SAMPLING METHODS IN CHEMISTRY

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Dana Vlascici, VladChiriac, DorinaModra, Mariana Albulescu, OtiliaBizerea, Gabriela Preda, Vlad-Oros Beatrice, Laura Pitulice, Daniela Dascalu

Trainers Dana Vlascici, VladChiriac

1. Preparation and sampling considerations

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed.
2. Obtain the necessary sampling and monitoring equipment.
3. Decontaminate or pre-clean equipment, and ensure that it is in working order.
4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
5. Perform a general site survey prior to site entry.
6. Use stakes, flagging, or buoys to identify and mark all sampling locations. If required the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. If collecting sediment samples, this procedure may disturb the bottom.

In order to collect a representative sample, the hydrology and morphometric of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons, or impoundments, flow patterns in streams, and appropriate sample locations and depths.
Water quality data should be collected in impoundments, and to determine if stratification is present. Measurements of dissolved oxygen, pH, and temperature can indicate if strata exist which would affect analytical results. Measurements should be collected at one-meter intervals from the substrate to the surface using the appropriate instrument.
Water quality measurements such as dissolved oxygen, pH, temperature, conductivity, and oxidation-reduction potential can assist in the interpretation of analytical data and the selection of sampling sites anddepths when surface water samples are collected. Generally, the deciding factors in the selection of a sampling device for sampling liquids in streams, rivers, lakes, ponds, lagoons, and surface impoundments are:
1. Will the sample be collected from shore or from a boat?
2. What is the desired depth at which you wish to collect the sample?
3. What is the overall depth and flow direction of river or stream?
4. What type of sample will be collected (i.e.water or lagoon liquids)?

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Some variables being sampled must be analyzed within 48 or 72 hours of sampling,depending on the parameter or else the results are rendered invalid. It is essential thatsamples be shipped to the laboratory as soon as possible after collection to avoid alengthy time delay before analysis.
There are two primary interferences or potential problems with surface water sampling. These include cross contamination of samples and improper sample collection.
1. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary.
2. Improper sample collection can involve using contaminated equipment, disturbance of the stream or impoundment substrate, and sampling in an obviously disturbed area.

2. Taking samples

- Sample bottles shall be labelled indelibly prior to sampling with a unique sample number, the location, date and analyses required.
- Sample directly into the sampling bottle or jar unless a mixed sample is necessary, in which case ensure that the larger mixing container has been prepared in the same manner as the sampling container.
- Use disposable gloves in polluted waters.
- When sampling water in streams or dams, submerge the bottle carefully. The mouth of the bottle should be held at least 10 cm below the surface.
- It is necessary that the person taking the samples use their discretion while collecting, so as not to take a non-representative sample. When sampling waters, flowing or well mixed water is preferable to use for sampling, but this may not always be available, particularly when very still conditions cause stratification in dams or lakes. In this case, attempt to collect three equally sized samples, from the surface, midzone and deeper waters mix them together and sub-sample the mixture.
- Do not rinse the sampling container in the sample stream when sampling waters. If it has been correctly prepared the sample container should not contain any contaminants.
- When sampling waterbodies avoid dislodging benthic algal mats, scraping against walls or floors of waterbodies, or otherwise disturbing the sediment. Care should be taken so that no larger animals or algae mats are included in the sample, unless that is what you specifically wish to sample.
- In flowing water, always ensure that your hand is downstream of the collecting bottle's mouth and that the mouth of the bottle is facing into the current. Ensure that the sample is taken midstream.
- When collecting bacterial samples use clean hands, disposable gloves and sterile collection procedure - that is, only break the seal just prior to collecting the sample, hold lid and bottle opening facing downwards, do not put the lid down on a surface, ensure hand is held downstream of the bottle, and cap the sample immediately after collecting.
- Record relevant details on the sampling record sheet, and also on the chain-of-custody record for samples being sent away for testing.
- Sample bottles for nutrient analysis should be filled to the top and the last air squeezed out of the sample bottle prior to sealing, to minimise the chance of nitrogen fixation prior to testing. Samples should be chilled immediately, and stored in a freezer before dispatch to the testing laboratory in an ice-filled esky.

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- Samples for chlorophyll and bacteria require an air space.
- When sampling soils, try to avoid large rocks and large pieces of organic materials.

A) Bridge Sampling

Tie the free end of the rope to the bridge railing to secure the sampler. To allow sample bottles to fill with fewer casts, swing sampler as far upstream as possible before releasing it. Try to avoid sampling near bridge supports, or any other objects that may interfere. It is always preferable to sample from the upstream side of a bridge, however safety is paramount. The bridge walkway must always be used regardless of which side it is on. Additionally, in very fast currents it may be necessary to sample on the downstream side on occasion, to prevent the multi-sampler from being swept too far under the bridge.

B) Sampling from Shore or by Wading

Wading is one of the easiest methods for collecting samples, but it can also be one of the most dangerous. Wading permits the collector to examine steam flow and to decide where to sample. Rubber boots or hipwaders are standard equipment. Chest waders should not be used due to safety concerns. A wading rod or similar probing instrument is often useful to estimate the current and to locate holes and unsafe footing.
If sampling from shore, ensure a safe footing, and make sure you are well balanced, keeping in mind that the current may pull the multi-sampler sharply downstream. Note that water levels for some rivers can change height within seconds. When sampling from shore always collect samples while facing upstream. The multi-sampler should besubmerged to the length of the handle below the surface. If bottom sediment is stirred up when wading,allow it to flow away from the sampling spot before collecting the samples. If sampling from a rocky outcrop on the shore, submerge the sampler to the length of the handle, and allow the bottles to fill.
If it is not practical to use the multi-sampler (i.e., if the water is too shallow), then fill the bottles one at atime. Uncap the bottle immediately before sampling. Stand perpendicular to the flow facing upstream. While holding the cap in one hand, plunge the opening of the bottle into the river with the opening facing upstream into the current until it is filled. If sampling from a stationary water body, with the bottle cap removed, lean out and plunge the bottle below the surface and force the bottle through the bottle away from you until it is filled. Lift bottle out of water, decant a small amount if required, and re-cap immediately. Ensure that your hands do not come into contact with the insides of the bottles or caps.

Once samples have been collected, the following procedure should be followed:
1. Transfer the sample(s) into suitable, labeled sample containers.
2. Preserve the sample if appropriate, or use pre-preserved sample bottles. Do not overfill bottles if they are pre-preserved.
3. Cap the container, place in a ziploc plastic bag and cool to 4^{o}C.
4. Record all pertinent data in the site logbook and on field data sheets.
5. Decontaminate all sampling equipment prior to the collection of additional samples with that sampling device.

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Sample filtration in the field can extend the period of time in which accurate results can be obtained from analysis. For example:

- Concentrations of ammonia or nitrate can decrease over time in water samples. Filtration extends the period of time that a representative result can be returned from a sample following collection.
- For samples requiring analysis for the soluble metals content filtration soon after collection can remove colloidal or particulate material which provides additional facies for adsorption.

There are two main methods employed in the filtration of water samples, pressure systems employing syringe or gravitational pressure and vacuum filtration systems.
Syringe filtration:

- Agitate sample bottle to ensure thorough mixing.
- Draw an aliquot of the sample into the syringe from the sample collection container taking care to maintain an air gap between the base of the plunger and the sample to minimize contact and potential contamination.
- Dispense aliquot to waste to rinse syringe. Repeat.
- Draw an aliquot of the sample into the syringe taking care to maintain an air gap between the base of the plunger and the sample to minimize contact and potential contamination.
- Affix appropriate filter unit to syringe (between 0.4 and 0.5 μm) and dispense to laboratory sample container.
- Add any preservative to be used, reseal laboratory sample container and invert to mix thoroughly.

3. Integrity of samples

To ensure the reliability and interpretability of the collected data, appropriate documentation should be incorporated into the monitoring program that records sample movement from collection to data reporting and ensures that analytical data is ascribed to the correct location. Appropriate chain of custody information for collected samples commences with the completion of a sampling report. Sampling reports should contain at least the following information:

- Location (and name) of sampling site, with coordinates and any other relevant information.
- Details of sampling point.
- Date of sampling.
- Method of sampling.
- Time of sampling.
- Name of sampler.
- General environment and climatic conditions.
- Nature of pre-treatment.
- Preservation procedure.
- Water quality parameters collected in the field.
- Any information which may affect the results of analysis.

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Once collected, samples should be stored, handled, and transported in such a manner as to: prevent damage to containers or labels, minimize or eliminate degradation of the sample, and prevent contamination of the sample.
At each sample location, details relevant to the subsequent analysis and interpretation should be recorded on the field sheets. The details included on field sheets will vary according to the objectives of the sampling program but should include all the information necessary to assist in data interpretation and repeatability of sampling efforts. Information which could be considered for inclusion on field sheets includes:

- Name and location of sampling point.
- Date and time of sample collection.
- Any relevant descriptive information, e.g. water level/flow
- Sample appearance at the time of collection, egcolour, clarity and odour.
- Field parameters measured or results of any on site analysis, eg alkalinity.
- Sample treatment post collection, eg filtration, acidification, etc.

The choice of sample collection device is influenced by the nature of the sample site and the type of sample required. For example, a sample pole and container may be necessary where steep banks make accessing the water a safety risk. A clean pair of gloves should be worn at each sample site to minimize potential contamination problems. To collect a grab sample from shallow water body or a channel of flowing water:

- Select a point in the stream that is downstream of any channel braiding or inputs from tributaries to allow thorough mixing.
- Remove sample container lid (for locations with known very low concentrations of analytes this may need to be performed beneath the surface of the water to reduce contamination risk)
- Immerse sample container with the opening pointing directly down to maintain a volume of air in the container, thereby avoiding the collection of any surface films.
- Once under the surface of the water point the mouth of the sample container up stream so that gloved hands, sample container and/or sample collection device is downstream of the sample being collected.
- When sampling from a shallow water body, where possible select a point that is a reasonable distance from the edge. If the water is still (or flowing very slowly) move the sample container forward away from the sampler and any equipment to collect a continuous uncontaminated sample.
- Fill container, rinse and empty rinse water downstream or at a sufficient distance from sample site to prevent mixing of rinse water with the water to be sampled. Repeat.
- Fill container completely to exclude air and replace cap.
- Perform necessary filtration and/or preservation procedures, ensuring that sufficient sample is collected to perform the required analyses and any repeat analyses necessary.
- Complete sample labels and field data sheets.

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4. Handling preservatives

Strong acids or bases used for the preservation of water samples should be storedand handled with care. Always store sample kits in an upright position before use asindicated by the "up arrow" on the outside of each kit. Store in a location where thepreservatives will not freeze or overheat.
If a preservative does come into contact with your skin, the affected area shouldimmediatelybe flushed with large amounts of water. The area may have to beflushed for as long as fifteen minutes. If a preservative gets into your eyes, flush them immediately with plenty of water this includes the outside of the eyes. It may be necessary to hold the eyelids open duringthe washing procedure. Continue the rinsing for at least 15 minutes. After first aid, all eye injuries must be professionally treated as soon as possible.

5. Sampling materials

The materials required for taking samples:

- new, prepared sample bottles (waters) or wide topped jars or whirl-pack bags (soils), labelled with marker pen
- clean trowel, spade or auger for soil sampling
- sterile disposable gloves for bacterial sample collection
- ice or dry ice
- any equipment needed for taking on-site tests (thermometer, conductivity meter, pH meter, etc)
- sampling record sheet

The appropriate sampling device must be of a proper composition. Selection of samplers constructed ofglass, stainless steel, PVC or PFTE (Teflon) should be based upon the analyses to be performed. The containers for water samples are also influenced by the analysis that will be performed (table 1):

Table 1: Containers for water samples

Test	Sample Bottle	Wash	Storage & Transport
Turbidity	Polyethylene	Detergent then Dist H_2O	Store at 1-4° C
Colour	Polyethylene	Detergent then Dist H_2O	Store at 1-4° C. Test within 48 hours.
Major Ions	Polyethylene	Dist H_20	
Nutrients	Polyethylene	Dist H_20	May be frozen, or test within 24 hours.
Suspended and Settleable Solids	Polyethylene	Detergent then Dist H_20	Store at 1-4° C. Test within 24 hours.
Heavy Metals	Polyethylene	Acid wash then rinsed with Dist H_2O	Store at 1-4° C
Pesticides	Amber Glass	Acid wash then rinsed with Dist H_2O	Store at 1-4° C

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Herbicides	Amber Glass	Acid wash then rinsed with Dist H_2O	Store at 1-4° C
Bacteria	Sterile IDEXX jars	Do not wash. Fill to the mark only.	Transport at 4° C. Test within 6 hours for public health testing, within 24 hours for environmental samples.
Chlorophyll	Opaque Polyethylene	Dist H_20. Fill to the shoulder only.	Transport at 4° C.

6. Transport and storage

While sample preservation will limit degradation, it is recommended that dispatch to the laboratory for analysis occurs as soon as practicable.

The appropriate method and period of storage is dependent on the analyte of interest and should be followed to ensure that representative results from analysis are obtained.

Water sample storage and preservation procedures for common analytes of interest. Determinant	**Type of container**	**Preservation procedure**
Acidity and alkalinity	Plastic or glass	Fill container completely to exclude air and refrigerate.
Ammonia	Plastic or glass	Refrigerate.
Metals	Acid washed plastic or glass	Acidify with nitric acid to pH 1 - 2 and refrigerate. Filtration of the sample must be performed prior to acidification.
Major cations, eg Calcium	Plastic	Acidification is not required, though the addition of nitric acid sufficient to lower pH to 1 -2 will enable determination of concentration with metals analysis.
Chloride	Plastic or Glass	None required.
Cyanide	Plastic or Glass	If no interfering compounds are present, then add sodium hydroxide to a pH greater than 12.

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Nitrate	Plastic or Glass	Filter on site and freeze.
Nitrite	Plastic or Glass	Freeze
Total Nitrogen	Plastic or Glass	Freeze
Phosphorus	Plastic or Glass	For dissolved concentration determination filter on site and freeze. For total concentration determination, freeze.
Sulfate	Plastic or Glass	Refrigerate
Hydrocarbons	Glass, solvent washed.	Do not pre-rinse sample container. Do not completely fill sample container. Acidify with sulfuric acid or hydrochloric acid to pH 1 to 2 and refrigerate.

7. References

Kim, A.G., and Cardone, C.R. *Scatterscore: a reconnaissance method to evaluate changes in water quality.* Environmental Monitoring and Assessment, 2005, 111:277-95.

Ahlers, W.H., Reid, M.R., Kim, J.P., and Hunter, K.A., *Contamination-free sample Collection and Handling Protocols for Trace Elements in Natural Fresh Waters.*Australian Journal of Marine and Freshwater Research, 1991, 41:713-20.

Chen, J. P., Chang, S.-Y., Huang, J.Y.C., Bauman, E.R., and Hung, Y,-T. *Gravity Filtration.*In Handbook of Environmental Engineering, Volume 3.Physicochemical Treatment Processes. Ed: Wang, L.K., Hung, Y.-T., and Shammas, N.K. The Humana Press Inc. Totowa, NJ.

Shammas, N.k., and L.K. Wang.*Pressure Filtration.*In Handbook of Environmental Engineering, Volume 6.Biosolids treatment processes. Ed: Wang, L.K., Hung, Y.-T., and Shammas, N.K. The Humana Press Inc. Totowa, NJ.

-- 2007b.*EPA Guidelines. Regulatory monitoring and testing: Groundwater sampling.* Adelaide

-- 2006. *EPA Guideline. Regulatory monitoring and testing: Monitoring plan requirements.* Adelaide

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