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Circular 1407

Water Quality Monitoring Programs for Environmental Assessment of Citrus Groves[1]

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Monitoring versus Sampling

Monitoring is the process of checking or testing in order to regulate or control something. This definition implies three elements: continuity, organization or systematic testing, and purpose. Water quality monitoring costs money, it takes time, and results can be difficult to interpret. There are many reasons to monitor, some more desirable than others. In fact, it may be hard to find any other water-related issue that growers are more emotional about than monitoring, except perhaps regulation. Before starting a water quality monitoring program, it is important to determine how it can benefit you and how to design a proper monitoring program. This document does not attempt to list all possible uses of a monitoring program, but rather describes basic principles on which one is able to build a valid program while minimizing both investment in the field and operational costs.

A single sample in time and space does not constitute monitoring. The difference between monitoring and a single sample (sporadic sampling) is that the former is able to describe the behavior of the water system, while the latter only provides a snapshot of the same system at a specific time and place. It should be kept in mind that at best, a single sample is indicative of the instantaneous status of the water and it has a good chance of not being representative of the overall water condition. Making a long-term commitment and/or decision based on a single sample is risky and bound to lead to unexpected complications.

A number of samples taken sporadically over time should not be considered monitoring, even if the samples are analyzed for the same set of parameters. In fact, even if the samples are analyzed for the same parameters but the sampling method is altered or the time interval is varied without a predetermined reason, the sampling cannot be considered monitoring in the strictest sense of the term. Since random sampling lacks continuity or organization, the data provided may not hold up in the face of a challenge and therefore should not be considered as monitoring.

The purpose of a water monitoring program can vary widely, depending on each particular grove or operation. To assure that the design serves the intended purpose, the object of the program must be clearly stated and understood. The objectives based on the purpose are the foundation for the entire program. The objectives of a monitoring program determine the means of sampling, system design, parameter selection, analytical services selected, cost, and the applicability of the data. If the statement of purpose and objectives for a monitoring program are weak, the monitoring program results will be weak also. However, well-defined and thoroughly thought-out objectives, plus a program built around them, should result in a successful program and save money and effort.

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Need for Monitoring

The need for monitoring can be divided roughly into three categories:

1. The monitoring one wants to do — **Grower interests**.

2. The monitoring one should do — **Market interests.**

3. The monitoring one must do — **Governmental interests.**

It is obvious that a number of intermediate stages exist and it is feasible to expect one monitoring program to serve several interests.

Recent trends in agricultural technology have led the scientific community as well as growers to search for cause/effect relationships in crop management systems. Water constituents and characteristics are an integral part of that management scheme.

The governmental agencies concerned with human health and the environment require ever increasing assurances of proper growing practices when related to food safety and are pushing towards no impact on the environment at or beyond the grove. In addition, those marketing fruit both within the US and abroad are under pressure to show that their merchandise has been produced using environmentally sound and safe practices. These requirements usually result in the transfer of the burden of proof to the growers. This translates to an increased need to monitor for the influence of the water on the crop, as well as for the environmental impact of the growing practices.

<u>Voluntary Monitoring</u>

In normal business environments, one wants to know what helps increase profits or minimize losses. This means obtaining information that must be economical and focused on:

- Cost savings
- Cultural controls
- Crop improvement

The cost savings can include such concerns as water quality impact on crop protection chemicals. For example, a number of materials in the present market are pH sensitive, and the efficacy of the spray or other application may depend on proper pH in the carrier water. A water pH monitoring program will allow the grower to avoid costly mistakes and minimize material usage.

Improving profitabilty of the cultural program may require information describing the impact of rain on the quality of surface water or shallow wells. Knowledge of the concentration variation of Calcium (Ca) and Magnesium (Mg) in the irrigation water can help in making proper changes to a liming program, or there may be a concern about mineral components in the water in general, and a desire to assess their contribution to the overall growing practices.

Measurement of the irrigation water salinity may indicate a need to select different fertilizer materials or alter irrigation strategies in order to improve yield and crop quality. It can also warn the grower if a steady increase in salinity is observed. Depending on the water source, the trend may warn of impeding saltwater intrusion or overirrigation, dissolution, and transport of the fertilizer into groundwater or ditches and canals.

In all these cases, equipment and services needed are available at very economical costs. Good portable pH and salinity meters cost anywhere from $200 to $500 and many of the needed wells or sampling points can be hand installed using various sizes of PVC pipe. More detailed water analysis can be determined at analytical laboratories commonly used for soil and leaf testing. The crux of a good monitoring program is not the equipment, but the continuous and systematic approach that must be established and adhered to in order to meet the intended goals of the program.

<u>Monitoring that should be done</u>

While the food supply is safer than it has ever been, our ability to determine residual pesticides at the part per trillion (ppt) level allows extremely detailed analysis of citrus and citrus by-products. The dissemination of this information by the media and interest groups (oftentimes without adequate scientific scrutiny) has resulted in public concerns about the wholesomeness of their food supply. Recent interest in organically grown fruit and juice attest to the fact that citrus products perceived as environmentally and humanly safe can be sold at a premium in retail outlets. Globally the trend is directly correlated to technological advancements: the higher the level of industrialization, the higher the concern. Fortunately, these concerns are largely unfounded. However, once negative public concerns become highly publicized, growers must be able to refute negative public concerns with valid data.

Any negative news associated with the wholesomeness of fruit initially results in scrutiny of the retail store, and then on to the producer. Inability to show that the fruit was grown, harvested, packed, shipped, and handled properly may significantly increase financial losses. Unfortunately, negative news is often fueled by media and public hysteria, and scientific reason is forgotten. In these cases, both the retailer and the grower will suffer. To what degree depends on how well each of them is prepared to address the situation. Therefore, globalized concern has often necessitated that citrus growers monitor water quality parameters in order to assure that the crop is grown with sound practices in regards to:

- Environmental stewardship — Discharge water quality and its impact on the downstream system
- Inputs to the growing crop — Irrigation water quality
- Food safety — Bacterial and chemical quality of the water that comes in contact with the fruit

The environmental stewardship and inputs to the crop are some of the burden buyers and marketing branches are transferring to the grower. Food safety is a primary concern of packing houses and processing facilities. An environmental stewardship monitoring program may include such elements as characterizing incoming and outgoing water quality and monitoring aquifers and the shallow water table under citrus groves. The main concerns are nitrogen (N), phosphorus (P), salinity, turbidity, certain pesticides and some metals. With wise planning, the environmental stewardship monitoring program can aid in:

- Characterizing crop inputs
- Developing a nutrient application program and aid in irrigation scheduling
- Assuring customers that the fruit is wholesome

In essence, the monitoring can help by optimizing inputs. It also allows maximization of profits by eliminating unnecessary waste while tuning the application-irrigation relationships. A monitoring program can help meet criteria of environmentally sensitive buyers and many regulatory requirements as well.

The Food Quality Protection Act (FQPA), which is enforced by the Enviornmental Protection Agency (EPA) in the US, will probably result in a reduction in the number of available crop protection compounds available to growers.

To contradict these trends, growers need to show that their actions have minimal impact on the environment. Region-wide water quality monitoring programs can not only protect growers from environmental cleanup liability, but also ensure that their fruit can be freely marketed.

This type of monitoring provides some distinct benefits. The cost of the sampling goes down as well as the cost of analysis. Maintenance of the equipment and data handling can be centralized or each participant can supply his/her portion to the central organization or consultant. Therefore, participants get the best possible data at the lowest possible cost with little or no involvement on their part. This allows the grower to concentrate on growing while reaping the benefits of monitoring. This requires close contact between the grower and the monitoring entity so that the data provided is in such a form and is reported in such intervals, that allow the grower to use the data for his/her growing purposes as well.

In its simplest form, a region-wide monitoring program may consist of a number of individuals that have chosen to allow a single group (typically associated with cooperative or marketing association) to administer the monitoring instead of each doing their own. This arrangement lends:

- reliability due to independence of the monitoring entity
- uniformity due to single group administration
- continuity since dropping of one grower from the group will not necessarily affect the other
- validity since the work is done by professionals
- confidentiality due to region-wide reporting without identifying any grower

To design a region-wide monitoring system with net inputs and net outputs in mind is a complex task. In many cases, this may not even be possible unless the area is predominantly a monoculture. One must consider environmentally sensitive areas within the region and determine any potential connections to them. Other questions concern:

- What is the role of other land uses?
- What is the source water quality and where does it come from?
- What are the ecological interrelationships?

A number of professionals from several disciplines of science should be consulted to reach a satisfactory, defensible monitoring network that is economically feasible. The list of expertise should include chemistry, hydrogeology, ecology, biology, agriculture, and sociology.

Required Monitoring

Most water monitoring programs in place today fall under this category. These monitoring programs are initiated by governmental agencies (usually environmental) in order to cause a change in the downstream or surrounding environment. An example of this is the extensive monitoring and sampling program in the Everglades Agricultural Area, designed to change water quality going to the Everglades National Park. This program is administered by South Florida Water Management District. Another program is related to the restoration efforts made by the St. John's Water Management District in regards to the St. Johns River. The Florida nitrate bill also requires monitoring in sensitive areas. Today, monitoring is done by the state agencies. However, concerned citrus growers should consider water quality monitoring in order to establish long-term data that document the effects of their practices on the environment. Monitoring requirements vary from periodic grab samples to continuous discharge monitoring, where samples are proportional to flow or within certain time intervals.

Types of Monitoring

Monitoring can be either descriptive, warning, or controlling. A water quality monitoring program should provide information that can be used to:

- draw cause-effect relationships
- warn of a change
- automatically control the system when water characteristics change.

Descriptive Monitoring

Descriptive monitoring is most often based on physical and chemical characteristics of the water. The samples are taken systematically over time in a prescribed manner, allowing one to correlate system responses to other external events or vice versa and derive cause-effect relationships. This type of monitoring program seeks to determine what things are happening and why. Therefore, this type of monitoring program serves four important functions:

- It provides information about the system responses to various conditions
- It establishes behavioral limits of the system
- It shows the direction, speed and magnitude of a potential change
- It allows reliable assessment of impact on a secondary system such as soil and/or plants

As a result, there is a two-directional process that considers the impact of inputs and environment on the character and behavior of the monitored water, and assesses the impact of the water on any system it comes in contact with. The monitoring program types and their general function are displayed in Fig. 1. The dotted line from the "Water to environment" box to the "Change" box denotes a need for additional information besides that provided by the monitoring system alone.

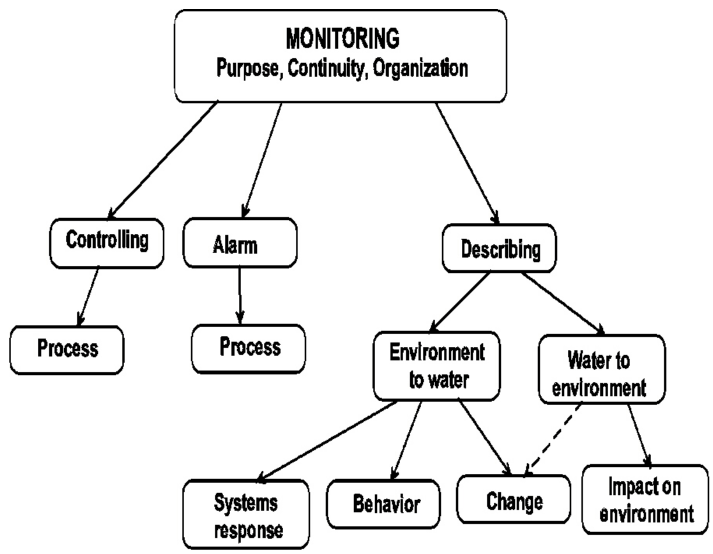

Figure 1. Types of monitoring and their general function.

Warning Monitoring

Monitoring where devices with alarms are used is actually a subcategory of the controlling monitoring. When a predetermined value is reached an appropriate action is required to take care of a problem. The alarm sensors are usually special systems measuring pH, salinity, temperature, turbidity, chlorine, nitrogen, and ammonia.

A potential use of these types of sensors can be where chlorination is used to maintain bacteria-free irrigation lines. When liquid fertilizer is injected, the chlorination should be turned off; a sensor that prevents fertilizer injection before chlorination is turned off, or sounds an alarm, is a good safety measure. If the chlorination is not turned off, there can be a number of problematic reactions at the point where the chlorine meets the fertilizer. Depending on fertilizer formulation, type of chlorine used, and concentrations of each compound, the reactions can range from overheating, precipite formation, inactivation of chlorine, or an explosion.

These devices are commonly used in water, waste water, and chemical plants to help with process control. The technology is well established. However, adjustments and / or modifications to the technology may be needed in order to adapt them to agricultural operations.

Control Monitoring

Control monitoring is basically threshold monitoring with associated alarms or controls. Threshold monitors are devices commonly used in the chemical industry and water and wastewater treatment plants to monitor water pH, salinity, chlorine, chemical concentrations etc. These monitoring devices consist of special sensors (characteristic to the parameter measured) that are installed into the water line or mixing container. The sensor measures the concentrations, color, turbidity etc. within the water stream. Should preset values be exceeded, the units may be programmed to sound an alarm and adjust the chemical feed into the water stream, or stop the process.

In agriculture, the use of such monitoring devices is generally limited to fertilizer or chemical feed systems in irrigation systems. However, chemical feed systems and controls are being used to alter the characteristics of agricultural waters in reservoirs, canals, lakes and ponds as well.

Costs of Monitoring

The minimum cost of any monitoring system is determined by the purpose of the program. This cost generally consists of the following:

- Equipment and maintenance — equipment, parts, man-hours
- Sample collection and shipment — man-hours, shipping costs
- Analysis — cost of analytical services
- Results — man-hours (data review, analysis, filing)

As a rule of thumb, once a program is in place it is relatively inexpensive to expand the spectrum of analyses as compared to the field portion of the costs for the program. This is because usually the same effort that is used to collect samples for several parameters is needed to collect samples for one or two analyses. With this type of program expansion, care must be taken that the initial purpose of the program is not compromised. The temptation to compromise or try to get by with the minimum is especially great when the pressure to monitor comes from outside. Inadequate planning often leads to vastly increased field time and cost because of continuous repairs, resampling, data retrofits, and eventual revamping of the entire sampling station design. If a company has several monitoring sites in various places, expenditures spent in this manner can be quite significant. To avoid this problem, one needs a clear focus and well-defined purpose combined with wisely spent money, experienced consultation, and proper equipment.

Some of the pitfalls that increase field cost are a lack of careful planning, no distinct objectives, inappropriate equipment, erroneous programming or alteration of the programming, lack of systematic maintenance, change in focus which is not carried all the way to the instrumentation, and incompatible add-ons. All of the above also increase the data analysis time due to mismatched or missing data. While the system design directly influences the operational costs, the work required to analyze the data is often ignored in initial cost assessment. This may be due to the lack of a defined purpose for the program, or because the data collection program is meant to solely meet the needs of a government agency. In designing a monitoring program, this is not sufficient. The data resulting from the sampling should be the reason the program was initiated in first place. In any monitoring program, the receipt and review of the data are the most important of all of the factors to be considered. Where the importance of the monitoring is acknowledged, it is not uncommon for a manager to spend a considerable amount of time reviewing and analyzing the data that are collected.

Cost should not be the only consideration in a monitoring program. Careful systematic planning when it comes to water monitoring is essential. While the initial dollar figure is meaningful, one must remember that it will (in most cases) be the least of the total expenditures. If one decides that the equipment needed is too expensive, he probably should not begin a monitoring program with lesser equipment. Inappropriate, poorly constructed equipment may waste manpower and effort. To avoid some of the common pitfalls, the process of the program design should consider the following:

1. Determine the general needs and have a written statement.

2. Determine whether monitoring can provide all or part of the necessary information. Describe the information needed.

3. Make a good faith estimate of the equipment and operational costs.

4. Determine the purpose of the monitoring program and prepare a written statement.

5. Determine the need for additional information to be combined with monitoring data such as purpose, collection method, intervals, etc.

6. Decide how the monitoring data are to be collected. Have a written statement that specifies the degree of automation, frequency, and sampling sites.

7. Determine what data are needed and why they need to be collected. Record the specific details of the analysis and characterization processes.

8. What are the requirements for data validity? Begin to establish a QA/QC (quality assurance/quality control) program, including sample preservation, storage time, and collection method.

9. Determine what equipment is needed, what it is supposed to do, and how the equipment functions. Determine type, cost, configuration, maintenance needs, and tolerance to the environment.

10. Speak to the analysis laboratory and other service providers to clarify their role, what they will provide, how they will perform the analysis, and how much it will cost. Determine whether a contract is needed.

11. Develop a record system and a written description of the programs and their purposes.

12. Establish a maintenance schedule in writing.

13. Provide time for test runs and record problems, needed improvements, etc.

Assess Cost Benefit Ratio

There are many ways to assess a water quality monitoring program. Does the water respond to the environment as it used to? If not, what is changing and why? Is the water within acceptable or usual parameter limits? If not, where is the change coming from? Is there a value one can attach to the knowledge that the quality of water one uses now is the same as it used to be five or ten years ago? Maybe something is being done right all along. Maybe material and effort are being saved because one is able to use the right adjuvant materials for the pest and weed-control programs, and is not losing the primary product efficacy due to water quality problems.

Often the water quality impact on soil is measurable and should be factored into the formulation of cultural programs. Without a monitoring program, this cannot be done. Is there a way to assess the value of this type of information? The answer depends greatly on the purpose of the monitoring program and how good the past record keeping has been. For example, using monitoring to adjust fertilizer and irrigation programs in regards to N application may allow one to use less expensive mixes and gain higher application efficiency. Knowing the calcium and magnesium contribution of the irrigation water may allow reductions in lime or dolomite applications.

Accuracy

No one wants to pay for something that is not useful. Since monitoring data will be relied upon and critical decisions will be based on them, the results must be valid. To insure this, the monitoring program must have strict quality requirements. There must be sufficient information to ensure that the results are accurate.

The data quality and their accuracy are described by two variables: bias and precision. Bias is the measure of the systematic error in the process. Precision describes the repeatability of the process (Fig. 2).

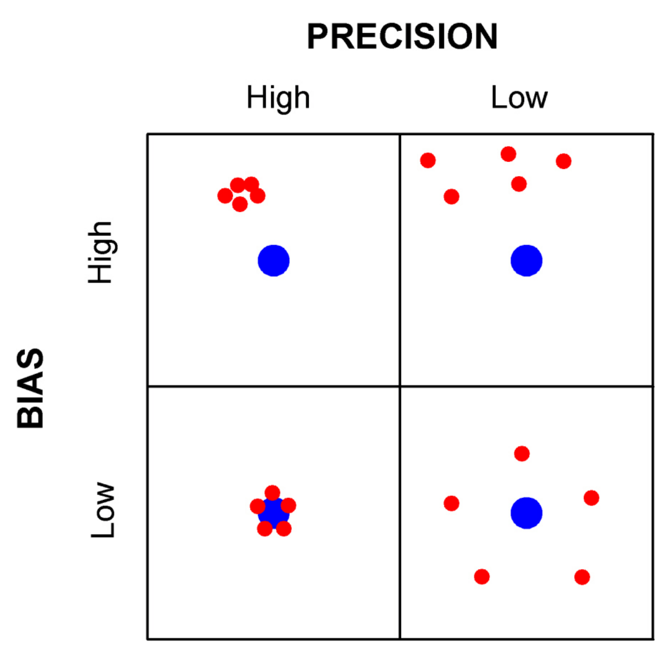

Figure 2. Illustration of how bias and precision affect accuracy.

Understanding these concepts while designing sampling regimes and intervals is essential. Faulty repair of a sampling device can skew results well off the baseline. For example, locating a sampling point close to the canal bank leads to consistently biased results due to sampling location within the stream. Use of soda cans, milk containers, and such introduce uncontrolled contamination to the samples and therefore decrease precision. Another factor to consider is the laboratory that is used for analysis. All laboratories have a bias and precision that is unique to their operation.

One other factor that should be considered is consistency. Consistent use of the same methods and laboratory permits reliable comparisons with the same techniques and lab procedures. It makes comparative analysis of the observed trends and/or changes much easier since differences in procedures do not have to be factored in. This principle pertains also to the entire monitoring operation—consistent sampling methods, time intervals, protocols, analytical parameters etc. Consistency in all of the above increases the reliability of the data.

What to Monitor

The decision as to what to monitor greatly depends on the initial question: What do we need to know? Possibilities are numerous and some broad direction can be pointed out, depending on the type of water one is dealing with. Table 1 identifies some of the parameters that may be included in typical monitoring programs.

The analysis of incoming or outgoing water quality may quantify only total N and total P, or it may be expanded to include metals such as Cu, Zn, Fe, Mn, or elements such as B and S. All of these can be obtained from one single acidified sample. Electrical conductivity and pH must be measured on site, since they are subject to change in transport or are purposely changed for the preservation of the other elements in the solution. Turbidity, pH, and TDS require monitoring equipment at the sampling site. Total suspended solids (TSS) may need to be measured at a lab. Another set of parameters consists of organic compounds: pesticides, natural compounds, and their derivatives. Each compound may require specific sampling methods, and therefore an analytical laboratory should be consulted before attempting to determine if organic compounds exist in the samples.

Combining data sources

A monitoring program may focus on water alone, but to use the data for maximum benefit, a number of other parameters should be included and recorded along with the data from the monitoring program. Some of these are:

Rainfall - dates, duration, amount, distribution within large groves

Fertilization - application dates, material, rate, application method

Irrigation - dates, time, duration, applied water

Chemical applications - dates, material, rate, application method

Intake water analysis

Soil analysis

Plant analysis

Crop survey - yields, quality, tree condition, etc.

Most of these additional data are routinely observed (if not recorded) by the grower. Systematic recording of the data generally does not necessarily increase the workload. The importance is to bring the different data sources together and sort them in a fashion that allows a meaningful analysis to be performed. This method can be used to obtain useful information that otherwise might have been cost prohibitive to generate.

Constituents

Water samples can be analyzed for numerous chemical properties. The most important constituents concerning runoff from citrus groves include pH, electrical conductivity (EC), total solids, hardness, chloride (Cl), nitrogen (N) and phosphorus (P). Total-N and Total-P measurements account for all nitrogen and phosphorus, respectively, in organic and inorganic forms, measurable using standard chemical analysis procedures.

Nitrogen

Nitrogen is an indispensable part of the life cycle. However, even though plants, animals and most micro-organisms require some form of combined nitrogen for growth and reproduction, concentrations above certain levels can present problems. Total-N is the sum of organic nitrogen, nitrate (NO_3^-), nitrite (NO_2^-), and ammonia (NH_4^+). Total Kjeldahl Nitrogen (TKN) includes organic nitrogen and ammonium-N (NH_4-N), but not nitrate-N (NO_3-N). Total Dissolved Kjeldahl Nitrogen (TDKN) is the fraction of

TKN that passes through a 0.45 micron filter. Inorganic nitrogen is normally found in soil water as NH_4^+, NO_3^-, and NO_2^-. Ammonia, a product of microbiological decay of plant and animal protein, is used in commercial fertilizers. Its excessive presence in raw surface waters usually indicates domestic or agricultural pollution. Above certain levels it is toxic to fish. Excessive amounts of nitrate or nitrite in water can cause infant death, adult illness, and produce spontaneous abortion of cows. Fairly low levels of nitrite can be harmful to humans and aquatic life.

Phosphorus

Phosphorus parameters commonly analyzed for are Ortho-Phosphate (PO_4^{---}), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), and total-P (TP). Particulate phosphorus is calculated as the difference between TP and TDP. Phosphorus occurs in natural waters as one of the following forms: ortho- (or reactive) phosphate, meta- or poly- (condensed) phosphate (requires hot acid digestion) and organic phosphate (requires severe digestion). Phosphates enter water supplies from runoff, cleaning operations, water treatment, sewage disposal, and natural decay of plants and animals. Although essential for plant growth, too much phosphorus often results in excessive growth of aquatic plants and eutrophication of fresh water bodies. TP includes particulate and dissolved forms of phosphorus, the amount of which can be greatly influenced by sampling procedures. Therefore, it is advisable to also analyze samples for TDP.

Electrical Conductivity (EC)

Electrical conductivity is a measure of the ability of water to pass an electrical current. Conductivity in water is affected by the presence of inorganic dissolved anions (negative charge) such as chloride, nitrate, sulfate, and phosphate and cations (positive charge) such as sodium, magnesium, calcium, iron, and aluminum. Organic compounds do not conduct electrical current very well and therefore have a low contribution to conductivity when in water. Conductivity is also affected by temperature: the warmer the water, the higher the conductivity. For this reason, conductivity is commonly reported as conductivity corrected to 25^o C.

EC measurements are taken with platinum electrodes and presented in units of conductance. The drop in voltage caused by the resistance of the water is used to calculate the conductivity per centimeter. The SI unit of measurement is deci-Siemens per meter (dS/m) which is equal in magnitude to the commonly used conductance term of milli-mho/cm (mmho/cm).

pH

The term pH is used to indicate the alkalinity or acidity of a substance as ranked on a scale from 0 to 14. Acidity increases as the pH decreases. The pH of water affects many chemical and biological processes in the water. The largest variety of aquatic animals prefer a range of 6.0-8.0. When pH is outside of this range, reductions in diversity within the water body may occur due to stresses in the physiological systems of many organisms. Reproduction may also be reduced when pH is not within the optimal range for the organisms. Low pH can also allow toxic elements (i.e. copper) and compounds to become mobile and available for uptake by aquatic plants and animals. This can lead to conditions that are toxic to aquatic life, particularly to sensitive species.

The pH scale measures the logarithmic concentration of hydrogen (H^+) and hydroxide (OH^-) ions, which make up water ($H^+ + OH^- = H_2O$). When both types of ions are in equal concentration, the pH is 7.0 or neutral. The pH value is the negative power to which 10 must be raised to equal the hydrogen ion concentration. Mathematically this is expressed as:

$$pH = -\log [H^+]$$

Below 7.0, the water is acidic (there are more hydrogen ions than hydroxide ions). When the pH is above 7.0, the water is alkaline, or basic (there are more hydroxide ions than hydrogen ions). Since the scale is logarithmic, a drop in the pH by 1.0 unit is equivalent to a 10-fold increase in H^+ concentration.

Generally, pH can be analyzed in the field or in the lab. If it is analyzed in the lab, you must measure the pH within 2 hours of the sample collection. The pH of a sample can decrease (become more acidic) due to carbon dioxide from the air dissolving in the water.

Hardness

Hardness in water is caused primarily by calcium and magnesium, although iron and manganese also contribute to the actual hardness. Hardness may be divided into two types: carbonate and non-carbonate. Carbonate hardness is the portion of calcium and magnesium that can combine with bicarbonate to form calcium and magnesium carbonate. Total hardness (carbonate and non-carbonate) is customarily expressed as equivalent calcium carbonate ($CaCO_3$).

Total Solids

Total solids are dissolved solids plus suspended and settleable solids in water. In stream water, dissolved solids consist of calcium, chlorides, nitrate, phosphorus, iron, sulfur, other ions, and particles that will pass through a filter with pores of approximately 0.45 microns (0.00045 mm) in size. Suspended solids include silt and clay particles, plankton, algae, fine organic debris, and other particulate matter. These are particles that will not pass through a 0.45 micron filter.

Total solids also affect water clarity. Higher solids decrease the passage of light through water, thereby slowing photosynthesis by aquatic plants. Water will heat up more rapidly and hold more heat (especially is solids are dark colors), possibly affecting aquatic life that has adapted to a lower temperature regime. The measurement of total solids can be useful as an indicator of the effects of runoff from urban and agricultural areas.

Concentrations of solids often increase sharply during rainfall. Regular monitoring of total solids can help detect trends that might indicate increasing erosion in developing watersheds. Total solids are related closely to canal flow and velocity, and should be correlated with these factors. Any change in total solids over time should be measured at the same site at the same flow.

Total solids are measured by weighing the amount of solids present in a known volume of sample. This is done by weighing a beaker, filling it with a known volume, evaporating the water in an oven, completely drying the residue, and then weighing the beaker with the residue. The total solids concentration is equal to the difference between the weight of the beaker with the residue and the weight of the beaker without it.

Chloride

In some areas of the state, chloride (Cl^-) concentration in agricultural runoff is of concern due to detrimental effects on downstream water users. Chloride is found in most natural waters and generally is not of concern at low levels. However, at high concentrations it is toxic to some plants. In addition, the Cl^- ions contribute to the total salt content (electrical conductivity) of the water.

Sampling Preservation and Analysis

Sample Collection and Storage

Water sample collection devices vary widely in complexity and cost; samples can be manually dipped from a body of water, one at a time, using specially prepared containers. Sophisticated autosamplers are available for collecting a series of samples at specific time intervals, at preset times, or in amounts proportional to flow.

Containers for collection of water samples for nitrogen and phosphorus analyses should be made out of nalgene, polyethylene, or some other inert material. Sample bottle sizes generally range from 250 to 1000 mL (depending on analysis) to ensure that an adequate sample will be available for re-analysis when necessary. The cost of the bottles varies according to size and style.

Prior to use, the sample bottles should be washed with a phosphate-free detergent, rinsed with distilled water, rinsed in a dilute hydrochloric acid (HCI) solution, rinsed with distilled water again, and dried. The bottles should be capped with foil, saran wrap, or bottle caps (washed and rinsed in the same manner as the bottles themselves) to protect against dust particles and other contaminants (i. e., free ammonia in the air, insects, etc.) from entering the containers during storage. Once prepared for receiving water samples, nothing except the water to be sampled should come in contact with the inside of the bottles or caps.

Proper labeling of sample bottles is critical to a successful water quality monitoring program. Bottles should be labeled in the field as the sample is being collected to ensure proper identification. Prelabeling bottles in the laboratory before taking them to the field can cause confusion for the person collecting samples as he/she searches for the appropriate bottle. It may be desirable to label a bottle for a site even if no water is available to sample at the site. This ensures that the receiving personnel in the laboratory know that the site was visited and no sample was available. The label should include the time, date, site, station, and name of the person collecting the sample. For best results, use waterproof, permanent marking pens and write directly on the bottle. The writing will be removed by the washing procedure. Alternatively, self-adhesive waterproof labels can be used. Removal of the labels, however, can be a time consuming task.

Grab Samples

Grab samples are manually collected at the site. They may be taken from a water body randomly, systematically, or at regular intervals such as daily, weekly, or monthly. These samples are generally used for establishing nutrient concentrations at specific points in time. Grab samples are useful for establishing long-term trends or point-in-time concentrations. Grab samples can be dipped manually or pumped from a body of water.

If using a pump, a suction strainer assembly and a peristaltic pump are necessary. The suction strainer is simply a coarse filtering device with holes small enough to prevent the passage of material that is too big to pass through the suction hose. These strainers are commercially available from several different companies that manufacture water sampling instruments. Alternatively, suction strainers can be constructed out of noncorrosive, chemically inert materials. The strainer should be attached to a rigid shaft for ease in lowering the unit to the desired depth in the water body. A hose should be attached to the strainer and can be connected to the pump inlet hose. A battery-operated peristaltic pump is used to pump the sample into the bottle from the desired depth.

Where adequate water is available for grab samples (i.e., in canals or ditches full of water), the sample bottle should be rinsed with water from the source being sampled. To do so, simply collect a sample as would normally be done, and empty the bottle before collecting the sample for return to the laboratory. Do not just dip water from the surface for the rinse process since the surface of the water body may have a different chemical and biological make-up than the water at the desired depth.

<u>Autosamplers</u>

An autosampler is a device that automatically collects water at preset times, on preset intervals, and in preset volumes (Fig. 3). The instrument consists of a timer, controller, pump, sample distributor, and sample bottles (Fig. 4). The timer unit can be programmed to initiate a sampling event and to continue taking samples at set time increments. Alternatively, electronic pulses from flow sensors can be used to trigger sample collection. Sample size typically can vary from 100 mL up to 1 liter. Samples are collected in custom-fitted polyethylene or glass bottles. A standard feature of most autosamplers is a bottles-per-sample or samples-per-bottle multiplexer, which allows several bottles to be filled at each sampling interval, or several samples to be placed in each bottle.

Autosamplers normally use a peristaltic pump system to transport the sample from the source to the sample bottle. The only materials in contact with the sample are the vinyl or teflon suction line, the inlet strainer, the silicone rubber pump tubing, and the polyethylene (or glass) sample

Figure 3. Typical programmable autosampler.

Figure 4. Eight-bottle collection chamber from autosampler.

bottles. Each sampling cycle includes an air prepurge and postpurge to clear the suction line both before and after sampling.

Samples can be based on either time or flow. The flow mode is controlled by external flowmeter pulses. This requires a separate flow meter to be attached to the control box on the autosampler by a cable. The flow meter is then programmed to trigger the collection of a sample after the passage of a preset flow volume (for example, a sample would be collected after every 1000 gallons passed the monitoring station), resulting in a composite sample that is composed of subsamples proportional to flow rates. Costs for autosampling units range from about $2,000 for a basic unit with no depth, rain, or flow measurements to over $7,000 for units with advanced measurement and data recording capabilities.

Soil Solution Sampling/Suction Lysimeters

The suction lysimeter is installed in the soil so that there is a tight fit between the porous cup and the soil. Without the tight fit, the unit will not extract water from the soil unless the cup is below the water table. The assembly should be left in the field for a suitable period of time prior to use for collecting samples for analysis. This allows the ceramic cup to physically and chemically equilibrate with the soil water. It is also advisable to pump samples through the system to flush it prior to use.

Any section of the lysimeter tube that protrudes above the ground surface should be painted black. Sunlight will pass through the thin walled white PVC pipe and allow the growth of algae within the tube. Painting the unit black will alleviate this problem. When sampling, the user must first apply a vacuum to the unit. The vacuum must be held in the lysimeter for enough time to ensure that an appropriate amount of water will enter the tube. If the cup is below the water table, little time will be needed. For suction lysimeters located above the water table, 2 or more hours of vacuum may be required.

Samples collected in the lysimeters can be extracted from using a peristaltic pump. The pump hose should be rinsed with distilled water before pumping a sample to avoid cross-contamination between lysimeters. It is important to make sure that all rinse water is pumped out of the tubing prior to filling the sample bottle. Pumping some lysimeter water through the tube prior to filling the sample bottle will ensure that the sample constituent concentrations are not diluted with rinse water. Alternatively, a vacuum flask and vacuum pump can be used to extract the sample without passing the sample through the pump tubing. This method is preferred if small sample volumes are available.

Suction lysimeters can be purchased preassembled or they can be constructed using commercially available parts. Each unit costs about $60. A service kit that includes a hand vacuum pump must also be purchased. This kit typically costs about $100.

Sample Preservation

Surface water grab samples and soil solution samples are collected manually and typically require little in the way of sample preservation in the field. Essentially all that is required is that the samples be kept cool (40^o F) during transportation from the field to the laboratory. This is easily accomplished by placing samples in an ice chest or cooler filled with ice.

Autosamplers were originally designed to collect numerous samples automatically over a variable length of time. Each sample, therefore, has a different length of time that it remains in the sampler between collection and pick-up times. Autosamplers generally collect up to 24 samples, enabling the sampler to operate over long time periods prior to pick-up. Thus, autosamplers require more sophisticated means of maintaining the viability of collected samples. Preservation begins in the field with the appropriate shelter. The shelter should protect the autosampler from direct sunlight while ensuring adequate ventilation. Refrigerated shelters are available for instances where the time between sampling and pickup is considerable. In other cases, a ventilated shelter will suffice if ice is placed in the autosampler base where the sample bottles are stored. Some autosamplers have insulated bases and allow ice to be added to the collection chamber to keep sample temperature well below ambient for several hours. Samples that will be analyzed for ammonia, total phosphorus, TKN, and hardness should be acidified with sulfuric acid (H_2SO_4) to a pH less than 2.0 upon collection.

Once the samples are brought into the laboratory, preservation activities must continue. There are a number of procedures to be used, depending on the constituent parameters to be measured. The storage and preservation specifications for chemical parameters most often measured in agricultural water are listed in Table 2.

Laboratory Procedures

Water samples can be filtered in the field, and should be if grab samples are being collected. Special equipment exists, enabling the filtration of the sample to occur as the sample is being pumped from the water body. Obviously, when numerous autosamplers are in use, field filtration techniques are not applicable nor practical.

When samples are brought in from the fields, they are filtered immediately. The filtration step allows for the determination of the concentrations of dissolved nutrient species (i. e., NO_3^-, NH_4^+, TDKN, ortho-P, and TDP) without interference from particulate matter. The filtration process involves passing the sample through a 0.45 micron chemically inert (polysulfone) filter membrane into a properly prepared vial. The filter membranes should be rinsed with deionized water prior to use. Once rinsed, to avoid contamination, they should not be touched directly by hands. Each filter membrane should only be used once. A vacuum filtration apparatus can be purchased to accelerate the process or a high-capacity vacuum filtration unit can be constructed out of readily available materials.

Sample Digestion

Water samples are digested prior to analyses for TDKN, TKN, TDP, and TP analyses. The Kjeldahl digestion process involves adding acid to the sample and heating it at 400º F for 1 hour. The heat is then turned up to 700º F for 1½ hours to break down complex chemical compounds into ones suitable for colorimetric analyses. Primarily, the process converts complex compounds of nitrogen and phosphorus to NH_4^+ and PO_4^{---}, respectively.

pH

The pH of water is measured using a pH meter. Surface water samples will generally range in pH from 5-8. Due to the limestone composition of most aquifers in Florida, most well water is alkaline, with pH values ranging from 7 to 8.5.

Turbidity

The standard methods for the determination of turbidity are the nephelometric and visual methods. The turbidity of a water sample measured using a nephelometric method is reported in nephelometric turbidity units (NTUs). The visual Jackson Turbidity Method reports turbidity in Jackson turbidity units (JTU's). Meters for measuring turbidity range in cost from about $600 to $2,000.

Nitrogen and Phosphorus

Colorimetry is one of several method of analysis used to determine the concentrations of nitrogen and phosphorus in a water sample. The procedure involves the use of a colorimeter as a detection device. Essentially, upon chemical treatment in an explicit manner, a water sample will yield unique color traits, dependent on the concentrations of nutrients in the sample.

Colorimeters range from simple to extraordinarily sophisticated instruments. In situations that require analyses of a large number of samples in a limited amount of time, it is advantageous to use an autoanalyzer. An autoanalyzer is simply a colorimeter that has most of its functions automated, including the addition of the chemicals necessary to produce the measurable color. Autoanalyzers are capable of analyzing an extremely large number of samples while eliminating much of the potential for human error. The instruments are, however, subject to the usual maintenance problems associated with electronic and computerized equipment operating in wet chemistry environments.

Field Test Kits

Many field test kits (Fig. 5) are available for analyzing water samples for various constituent concentrations. Accuracy, range, and detection limits vary among kits. Field test kit data are useful as indicators of nutrient concentrations, with the general consensus being that the resulting concentrations will be ball park figures. The user must also be extremely careful regarding what nutrient species are actually being measured. For example, a kit measuring total phosphorus, with no digestion procedure involved, is probably only measuring total soluble inorganic phosphorus.

Figure 5. Field test kit for acidity, alkalinity, carbon dioxide, DO, hardness, and pH with color wheel and digital titrator.

The test kits are reliable as long as the user is aware of their inherent limitations. Generally, field test kits should not be looked upon as inexpensive substitutes for laboratory analyses. However, several of the available test kits have been certified by the EPA as accepted methods for determining and reporting some of the water quality constituents.

Quality Assurance/Quality Control (QA/QC)

Quality assurance is attained by employing adequately trained and experienced personnel, having good physical facilities and equipment, using certified reagents and standards, frequently servicing and calibrating instruments, and using replicate and known-addition sample analysis. It is desirable that QA/QC programs be acceptable to the Florida Department of Environmental Protection (FDEP)/ and the Florida Dept. of Health.

A good analytical quality control program consists of an organized plan for sampling procedures, sample custody, analytical procedures, calibration procedures and frequency, routine maintenance of equipment, quality control checks (matrix spikes, method blanks, standard calibration, check samples, laboratory duplicates, field quality controls, precision, accuracy), data reduction, data validation, and reporting. Each organization or laboratory involved with sample collection or analysis has the responsibility of implementing procedures that assures that the precision, accuracy, and comparability of the data submitted is of a known and documented level of quality.

References

Taylor, L. A., F. T. Izuno, and A. D. Bottcher. 1982. Water quality sampling and analysis instruments and procedures. Univ. of Florida, IFAS Coop. Ext. Serv. Circ. 1040.

Table 1. Parameters to include in a basic water monitoring program.

Surface Water	Well water	Soil water
Incoming water quality	Water quality at the well	Soil water extract
Outgoing water quality	pH	pH
pH	Electrical conductivity	Calcium
Electrical conductivity	Hardness (Ca, Mg)	Magnesium
N, P, K	Alkalinity (CO_3)	Copper
Turbidity (TSS)	Iron	Nitrogen
Pesticides	Sulfur	Phosphorus

Table 2. Required water sample containers, preservation techniques, and maximum storage times suggested by EPA (1984).

Parameter	Container*	Preservation	Maximum storage time
Ammonia	P, G	Cool, 40°F, H_2SO_4 to pH<2	28 days
Color	P, G	Cool, 40°F	48 hours
Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
pH	P, G	None	Analyze immediately
Kjeldahl and organic N	P, G	Cool, 40°F H_2SO_4 to pH<2	28 days
Nitrate	P, G	Cool, 40°F	48 hours
Nitrate+Nitrite	P, G	Cool, 40°F	28 days
Nitrite	P, G	Cool, 40°F	48 hours
Phosphorus (Total)	P, G	Cool, 40°F, H_2SO_4 to pH<2	28 days
Turbidity	P, G	Cool, 40° F	48 hours
*P = plastic, G = glass			