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Sampling and Monitoring

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For further information about this and other documents in the series, contact the project team leader (see below) or visit the following website:

www.dhs.ca.gov/ps/ddwem/dwsap/DWSAPindex.htm

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Cover photo: Hydrologist collecting snow samples in the Sierra Nevada

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Water quality data are only as good as the water samples from which the measurements are made. Even the most precise laboratory analysis of a water sample cannot compensate for improper sample collection or physical and chemical alteration of a sample due to inappropriate transport and storage.

A technically sound sampling program is therefore the cornerstone of good water quality management. Such a program includes well-specified controls throughout the sampling process to guarantee the long-term reliability of the data collected.

This booklet outlines the basic principles of water sampling and monitoring. It provides the reader with a fundamental understanding and appreciation of the elements of water sampling—both for groundwater and for surface water. Many of the principles apply to other environmental sampling procedures as well. Of course, this brief guide is not a substitute for proper training of laboratory or field technicians involved in water sampling and monitoring.

Technician measuring water quality in the field

Key Factors in Sampling

Whether we monitor groundwater from wells, water from above-ground sources such as streams and ponds, or drinking water issuing from a tap, an important aspect of sampling is the location or set of locations from which the sample is taken, and the size of the sample. The location, timing, and size of the sample determine to a large degree the value of the sample and what part of the aquifer, watershed, or drinking water distribution system the sample may represent.

Another important aspect of making good water quality measurements is the set of analytical procedures employed to determine the concentrations of the constitutents of interest. This is usually done by certified laboratories, which follow detailed protocols to control the accuracy, precision, and repeatability of their determinations. The procedures and protocols they use are not described in this booklet. Instead, we focus on the sampling process itself, as implemented by consulting engineers and hydrologists, environmental technicians, utility employees, property owners, or private citizens. Sampling programs and procedures described herein assume that sampling locations have been determined, that the constituents of the water analysis are known, and that a certified laboratory will be employed to carry out the chemical analyses.

The sample collection process is also an important factor. That process includes a number of key elements. First, *sampling objectives* must be defined. The objectives, in turn, determine what kind of *sampling plan* needs to be followed. Then comes sampling itself, which includes *sampling prepartions*, *sampling procedures*, and *post-sampling activities*. Finally, the quality of the sampling process may be assessed and verified through *quality assurance and quality control procedures*. The following sections provide an overview of each of these elements.

Defining Sampling Objectives

What exactly is it that needs to be determined by the sampling program? A precise and well-thought-out answer to this question will lead to well-defined objectives for the sampling program. Those objectives must be clearly defined prior to designing a sampling plan.

For More Information

Water sampling procedures have become well established during the past 30 years. Protocols are now available, primarily through the U.S. Environmental Protection Agency (EPA), for collecting samples and measuring the chemical and physical characteristics of water. Many of the EPA's publications are available via the agency's website (www.epa.gov). Sample forms, examples, and other useful hands-on information are available in books such as *Environmental Sampling and Analysis for Technicians*, by M. Csuros (1994).

Sampling objectives determine the sampling locations (i.e., the layout of the monitoring network), the sampling frequency, the water constituents that will be analyzed, and the details of the sampling procedures. (Sampling procedures depend greatly on the type(s) of constituents to be analyzed.)

Without well-defined objectives, it is impossible to determine exactly what constituents should be analyzed. As a result, a sampling program may over-analyze or under-analyze a water sample. Analyzing for too many constituents adds unnecessary analytical cost. It may also increase the complexity—and therefore the cost— of the sampling procedures.Analyzing for too few constituents, on the other hand, often means that the entire sampling program is worthless, because it does not allow for appropriate interpretations of the results. Unfortunately, sometimes mistakes in a poorly-designed sampling program go undiscovered until several years after the program has been initiated. In such cases, the loss often is irretrievable, meaning that much effort has been invested with little to show for it.

Sampling objectives define the scope and purpose of a sampling project. Therefore, they can be very broad or very specific. Typical activities for which a sampling project will be designed are:

- planning (e.g., water resources management, groundwater management, resource use)
- permitting (e.g., project environmental impact review for landfills, industrial activities)
- compliance (e.g., drinking water, discharge requirements, groundwater quality requirements)
- enforcement (e.g., environmental cleanup)
- design (e.g., production well drilling, reclamation, remediation)
- research and development

The type of activity will determine the sampling objectives.

Preparing a Sampling Plan

Once the sampling objectives are determined, a sampling plan is developed that lays out, in detail, the actual sampling procedures and ensures that the sampling protocol meets the sampling objectives.

Sampling Campaign

The sampling plan identifies the overall type of sampling campaign, which can be classified as one of the following:

Sampling is limited in time (single sampling event):

- reconnaissance survey, covering an extensive spatial area (e.g., distribution network, watershed, or aquifer)
- point source characterization, focused on a single sampling location (e.g., waste discharges, water intake, production wellhead, household water faucet with conspicuous water quality)
- intensive survey, covering a larger spatial area with many sampling points

Continuous or repeated monitoring (ongoing, indefinite ending date, prescribed interval):

- fixed station monitoring, (e.g., within a water-filtration or treatment process, in a drinking water system, or on production wellhead)
- network monitoring, (e.g., monitoring wells located around a landfill, or wells installed in a watershed used for drinking water production)
- special surveys

Sampling objectives further provide guidelines in developing the proper sampling frequency (how often and when to take samples) and sampling density (number of sampling locations within the watershed, field site, aquifer, or water distribution system) and the type of sample to be collected.

Sampling Frequency

Depending on the objectives, depending on the anticipated changes in pollutant concentrations over time, and depending on the size of the sample (see below), samples may be taken continuously (e.g., salinity or pH measurements), hourly (e.g., in streams during storm events or in waterworks as part of a daily composite sample), or once to several times daily, weekly, monthly, or annually. Groundwater samples, particularly those taken from deep production wells that are subject only to very gradual changes in water quality, might be needed only once every few years (e.g., for drinking water compliance of small water supply systems).

Sampling Density

The number of samples within the area of interest follows from the sampling objectives and is determined primarily by the amount of spatial variability in water quality expected throughout the area of interest. The objectives also must define what constitutes a "significant" change: Is it important to know the change of a water constituent by 1%, by 10%, or by an order of magnitude? The answer to this question depends on the water constituent of interest: some water quality parameters vary much less over space and time than others. Total dissolved solids (TDS) in potable aquifers, for example, typically varies over less than two orders

of magnitude, from less than 100 mg/l in uncontaminated groundwater to several thousand mg/l in very salinized or contaminated waters. Organic contaminants such as TCE or MTBE on the other hand, are highly variable in their concentrations even within a contaminant plume. Three to five orders of magnitude difference from location to location are not uncommon, especially when the sample volume is small.

Sample Type

Samples collected at each sampling event within the sampling campaign are either grab samples or composite samples. A *grab sample* is an individual sample collected at a particular time and place. Such a sample represents conditions only at the time it is collected and for the location from which it was removed. Since most water samples rarely exceed a few liters in size, they represent a very small portion of the volume of water of concern (typically a watershed, a river, an aquifer, or a drinking water system). In light of natural variability, the representative value of a grab sample relative to the volume of interest must be carefully considered. A single grab sample should not be used as a basis for a decision about pollution abatement. Fortunately, in many cases, preliminary testing or existing data demonstrate that natural variability (in space or time) has only a minor influence on the sampling outcome. In such cases, grab samples are valuable representations of a much larger volume.

A composite sample, if collected properly, is a mixture of multiple grab samples collected either at a single point at different times within a given time period (e.g., samples collected hourly from water intake on a stream, over 24 hours), or at a specific time at different locations within the area of interest (e.g., soil samples taken during a single day at multiple locations throughout a field). The grab samples to be composited are collected in a single container, where they are carefully but thoroughly blended for analysis. The mixing process averages the variations in sample composition and minimizes analytical effort and expense. The volume of each grab sample should be the same at each time interval or field location. This assures that each sample has equal weight within the composite and hence contributes equally to the final measurement(s).

The laboratory analysis is rarely done on the entire composite sample. Rather, a subsample, or *aliquot*, is removed for analysis from the thoroughly mixed composite sample.

An analyte is an aqueous chemical constituent for which a chemical analysis is performed. For some types of analytes, the mixing process would result in changes of concentration that are unacceptable. For example, grab samples to be analyzed for Volatile Organic Compounds (VOCs), oil and grease, total recoverable petroleum hydrocarbon, or microbiological testing should never be composited. Instead, each sample is analyzed separately and averages are computed to provide a composite result.

Sample Collection,Preservation, Storage, & Delivery

Samples can be collected manually or automatically. Manual collection is labor-intensive and subject to differences in handling between sampling dates and sampling personnel. (The latter can be minimized by implementing a quality assurance plan, as described later in this document.) Automatic sampling equipment is now available commercially for many tasks; however, the cost of the equipment and equipment maintenance and concerns about vandalism at field sites often outweigh the disadvantages of manual sampling. In either case, the protocol for collecting the sample must be considered thoroughly. For example, when a water sample is to be analyzed for dissolved chemicals, the sample should be filtered immediately to remove any solids suspended within the water. That is because suspended solids can alter the chemistry of the sample during transport and storage, especially when the analyte of interest is strongly sorptive. The sampling devices and storage containers used and the cleanliness of all of these must be carefully weighed, too. The sampling plan therefore specifies procedures for cleaning, maintaining, and calibrating the sample bottles and field equipment.

If water samples are taken and not immediately analyzed in the field, they typically require preservation. Sample preservation assures that the water quality of the sample does not change during the time period between sample collection in the field and sample analysis in the laboratory. Preservation methods suppress chemical reactions that can occur in sample water due to degassing (lower partial pressure of dissolved oxygen, CO_2, etc.), or due to exposure to heat and light. The preservation method used depends on the water quality parameter(s) to be measured.

Preservation usually includes cooling the sample to 4°C (40°F). Samples must remain cool during shipping and storage. In many cases, preservation also requires the addition of strong acids or bases. These chemicals suppress certain reactions that would alter the water quality parameter of interest. Preservation methods depend on the anticipated holding time between obtaining and analyzing the water sample. For some parameters, any holding time is too long and they must be determined in the field (e.g., temperature, pH, chlorine). With proper preservation of the sample, most other parameters remain unaltered for a holding time of 1 week to 1 month.

If a water sample is analyzed for multiple parameters that require different preservation methods, it may be necessary to split the sample into multiple containers. Detailed guidelines for sample preservation have been developed by the U.S. EPA (Federal Register 40 CFR, Part 136; see Table 1). These guidelines should be followed whenever samples are submitted as part of a regulatory program or if results become part of litigation. Analytical laboratories should be consulted if there is any question about the proper preservation method. They often provide logistical support as well (such as appropriate sample containers, or even pre-preserved sample containers).

Prior to shipping, the sealed sample containers typically are put into ice chests, which are then packed with ice and transported to the analytical laboratory by express delivery service. At the lab, the samples are logged in, given sample ID numbers, and kept cool until the analysis occurs. A "chain-of-custody" form identifying each person who is handling the sample, from the time of collection to the time of analysis, accompanies the sample.

Sampling Preparations

Preparations necessary for the sampling trip should be listed in the sampling plan. Those preparations include:

- cleaning sample containers (bottles) and sampling equipment, such as filters, flow-through cells, pumping or bailing equipment, water level meters, etc. (see Tables 2 and 3);
- making sure the field kit includes equipment for preserving sample containers, such as ice, chemicals, tools, filtration equipment, and reference materials (Table 4);
- cleaning and calibrating field measurement equipment, such as probes and instruments for measuring temperature, pH, electric conductivity, dissolved oxygen, and reduction-oxidation potential;
- preparation of supplies for field spike samples, field blank samples, and for field calibration of measurement equipment (including an appropriate preparation log);
- preparation of field sampling labels and forms, such as container labels and shipping labels, field notebook (see Table 5), sample log sheets, and chain-of-custody forms; and
- loading the field vehicle and securing all equipment, while ensuring cleanliness (it is best to use a detailed checklist of all items to be loaded, including commonly needed repair tools and replacement parts).

Sampling Procedures

General Rules. Actual sampling procedures will vary greatly, depending on the type of sample (surface water, groundwater, drinking water, wastewater), the depth of the sample (in wells, lakes, rivers), the size of the sample, and the water quality parameters of interest. But common to all sampling procedures, the following general sampling rules should be understood and applied by sampling personnel (from Csuros, 1994):

- Samples should be collected first from the least contaminated sampling locations within the site, progressing gradually toward the more highly contaminated locations.
- Disposable latex gloves should be worn when sampling, and new, unused gloves must be used for each separate sampling point. For sampling hazardous materials, rubber gloves are recommended. Eating, drinking, and smoking should be avoided around the sampling site.
- When compositing samples, use a bowl and spatula to mix the sample. If the sample is to be analyzed eventually to measure trace organics and metals, use only mixing tools made of stainless steel, glass, or teflon. Samples should be mixed thoroughly and sectioned, and the quantity of each subsample should be recorded.
- The preferred order in sample collection is the following:

  (1) volatile organic carbons

  (2) extractable organics, including oils, grease, and TRPH

  (3) total metals

  (4) dissolved metals

  (5) microbiological samples

  (6) inorganic nonmetals

Groundwater Samples

Groundwater samples are obtained either from production wells (irrigation wells, domestic wells, municipal supply wells) or from *monitoring wells* especially designed for obtaining groundwater samples at specific locations and specific depths. Wells selected for sampling must meet the sampling objectives. Deciding whether to use a particular well typically requires having a good knowledge of the hydrogeologic setting and the construction details of the well. Particularly important is knowledge of the depth from which the well draws water (the part of the well that is "screened"—i.e., perforated or slotted to allow water to enter). General information on the hydrogeologic

Table 1: Recommendations for Collecting & Preserving Samples*

Parameter	Volume (ml)	Container	Preservative	Holding Time
PHYSICAL PROPERTIES				
Color	50	P, G	Cool, 4°C	48 hours
Conductance	100	P, G	Cool, 4°C	28 days
Hardness	100	P, G	HNO_3 to pH <2	6 months
Odor	200	G only	Cool, 4°C	24 hours
pH	25	P, G	None required	Analyze immediately
Residue, filtrable	100	P, G	Cool, 4°C	48 hours
Residue, non-filtrable	100	P, G	Cool, 4°C	7 days
Residue, total	100	P, G	Cool, 4°C	7 days
Residue, volatile	100	P, G	Cool, 4°C	7 days
Settleable matter	1000	P, G	Cool, 4°C	48 hours
Temperature	1000	P, G	None required	Analyze immediately
Turbidity	100	P, G	Cool, 4°C	48 hours
METALS				
Dissolved	200	P, G	Filter on site HNO_3 to pH <2	6 months
Suspended	200	P, G	Filter on site HNO_3 to pH <2	6 months
Total	100	P, G	HNO_3 to pH <2	6 months
Chromium +6	200	P, G	Cool, 4°C	24 hours
Mercury, dissolved		P, G	HNO_3 to pH <2	28 days
Total mercury	100	P, G	HNO_3 to pH <2	28 days
INORGANIC NON-METALLIC				
Acidity	100	P, G	Cool, 4°C	14 days
Alkalinity	100	P, G	Cool, 4°C	14 days
Bromide	100	P, G	None required	28 days
Chloride	100	P, G	None required	28 days
Chlorine	1000	P, G	None required	Analyze immediately
Cyanides	500	P, G	Cool, 4°C NaOH to pH >12	14 days
Fluoride	300	P, G	None required	28 days
Iodide	100	P, G	Cool, 4°C	24 hours
Nitrogen ammonia	400	P, G	Cool, 4°C H_2S0_4 to pH < 2	28 days
Kjeldahl - nitrogen	500	P, G	Cool, 4°C H_2S0_4 to pH < 2	28 days
Nitrate plus nitrite	100	P, G	Cool, 4°C H_2S0_4 to pH < 2	28 days
Nitrate	100	P, G	Cool, 4°C	48 hours
Nitrate	50	P, G	Cool, 4°C	48 hours
Dissolved oxygen, probe	300	G bottle and top	None required	Analyze immediately
Dissolved oxygen, Winkler	300	G bottle and top	Fix on site, store in dark	8 hours

Table 1: Recommendations for Collecting & Preserving Samples* *(continued)*

Parameter	Volume (ml)	Container	Preservative	Holding Time
INORGANIC NON-METALLIC *(continued)*				
Phosphorus, ortho-P, dissolved	50	P, G	Filter on site Cool, 4°C	48 hours
Hydrolyzable P	50	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Total P	50	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Total dissolved P	50	P, G	Filter on site Cool, 4°C H_2SO_4 to pH < 2	24 hours
Silica	50	P only	Cool, 4°C	28 days
Sulfide	500	P, G	Cool, 4°C 2 ml zinc acetate + 2N NaOH to pH > 9	7 days
Sulfite	100	P, G	None required	Analyze immediately
Sulfate	100	P, G	Cool, 4°C	28 days
ORGANICS				
BOD	1000	P, G	Cool, 4°C	48 hours
COD	50	P, G	Cool, 4°C	28 days
Oil and grease	1000	G only	Cool, 4°C H_2SO_4 to pH < 2	28 days
Organic carbon	50	P, G, G brown	Cool, 4°C H_2SO_4 to pH < 2	28 days
Phenolics	500	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Surfactants	500	P, G	Cool, 4°C	48 hours
Purgeable halocarbons	40	G, teflon lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$**	28 days
Purgeable aromatics	40	G, teflon lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$** HCl to pH < 2	14 days
Acrolein and Acrylonitrile	40	G, teflon lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$** pH 4 to 5	14 days
Phenols	1000	G, teflon lined cups	Cool, 4°C 0.008% $Na_2S_2O_3$**	7 days until extraction, 40 days after extraction
Phthalate esters	1000	G, teflon lined cups	Cool, 4°C 0.008% $Na_2S_2O_3$**	7 days until extraction, 40 days after extraction
Nitrosamines	1000	G, teflon lined cups	Cool, 4°C 0.008% $Na_2S_2O_3$** store in dark	7 days until extraction, 40 days after extraction
PCBs	1000	G, teflon lined cups	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitroaromatics and isophorone	1000	G, teflon lined cups	Cool, 4°C store in dark	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	1000	G, teflon lined cups	Cool, 4°C store in dark	7 days until extraction, 40 days after extraction
TCDD (Dioxin)	1000	G, teflon lined cups	Cool, 4°C 0.008% $Na_2S_2O_3$**	7 days until extraction, 40 days after extraction

Table 1: Recommendations for Collecting & Preserving Samples* *(continued)*

Parameter	Volume (ml)	Container	Preservative	Holding Time
ORGANICS *(continued)*				
Chorinated hydrocarbons	1000	G, teflon lined cups	Cool, 4°C	7 days until extraction, 40 days after extraction
Pesticides	1000	G, teflon lined cups	Cool, 4°C PH 5 to 9	7 days until extraction, 40 days after extraction
Soil, sediment, sludge, Organic extractable	8 oz	Widemouth G teflon lined cup	Cool, 4°C	ASAP
Organic volatile	8 oz	Widemouth G teflon lined cup	Cool, 4°C	ASAP
Metal	1 pint	P	Cool, 4°C	6 months
Fish samples		Wrap in Al foil***	Cool, 4°C Freeze	ASAP
Chemical wastes	8 oz	Widemouth G,*** teflon lined cup	None	ASAP
BACTERIOLOGY				
Total and fecal coli, Fecal streptococcus	100	P, G sterile	Cool, 4°C 0.008% Na_2SO_4	6 hours
RADIOLOGICAL				
Alpha, Beta, Radium	1000	P, G	HNO_3 pH < 2	6 months

** From 40 CFR, Part 136*

*** Required if residual chlorine is present.*

****Plastic containers may be used if only metals are required.*

KEY: *ASAP = As soon as possible; P = Polyethylene container; G = Glass container. Sample preservation = Sample preservation should be performed immediately upon sample collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, chemical samples may be preserved by maintaining 4°C until compositing and sample splitting is completed. Holding time = Samples should be analyzed as soon as possible after collection. Those listed should be the maximum time that samples may be held before analysis and still be considered valid. Dissolved parameters = Samples should be filtered immediately on site before preservation.*

setting and details of well construction and maintenance should be on file prior to the beginning of a sampling campaign.

Collection of water samples from groundwater wells occurs in five steps: (1) accessing the well,(2) measuring the water level, (3)purging the well, (4) collecting the water sample, and (5) securing the well. These steps are explained in detail below.

Access

Monitoring wells are usually secured with a locking cover or bolted metal housing, either at ground level (a traffic-rated utility or well box), or inside a 2 ft - 3 ft high metal pipe housing. Inside the housing, the actual monitoring well (usually a 2" or 4" PVC pipe) is sealed with an expandable rubber plug that can be locked tight. The plug is sealed with a keyed padlock. To gain access to the well, covers and locks are removed.

Access to production wells can be more tricky. Ideally, a sample valve or spigot is located in the water pipeline between the wellhead and the water storage or pressure tank. Sometimes, however, particularly when sampling domestic or irrigation wells, the closest access to water from the well is at the exit point of the water pressure tank (domestic wells) or the irrigation system (flood gates, sprinkler system hookup, etc.). The sampling plan should clearly identify the access point to production wells and must consider potential changes in water quality due to storage in pressure tanks and irrigation piping, due to the type of irrigation piping, or due to water treatment or filtration system(s) that may be present between the wellhead and the water sampling

Table 2: Cleaning Sampling Equipment In the Laboratory & in the Field*

Equipment should be cleaned before sampling and at the field between samples. At the end of the field trip, sample collection equipment must be labeled as "rinsed, ready for in-house cleaning". After sufficient cleaning in the laboratory, they should be labeled as "in-house cleaned, ready for field" with date cleaned and signature of the cleaner. Both house and field cleaning should be documented properly. Detergents specified for cleaning are Alconox (or equivalent) with <5% phosphate, or Liquinox (or equivalent) that is phosphate- and ammonia-free. The solvent used in routine cleaning should be pesticide-grade isopropanol. Analyte-free water is to be used as rinsing water and for preparation of blanks. The purity and reliability of the analyte-free water is shown by the results of the blank sample. Document all cleaning in a boundnotebook.

Cleaning Equipment in the Laboratory:

- Wash with hot soapy tap water and scrub with a brush.
- Rinse thoroughly with hot tap water.
- Rinse with 10% to 15% nitric acid (HNO_3). If nutrients are of interest, after the HNO_3 rinse, rinse again with 10 to 15% hydrochloric acid (HCl) or skip the HNO_3 rinse altogether and rinse only with HCl. Acid rinse solutions should never be applied to stainless steel or any other type of metallic equipment!
- Rinse thoroughly with de-ionized water.
- Rinse thoroughly with pesticide-grade isopropanol.
- Rinse thoroughly with analyte free water.
- Air-dry completely
- Wrap in aluminum foil for storage and transportation.

Cleaning Equipment in the Field:

- Use the same procedure as in-house cleaning, with the exception of hot water.
- First wipe or scrub the equipment to remove particles with the appropriate soap solution, rinse with tap water, followed by de-ionized water, and finally air-dry.
- For heavily contaminated equipment, use Acetone or Acetone-Hexane-Acetone rinse before regular field cleaning (decontamination or "decon")
- The rinse with analyte-free water is recommended, but optional.
- When only inorganic parameters are of interest, equipment may be rinsed with analyte-free water and with sample water.
- If proper cleaning of the equipment is impossible, it should be properly set aside until effective cleaning is possible.

Cleaning of Purging Equipment (*e.g., submersible pumps & non-Teflon hoses*)

- Wipe or scrub to remove particles with appropriate soap solution.
- Rinse with tap water.
- Rinse with de-ionized water
- Air-dry as long as possible before purging next well.

Care should be taken to completely clean the exterior of the pump and the exterior and interior surfaces of tubing.

Decontamination of Teflon Tubing (*alwys in laboratory; never in field*)

- Soak tubing in hot soapy water and if necessary use a brush to remove any particulate if necessary.
- Rinse tubing exterior and ends liberally with tap water.
- Rinse tubing surface and ends with 10 to 15% HNO_3.
- Rinse with tap water.
- Rinse with pesticide-grade methanol or isopropanol.
- Rinse with analyte-free water, then air-dry.
- Place tubing in clean aluminum foil.
- With teflon inserts, connect all of the hose used on site. Using the field-use peristaltic pump, assemble the system used in the fields, but use a larger size bottle hat has the same cap size as the collection bottles. (A large size bottle such as the type containing solvents or acids is suitable.)
- Pump copious amounts of hot, soapy water through the connected tubing. Follow this with tap water.
- With the pump running, draw at least 1 liter of 1 + 1 HNO_3 through the tubing. Close valve, and stop the pump. Let the acid remain in the tubing for 15 to 20 minutes. Pump an additional 1 to 2 liters of acid through the tubing, followed by 1 to 2 liters of tap water.
- Pump 1 liter of pesticide-grade methanol or isopropanol through the tubing. Let solvent remain in the tubing 15 to 20 minutes. Pump an additional 1 to 2 liters of solvent through the system.
- Finally, rinse with 2 to 3 liters of analyte-free water.
- Leave the teflon inserts between the pre-cut lengths, and cap or connect the remaining end.
- After the interior has been sufficiently cleaned, the exterior needs a final rinse with analyte-free water. Air dry.
- Wrap in aluminum foil and store in a clean, dry area. Label with the date of cleaning.

* *from Csuros, 1994*

point. Sometimes it may be possible to access the well casing through an access tube. If sampling directly from a production well via a portable submersible pump, bailers, or other collection devices, the production well turbines or pumps must be shut off and considerable care must be taken not to tangle or wedge the sampling equipment between the production line, electric cables, drive shaft, and other equipment suspended in the well casing.

Measuring water level

After gaining access to the well, the first measurement taken is a groundwater level measurement. Groundwater levels are measured to one one-hundredth of a foot (0.01 ft) accuracy, using a survey grade groundwater level meter. As part of the in-house sampling preparation, groundwater level tapes should be inspected regularly against survey-grade measuring tapes to account for and correct for gradual stretching of the tapes. The metering device must be properly decontaminated prior to and between sampling locations. For water level readings, the depth to water is measured from a fixed and identifiable reference point at the top of the well. For monitoring wells, the standard reference point is the north-side of the top of the PVC casing (not the top of the protective housing around the PVC pipe). Reference points should be marked to ensure consistency between sampling times. For production wells, the reference point can be the top of the access tube or access hole to the well casing. When taking water level measurements in production wells, the pump plant inside the casing must be off and great care must be taken not to tangle the measuring tape on the drive shaft, production line, or other cables suspended in the casing. If at all unsure about whether enough space is available, a styrofoam cylinder of the same size as the water level meter can be lowered on a sturdy string to test access

Purging

Prior to collecting a groundwater sample, the well is purged to remove any stagnant water in the well casing or gravel pack and to ensure that at least 95% of the water sample originates from the aquifer formation being sampled. As a rule of thumb, a minimum of three to five well volumes of water are purged (for definition of well volume, see Figure 1). Purging continues until temperature, electric conductivity, and pH level readings stabilize. The method and volume of water pumped and the water quality readings are logged in the field book. Additional purging may be necessary, if sampling occurs at the outlet of a water pressure tank, to remove stagnant water in the tank.

In production wells, the purging is implemented with the production pump. Typical equipment used for well purging in monitoring wells are electric submersible pumps (available in plastic materials and stainless steel for 2" and 4" wells, with constant or variable speed, pumping rates ranging from 100 ml/minute to 10 gal/min, lift up to 300'), hand pumps (inexpensive, available for small-diameter wells), peristaltic pumps (for small-diameter wells with water table depth less than 20 ft), air-lift samplers (pressurizes well casing to force water sample to the surface; not suited for volatile compounds), gas operated pumps (for small- diameter, deep wells; needs a source of nitrogen gas), or bailers (available in a wide variety of materials and diameters; inexpensive, but low-volume removal and degassing and aeration are possible).

Sample Collection

Sample collection usually occurs immediately after purging, but no later than six hours after purging. For sample collection, samples are generally removed at a lower pumping rate (if a pump with adjustable speed is used) than was used for purging. The reduced pump rate is necessary to avoid degassing or aeration of the water sample.

Sample containers should be properly labeled and checked immediately prior to collecting the samples. Bottles that are not pre-preserved are rinsed twice with sample water before filling with the final sample. (Exception: Never rinse bottles used for samples that

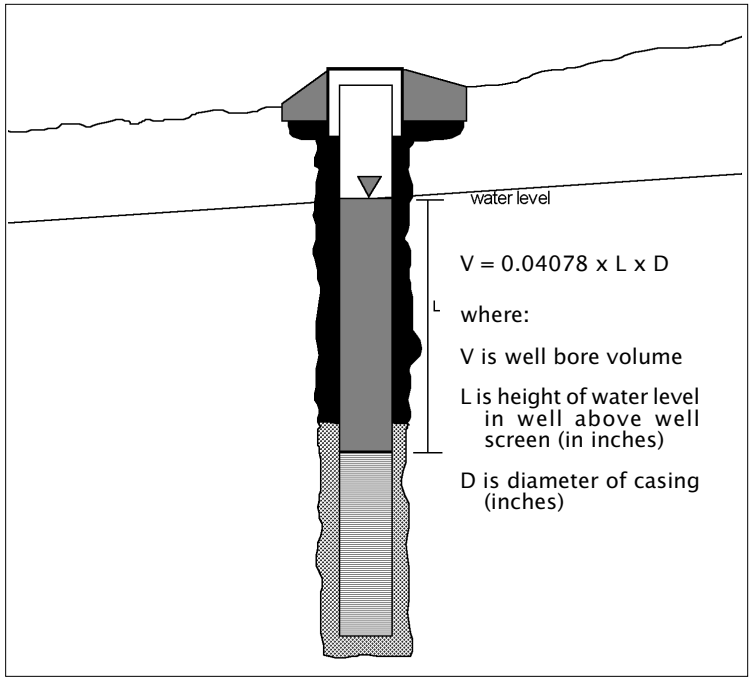

Figure 1. Definition of well-bore volume

Table 3: Preparing Sampling Containers*

Selecting Sampling Containers

The material that the sample container is composed of should be chosen so it will not react with the sample. The container should be resistant to leakage and breakage and should have the proper volume necessary for the analyte(s) of interest. Plastic bottles are the best for sampling inorganic parameters. The containers must have tight screw-type lids. Glass and teflon containers with teflon lined caps are suitable for organic analytes. However, there are some disadvantages. Glass is breakable and teflon is quite expensive. For purgeable organics, use 40 ml borosilicate glass vials with screw caps that have teflon-backed silicon septums. Sterile plastic cups, individually wrapped, or sterile whirl-pack plastic bags are adequate for microbiological samples.

Sample containers may be cleaned by the sampling organization or purchased from commercial vendors as precleaned equipments. If using the latter, make sure each container has been labeled with date of receipt, etc.) and their uses must be documented.

Cleaning Procedures for Sampling Containers

To eliminate sample contamination by the sample containers, these regulated cleaning procedures must be strictly followed:

CONTAINERS FOR PHYSICAL PROPERTIES & MINERAL ANALLYSIS

BOTTLE TYPE: Plastic or glass, minimum of half gallon capacity.

SOAP: Liquinox or equivalent.

- Wash bottles and caps with hot soapy water, and rinse liberally with tap water until suds are no longer present.
- Rinse bottles and caps with laboratory-pure water at least 3 to 5 times. Drain and store tightly capped until used.

to eliminate sample contamination by the sample container

CONTAINERS FOR NUTRIENTS, DEMANDS, & RADIOLOGICAL ANALYSIS

BOTTLE TYPE: Plastic or glass.

SOAP: Liquinox or equivalent (phosphate- and ammonia-free).

- Wash bottles and caps with hot soapy water, then rinse liberally with tap water until suds are no longer present.
- Rinse bottles and caps with 1+1 HCL, then follow by rinsing 3 to 5 times with laboratory - pure water.
- Drain and store bottles tightly capped until use.

CONTAINERS FOR METALS

BOTTLE TYPE: Plastic bottle with lid.

SOAP: Metal-free Acationox or equivalent.

- Wash bottles and caps with hot soapy water, then rinse liberally with tap water until suds are no longer present.
- Rinse bottles and caps with 1+1 HCL, followed by tap water rinse.
- Rinse bottles and caps with 1+1 HNO_3. Rinse three times with liberal amount of laboratory pure water.
- Drain and cap tightly until use.

CONTAINERS FOR EXTRACTABLE ORGANICS

BOTTLE TYPE: 1-liter narrow-necked glass bottle with Teflon lined caps. Plastic bottles and plastic or rubber lined caps are not acceptable.

SOAP: Alconox or equivalent.Do not use liquid or powdered detergent that has been stored in a plastic container.

- Wash bottles and caps in hot soapy water. Do not use brushes with rubber or plastic parts! The use of plastic gloves while washing or rinsing organic bottles is not recommended since they are another potential source of contamination.
- Rinse bottle five times with tap water until all soap is gone.
- Rinse each bottle with 10 ml of pesticide grade acetone, cap tightly and shake approximately 10 seconds. Care should be taken not to allow the interior plastic portion of the cap to come in contact with the acetone.
- The final aqueous rinse should be with organic-free water.There should be no acetone smell in the bottle. This means, rinse about five times.
- Drain bottles and cap until use.

CONTAINERS FOR VOLATILE ORGANIC COMPOUNDS (VOCs)

BOTTLE TYPE: 40 ml glass vial with teflon lined septum.

SOAP: Alconox or equivalent. Do not use liquid or powdered detergent that has been stored in a plastic container.

- Wash vials, caps, and septums in hot soapy water, using the same precautions as described under extractable organics.
- Rinse liberally with tap water and laboratory - pure water.
- Finally, rinse with pesticide - grade methanol.
- Dry vials, caps, and septums in oven at 105℃ for more than 60 minutes.
- Cool in inverted position and cap immediately after bottles are cool enough to handle.

* *from Csuros, 1994*

will be analyzed for oil, grease, and total recoverable petroleum hydrocarbons, because these compounds remain on the sampling equipment.) If sampling for dissolved and suspended metals, organic carbon, or nutrients, each sample should be filtered with a 0.45 µm membrane filter. The filter should be washed with deionized water prior to use. Easiest to use with pumps are disposable filters that can be attached to the end of the discharge hose. The filtrate (water sample) contains the dissolved compounds. The filter paper can be submitted to the lab for analysis of suspended metals. The water sample is then carefully placed into the sample container.

If unfiltered, the sample goes directly from the bailer or the discharge tube of the pump into the sample container. If a flow-through cell is used for continuous water quality monitoring, the flow-through cell should be bypassed for sampling collection, using a T-valve. Care should be taken that the discharge tube does not touch the sample bottle and to ensure that as little air as possible is entrained into the sample, particularly when sampling for volatile organic compounds (VOCs). The sample container should be almost full (completely full when sampling for VOCs), and then capped and properly stored immediately. When sample preparation with acid is necessary, the exact same amount of preservative should be added to all samples and to the field blank. Finally, the field log, preservation log, and chain-of-custody form are completed.

Securing Well Access

All locking covers, locks, and housing covers should be secured safely to ensure protection of the well.

Drinking Water Samples

Collecting samples of drinking water from private potable wells follows the same procedures as those described for groundwater samples. Sampling from the water distribution system also follows the same rules as sample collection from wells. If residual chlorine is present, and, if it is likely to interfere with the desired analysis (e.g., microbiological samples), add 0.008% (100 mg/l) sodium thiosulfate ($Na_2S_2O_3$) immediately after collecting the sample to inhibit the chlorine's action.

When samples are collected from faucets, the faucets must be clean and free from excessive dust, rain, snow, or other sources of contamination. The faucets should be flushed for several minutes prior to sampling. After flushing, the flow rate should be adjusted to allow for smooth sampling without splashing or spilling.

Surface Water Samples

Surface water samples may be taken from lakes, ponds, rivers, streams, and estuaries. The sampling locations depend on the sampling objectives and are often prescribed in general fashion by recommendations from state and federal agencies. The following general rules should be observed (from Csuros, 1994):

- If sampling with a boat, samples must be taken from the bow, away and upwind from any outboard gasoline engine.
- Samples, both water and sediments, should always be collected from downstream to upstream.
- Care should be taken not to disturb sediments when taking the water samples.
- When water and sediment samples are taken from the same area, water samples must be collected first.
- Do not take samples at or near dams, piers, or bridges because the unnatural water flow may make the sample unrepresentative.
- *Grab samples* are taken using unpreserved sample containers. Collecting grab samples is a common and accepted method because no additional equipment interferes with the procedure. Preservation, if necessary, should be done immediately after sample collection (see Table 5).
- *Composite samples* are taken when a given depth interval is desired for the sample. All subsamples should have equal volumes. Composite samples from depths may be taken using a peristaltic pump, bailer, or depth-specific samplers (Kemmerer samplers, Niskin sampler, etc.). A Kemmerer sampler is a 4- by 18-in. tube with end caps that close by means of a messenger and entrap a 4.2-L water sample inside.

Taking a surface water grab sample:

- Submerge the container into the water.
- Invert the bottle, so the neck is upright and pointing to the water flow, and return the filled container quickly to the surface.
- If an intermediate sampling vessel must be used, pour the sample into a sample container.
- Pour out a few milliliters of the sample to allow room for the preservative.
- Cap, close, and label the bottles.

Post-sampling Activities

After completion of sampling (including sample preservation), samples are packaged appropriately and shipped, usually by the field personnel or by a designated sample custodian. The chain-of-custody form (see quality control, below) must accompany the sample at all times. All personnel handling the sample from

collection to analysis must sign the chain-of-custody form at reception *and* upon release of the sample. After returning from the field or collection point, all sampling equipment, containers, etc., should be properly cleaned and re-calibrated, and all field logs should be completed.

Quality Assurance and Quality Control

Determining the water quality of a sample involves more than just a single measurement process. It is a system of many individual steps that, together, represent a "measurement" of the water quality. These steps include the proper preparation of the sampling equipment and sampling containers, proper sampling methods in the field, proper sample preservation and transport, and appropriate laboratory procedures to analyze the water sample. In order to ensure that the final concentrations reported are close to the true water quality of the sampled water, a "quality assurance" (QA) program is needed. The quality assurance program ensures that no unintended contamination or mistake occurred during any of the individual steps necessary to measure field water quality. The quality assurance program achieves this goal:

- through the use of appropriate "quality control" (QC) checks;
- by prescribing proper sampling protocols;
- by properly training field personnel;
- through proper recording and field documentation (including proper chain-of-custody records; and
- through prescribed procedures for frequent review, processing, and reporting of the data.

Precision, Accuracy, Sensitivity

A properly implemented quality assurance program with the right quality control checks will provide a water quality determination that has a high—and independently determined—*precision* and *accuracy* with known *sensitivity*.

The *precision* of a measurement refers to the small differences observed between repeated measurements of the exact same sample. Commonly (especially in laboratory analyses), duplicate measurements are made of the same sample to document precision. Precision is expressed as the "Relative Percent Deviation" (RPD) between the two measurement results. The RPD is the difference between two measurements relative to the average result of the two measurements:

$$RPD = (A - B) / [0.5 * (A + B)] * 100\ [\%]$$

where A and B are the two numbers measured. The *accuracy* of a measurement refers to its ability to come close to the true value. The accuracy of field or laboratory measurements is tested by measuring a sample with a known concentration (a "spiked" sample). The accuracy is expressed as "% Recovery":

$$\%R = \text{measured value} / \text{true value} * 100\ [\%]$$

In practice, RPD and %R determinations are made on a frequent basis, and statistics of their mean value and standard deviation are compiled. The *sensitivity* of a measurement refers to the lowest concentration that can reliably be detected, the so-called limit of detection

Examples of How to Achieve Accuracy & Precision

Example 1: Precision and accuracy of measuring length

Let's say we want to measure the length of a letter sized paper with a used wooden ruler that is marked every tenth of an inch. We measure the same paper twice in a row. Once it looks like the paper is 10.5 inches long. The second time, we measure more like 10.6 inches. The difference is 0.1 inches. The average of the two measurements is 10.55 inches. The RPD is (0.1 / 10.55) times 100 [%], or 1%. Hence, our measurement has a precision of 1%. But how accurate is the measurement? We know that the letter size paper is exactly 11 inches long. The accuracy is (10.55 inches / 11 inches) x 100 [%] or 95%.

Example 2: Precision and accuracy of a field water quality sample

Let's consider measuring nitrate concentration in well water. To measure the precision and the accuracy of our field sampling procedure, we need a "field duplicate sample" and a "field spiked sample." The duplicate samples were collected at the same time from the same well. The spiked samples were filled (in the field) with a carefully prepared solution of known nitrate concentration (10.0 mg/l). The laboratory analysis yields 6.1 mg/l and 6.9 mg/l nitrate in the two duplicate samples. Taking the difference between those two samples (0.8 mg/l) and dividing by the average of the two (6.5 mg/l) yields an RPD of 12%. Hence, the precision of the nitrate sample measurement is 12%. The spiked sample with 10.0 mg/l nitrate measured 13.5 mg/l in the laboratory. The % Recovery of the combined field sampling and laboratory analysis is therefore equal to 135% (13.5 mg/l divided by 10 mg/l).

Table 4: Preserving Samples*

Preservation is necessary for all samples according to Federal Register 40 CFR, Part 136. Table 5 lists the types of sample containers, methods of preservation, maximum holding times, and amount of sample for each parameter.

Sample preservation may be accomplished by using ready, pre-preserved bottles, obtained from the laboratory. Additional preservatives should be available in the field, if the measured pH of the preserved sample indicates the need for more preservative. Samples may be preserved in the field after sample collection. If the sample is preserved in the field, the following protocols should be followed:

- Preservations should be added to each sample container by pipet or premeasured dropper.
- Preservative should be reagent-grade chemical, or higher grade chemical.
- Fresh preservative must be obtained prior to each sampling trip.
- After addition of preservatives, the sample should be mixed thoroughly and the pH of the sample should be checked. Use narrow-range pH paper on an aliquot of preserved sample poured out into a disposable container. If the pH value isn't quite where it should be, add more preservative until the pH is satisfactory. Any supplemental preservative added to the sample must originate from the same source as the original preservative. The pH check, and the quantity of the additional preservative should be documented.
- The same amount of additional preservative must be added to all corresponding blank samples.
- Acid preservation should be done in a well-ventilated area to avoid build-up of acid fumes and toxic gases released from the samples. Any unusual reaction should be noted in the field documentation.
- Avoid spattering or spilling acids. Wipe up any spill immediately and flush the area with a generous amount of water.
- All chemicals transported to the field should be properly stored in the laboratory. Acids should be stored in acid-storage cabinets and solvent should be stored in solvent-storage cabinets. Chemicals should be separated according to their chemical character.
- During transport to the field, all chemicals should be stored in properly cleaned plastic or Teflon containers, to avoid breakage, and should be segregated from sample containers to avoid accidental contamination.

* *from Csuros, 1994*

(LOD), and the minimum concentration that can reliably be measured. The latter is referred to as the method detection limit. The LOD is the lowest concentration that can be determined to be statistically different from a blank sample.

Quality Control Checks

Quality control checks are procedures, built into the sampling and analysis program, that allow us to determine the precision and accuracy of the water quality determination, while at the same time distinguishing between various sources of errors introduced through inadvertent, improper preparation of sample containers and improper field sampling and cleaning procedures. They also arise due to errors committed during transport or due to problems in the analytical laboratory. In Example 2 (see box), the duplicate and spiked samples allowed us to determine the overall precision and accuracy of the water quality sample. But whether the imprecision and inaccuracy of the sample is due to improper sample preparation, to sampling problems, or to limitations in the laboratory is unclear. Laboratories therefore implement internal QA/QC plans to determine the precision and accuracy of the analytical procedure itself (independent of errors in the field sampling). Also, field quality control typically includes a number of checks in addition to duplicates and spiked samples. The following is a summary of the field quality control checks typically used in water quality sampling protocols (after Csuros, 1994):

Duplicate Samples

Duplicates are samples collected at the same time from the same source (field duplicates) or aliquots of the sample that are prepared and analyzed at the same time (laboratory duplicates). During each independent sampling event, at least one sample or 10% of the samples, whichever is greater, must be collected for duplicate analysis. This requirement applies to each of the water quality parameters measured.

Field Spiked Samples

Field spiked samples are environmental samples that have specific concentrations of various parameters of interest added, usually in the range anticipated from the sample. Spiked samples are used to measure the performance of the complete analytical system, including interference from sample matrix. Field

Table 5: Maintaining Field Notes*

Field notes should be made in a bound record book with pencil or permanent (non-water-soluble ink) pen. The notes should include:

- Name of researcher and all personnel participating in the sample collection.
- Date and time of sampling.
- Field conditions: weather and description of sample site.
- Description of the sample location: address, sample site, exact sampling points, etc.
- Sample type: grab, or composite. If collecting a composite sample, record the appropriate time intervals, volume of the subsamples, and the time duration of the composition process.
- Analytical parameters to be measured, type and number of containers, and preservation techniques. (For example: Total metals, 1/2 gallon plastic container, preserved with 3 ml 1+1 NHO_3 per 1 liter sample.)
- Methods employed when preparing preservatives, and information about chemicals used.
- Method by which pH of preserved sample(s) was measured. Also the value(s) of measured pH. If additional chemicals were used to adjust pH, the amount added should be noted, as well as the method used to prepare blanks.
- The sequential order in which samples are taken. (Each sample should have its own "sequence number.")
- In addition to sequence number, each sample should be assigned a field identification number (FID) with the type of chemical analysis requested.
- If duplicate samples are taken, properly identify by designating each sample as FD1 or FD2.
- If split samples are taken, correctly describe and identify by FS1 and FS2.
- Information about the preparation and the true value of the field Quality Control (QC) samples, used to check the accuracy of the field tests (if applicable).
- Spiked samples are marked as FSp1 and FSp2, if duplicate spiked samples are collected (if applicable).
- Field measurement data for temperature, pH, conductivity, dissolved oxygen (DO), residual chlorine.
- List of the purging and sampling equipment used.
- Field decontamination performed.
- Documentation for monitoring wells:
  - ~ well casing composition and diameter of well casing
  - ~ water table depth and well depth
  - ~ calculation used for volume purged
  - ~ total volume of water purged
  - ~ date and time well was purged
  - ~ measurements to monitor stabilization of wells

  Note: at least 3 volumes must be purged. If field measurements are taken, purging shall continue until the measurements are stable. If no measurements are taken, at least five well volumes must be purged before the sample collection can begin.
- Additional documentation for surface water:
- depth at which samples were taken
- Additional documentation for wastewater effluent:
- beginning and ending times for composite sample, if applicable
- Additional documentation for soil and sediment:
- depth at which samples were taken
- Additional documentation for drum sampling:
- type of drum and description of contents
- if stratified, what layer(s) was sampled
- Description of method by which samples are transported to the laboratory: packing, cooling, separated, carrier, etc.
- Sample transmittal form (usually the chain-of-custody form) must include the following information:
- site name and address
- date and time of sample collection
- name and address (and phone number) of person, responsible for obtaining and transporting (or shipping) the sample
- identification of sample, including field ID number, number of sub-samples, data and time sample collected, intended analysis, preservation, and any comments about the sample or sample container

  Note: Failing to fill out records properly could result in invalidation of data.

* *from Csuros, 1994*

preparation and transportation to the laboratory should be similar to the samples, and marked FSp. If spiked duplicates are collected, their identifications are FSp1 and FSp2. The sample that will be spiked may be selected by specific requirement, by a previous evaluation of the sample site, or by an on-site inspection.

Split Samples

Split samples are a replica of the same sample. The samples are given to two independent laboratories for analysis.

Equipment Blanks

Equipment blanks are used to detect any contamination from sampling equipment. At least one equipment blank should be collected for every 20 samples per water quality parameter group. Each type of equipment used in sampling must be accompanied with an equipment blank. This blank is prepared in the field before sampling begins, by using the precleaned equipment and filling the appropriate container with analyte-free water. Preservation and documentation of these blanks should be the same as for the collected samples. If equipment is cleaned on site, then additional equipment blanks should be collected for each equipment group.

Field Blanks

Field blanks are collected at the end of the sampling event. Fill an appropriate sample container with analyte-free (de-ionized) water, then preserve and document in the same manner as the collected samples.

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