

√	Prefield activity	Comments
	Contact information for site (relevant stakeholders)	Completed on _____, by _____
	Associated maps (topography, geology) of study site	Completed on _____, by _____
	GPS equipment and extra batteries	Completed on _____, by _____
	Field notebook and field sampling forms	Completed on _____, by _____
	Indelible marker pens	Completed on _____, by _____
	Add the preservative to the 200 ml sample bottles used for Cr(VI) determinations	Completed on _____, by _____
	Filtration equipment (0.45 µm membrane filters, disposable syringes)	Completed on _____, by _____
	Ice packs	Completed on _____, by _____
	Cooler for ice packs and samples	Completed on _____, by _____
	Gloves	Completed on _____, by _____
	Adequate deionized water and glassware beakers	Completed on _____, by _____
	Clean sample bottles	Completed on _____, by _____
	Prepared analytical blanks	Completed on _____, by _____
	Clean and test field monitoring meters (e.g. water level, pH, temperature)	Completed on _____, by _____
	Calibration instructions and standard testing solutions for field monitoring equipment	Completed on _____, by _____
	Tool box	Completed on _____, by _____
	Calculator	Completed on _____, by _____
	Camera	Completed on _____, by _____

Appendix 4:

Sampling forms for groundwater and surface water

