ANRA's Water Quality Monitoring Program: What We Test for and Why

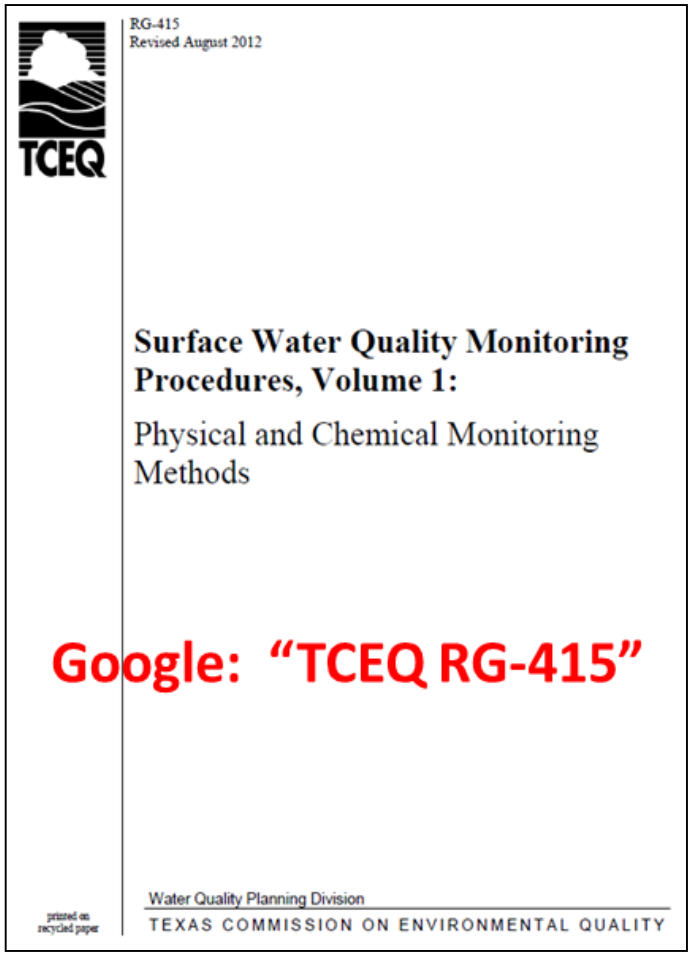
July 11, 2017

THE TEXAS CLEAN RIVERS PROGRAM

ANGELINA & NECHES RIVER AUTHORITY

Sampling Considerations

- Frequency and timing of sampling
- Type of sampling
- Where to sample
- Order of sample collection
- What parameters to collect



What Parameters to Collect

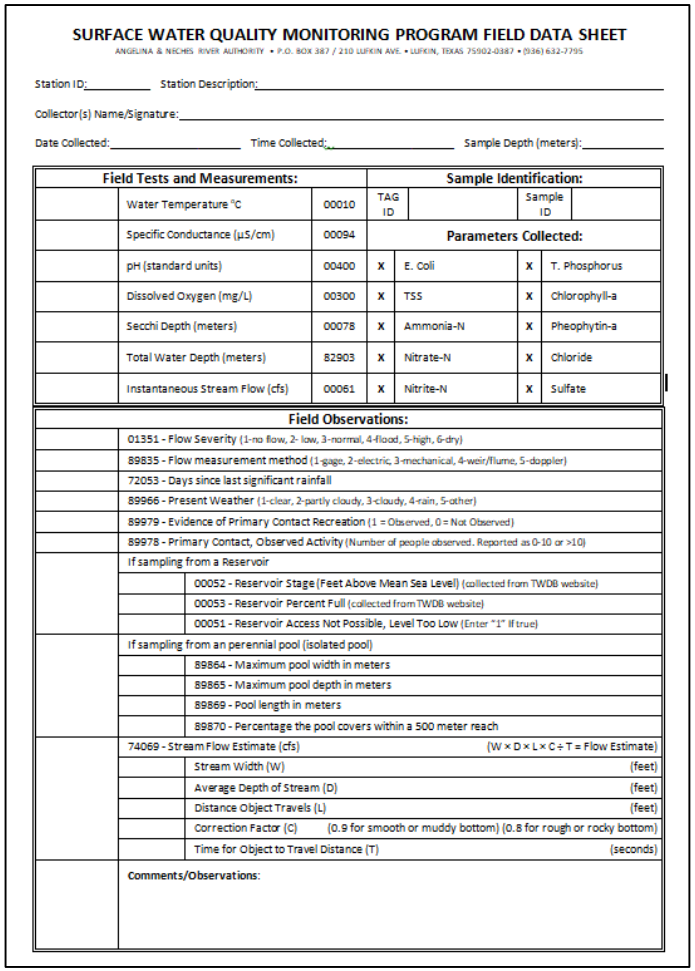
- Depends on purpose of sampling and watershed factors
  - Trend analysis
  - Watershed protection/drinking water supply protection
  - Permit support monitoring
- Basic Parameters
- Additional Parameters as needed

Table 3.1. Final format for reporting field data (rounding, significant figures).

Parameter	Parameter Code	Final Form for Field Data (Rounding, Significant Figures)
Water temperature (°C)	00010	Report temperature to the nearest tenth in degrees Celcius. (example: *25.94* to *25.9*, or *26.97* to *27.0*)
pH (s.u.)	00400	Report pH to the nearest tenth in pH standard units. (example: *7.94* to *7.9*, or *7.97* to *8.0*)
DO (mg/L)	00300	Report dissolved oxygen to the nearest tenth in mg/L. (example: *5.94* to *5.9*, or *6.97* to *7.0*)
Specific conductance (µS/cm)	00094	Report specific conductance to only three significant figures if the value exceeds 100—for example: *1532* to *1530*. Do not report ORP, which is displayed by some multiprobe instruments. For values < 100µS/cm follow standard rounding rules and report the nearest whole number. For example, report *88.7* as *88 µS/cm*.
Salinity (ppth)	00480	Report salinity values above 2.0 ppth to the nearest tenth in parts per thousand. Do not report salinity from freshwater or inland (brine) locations. In estuarine waters report the actual values displayed by the instrument above 2.0 ppt, and values less than 2.0 as < *2.0* (examples: *0.85* to < *2.0*; *1.5* to < *2.0*). Determine if a station is estuarine (experiencing periods where salinity is > 2.0 ppth), and always report salinity at this station, regardless of salinity during periods of high flow. In the absence of salinity data, use specific conductance and temperature to calculate salinity.
Secchi disk (meters)	00078	Report Secchi-depth transparency in meters to two significant figures (examples: *0.35 m* or *1.3 m*).
Days since last significant precipitation (days)	72053	Report whole numbers. If it is raining when the sample is collected, or has rained within the last 24 hours, report a value of < *1*. Otherwise report the actual number, if known, or a 'greater than' value.
E. coli (MPN/100 mL)	31699	First step: round the result to the nearest whole number to remove decimals. Second step: round to two significant figures (example: *347.1* to *347* to *350*). Adjust < and > results based on dilution. Do not report "zero" but < *1*.
Enterococci (MPN/100 mL)	31701	*First step:* round the result to the nearest whole number to remove decimals. *Second step:* round to two significant figures (example: *347.1* to *347* to *350*; *9.7* to *10*). Adjust < and > results based on dilution. Do not report "zero" but < *1*.
Fecal coliform (colonies/100 mL)	31616	Always report fecal coliform densities as a whole number. If no colonies are detected, report a less than value based on the volume filtered. For example: report < *1* (100 mL filtered), < *4* (25 mL filtered), or < *10* (10 mL filtered). For concentrations > 100, report two significant figures. Do not record "TNTC" or "0/100 mL."
Flow (Stream Discharge) (ft^3/s)	00061	Report instantaneous flow **values less than 10 but greater than 0.1 ft^3/s** to the nearest tenth (example: *9.35* to *9.4*). Report flow **values greater than 10 ft^3/s** to the nearest whole number (example: *20.62* to *21*). Actual flow **values less than 0.1 ft^3/s but greater than or equal to 0.01 ft^3/s** are reported and not subject to rounding (example: report *0.07* as *0.07*). Report flow **values < 0.01 ft^3/s** as < *0.01*. When there is **no flow** (pools), report 00061 as *0.0*. When there is no water, do not report a value for 00061.
Flow severity (1—No Flow, 2—Low, 3—Normal, 4—Flood, 5—High, 6—Dry)	01351	Report flow severity for freshwater streams and rivers only. When there is no flow (pools), report a flow severity of *1*, and the instantaneous flow (00061) as *0.0 ft^3/s*. If the stream is dry, record only the flow-severity value of *6*.
Note: For details on reporting final data sets to the TCEQ, see the *SWQM DMRG*.		

Basic Parameters

- Observations
- Field Parameters
- Conventional and Bacterial Parameters



SURFACE WATER QUALITY MONITORING PROGRAM FIELD DATA SHEET

ANGELINA & NECHES RIVER AUTHORITY • P.O. BOX 387 / 210 LUFKIN AVE. • LUFKIN, TEXAS 75902-0387 • (936) 632-7795

Station ID:_____ Station Description:_____

Collector(s) Name/Signature:_____

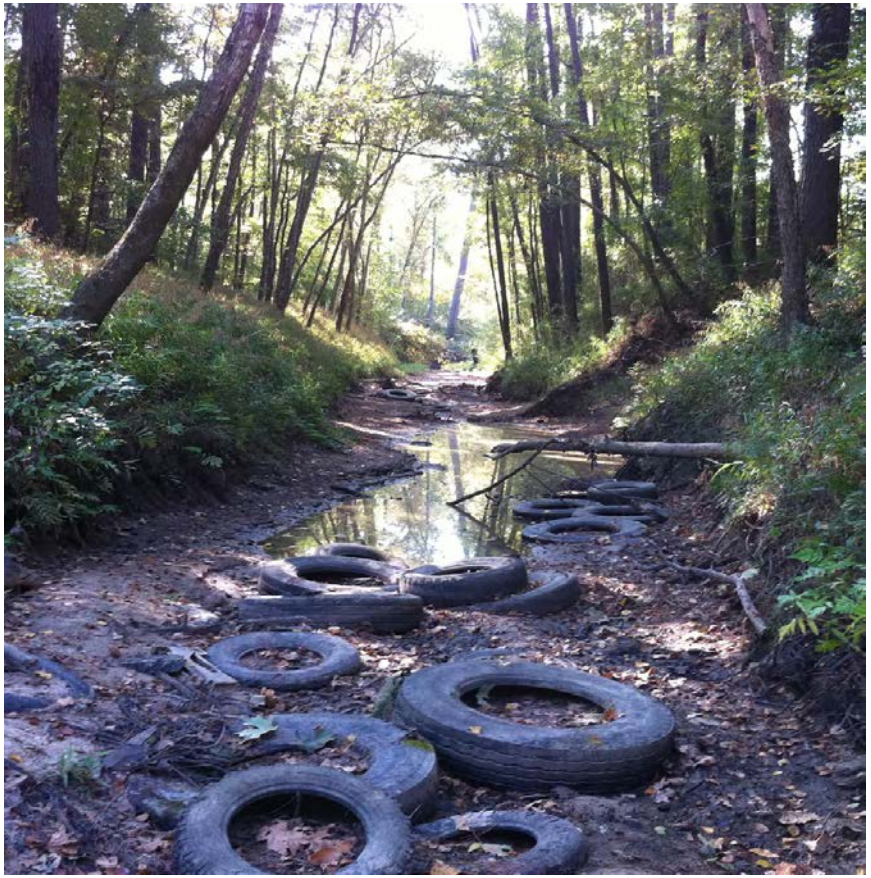
Date Collected:_____ Time Collected:_____ Sample Depth (meters):_____

Field Tests and Measurements:			Sample Identification:			
	Water Temperature °C	00010	TAG ID		Sample ID	
	Specific Conductance (µS/cm)	00094	Parameters Collected:			
	pH (standard units)	00400	X	E. Coli	X	T. Phosphorus
	Dissolved Oxygen (mg/L)	00300	X	TSS	X	Chlorophyll-a
	Secchi Depth (meters)	00078	X	Ammonia-N	X	Pheophytin-a
	Total Water Depth (meters)	82903	X	Nitrate-N	X	Chloride
	Instantaneous Stream Flow (cfs)	00061	X	Nitrite-N	X	Sulfate

Field Observations:		
	01351 - Flow Severity (1-no flow, 2- low, 3-normal, 4-flood, 5-high, 6-dry)	
	89835 - Flow measurement method (1-gage, 2-electric, 3-mechanical, 4-weir/flume, 5-doppler)	
	72053 - Days since last significant rainfall	
	89966 - Present Weather (1-clear, 2-partly cloudy, 3-cloudy, 4-rain, 5-other)	
	89979 - Evidence of Primary Contact Recreation (1 = Observed, 0 = Not Observed)	
	89978 - Primary Contact, Observed Activity (Number of people observed. Reported as 0-10 or >10)	
	If sampling from a Reservoir	
	00052 - Reservoir Stage (Feet Above Mean Sea Level) (collected from TWDB website)	
	00053 - Reservoir Percent Full (collected from TWDB website)	
	00051 - Reservoir Access Not Possible, Level Too Low (Enter "1" if true)	
	If sampling from an perennial pool (isolated pool)	
	89864 - Maximum pool width in meters	
	89865 - Maximum pool depth in meters	
	89869 - Pool length in meters	
	89870 - Percentage the pool covers within a 500 meter reach	
	74069 - Stream Flow Estimate (cfs)	(W × D × L × C ÷ T = Flow Estimate)
	Stream Width (W)	(feet)
	Average Depth of Stream (D)	(feet)
	Distance Object Travels (L)	(feet)
	Correction Factor (C) (0.9 for smooth or muddy bottom) (0.8 for rough or rocky bottom)	
	Time for Object to Travel Distance (T)	(seconds)
	Comments/Observations:	

Observations

- Weather
- Water appearance/odor
- Wildlife and human activities
- Algae/macrophytes
- Etc.



Water Quality Monitoring in the Upper Neches Basin

- Currently, ANRA monitors 40 sites quarterly for field parameters, conventional parameters, and bacteria.
- Additional monitoring in the Upper Neches Basin is performed by TCEQ (Region 5 in Tyler and Region 10 in Beaumont) and the Lower Neches Valley Authority (LNVA).

Parameters for Quarterly Monitoring		
Field Parameters	**Conventional Parameters**	**Bacterial Parameters**
Dissolved Oxygen	Ammonia-N	*E. coli*
Days Since Last Significant Rainfall	Nitrate-N	
Flow Severity	Nitrite-N	
Instantaneous Stream Flow	Chloride	
Evidence of Primary Contact Recreation	Sulfate	
pH	Chlorophyll-*a*	
Present Weather	Pheophytin-*a*	
Secchi Transparency	Total Phosphorus	
Specific Conductance	Total Suspended Solids (TSS)	
Total Water Depth		
Water Temperature		

Water Quality Monitoring: Field Parameters

Field parameters are performed on-site by direct monitoring in the water body. This data is collected using multiprobe instrumentation or with a Doppler flow meter, for in-stream flow measurements.

- Dissolved Oxygen (DO) – DO is a measure of the amount of dissolved oxygen that is available in the water. DO is vital for aquatic organisms to live. Where DO is too low, aquatic organisms may have insufficient oxygen to live.

- Days Since Last Significant Rainfall - The days since the last significant precipitation can help explain anomalous data due to runoff. Significant precipitation would be any amount that would produce runoff and influence water quality. (http://water.weather.gov/precip/)

- Flow Severity/Instantaneous Stream Flow - Flow is a measurement of the velocity of the water, measured in cubic feet per second (CFS). Flow combined with other parameters can be a good indicator of water quality. Flow can be affected by both natural and man-made sources.

Water Quality Monitoring: Field Parameters

- Evidence of Primary Contact Recreation –Are observations related to primary contact recreation that are needed to help the Water Quality Standards Group identify freshwater streams or rivers as suitable candidates for a Recreational Use Attainability Analysis. This information will also be considered as part of an existing RUAA to quantify the extent of existing primary contact recreation use. (https://www.tceq.texas.gov/assets/public/waterquality/swqm/monitor/manual/vol1/Chapt3_revFY15.pdf)

- pH - pH is a measure of the acidity or basicity of an aqueous solution. Most aquatic organisms are adapted to live within a specific pH range. pH can also affect the toxicity of many substances, which generally increase in solubility as pH decreases. The ability of water to resist changes in pH (its buffering capacity) is essential to aquatic life.

- Present Weather - Clear, partly cloudy, cloudy, rain, or other. Documenting any recent meteorological events that may have affected water quality include heavy rains, a cold front, or very dry or very wet conditions.

Water Quality Monitoring: Field Parameters

- Secchi Transparency - Secchi transparency remains an important secondary parameter for assessing eutrophication—the natural aging process in reservoirs and lakes—and for determining trends in water clarity. Eutrophication is accelerated by human activities that add nutrients to lakes, reservoirs, and the surrounding watersheds.

- Specific Conductance - Specific Conductance is the measure of the water's capacity to carry an electrical current and is indicative of the amounts of dissolved solids present in a water body. Dissolved salt-forming substances such as sulfate, chloride, and sodium increase the conductivity of the water.

- Total Water Depth - Measuring the depth of the water helps characterize a site. A site can be shallow, deep, or within a navigational channel. Rainfall and flow affect total water depth, so the total depth of a site can change depending on when it is sampled.

- Water Temperature - Water temperature affects the oxygen content of the water (dissolved oxygen). Temperature also has an impact on cold-blooded animals. Water temperature may be affected by alterations to the riparian zone, changes in ambient temperature, and discharges.

Water Quality Monitoring: Conventional Parameters

Conventional parameters are also evaluated as part of the monitoring plan. During routine monitoring events, water samples are collected for laboratory analysis of conventional parameters. Conventional parameters include nutrients, minerals, and particulates. For routine monitoring stations, ANRA collects and analyzes samples for the following conventional parameters:

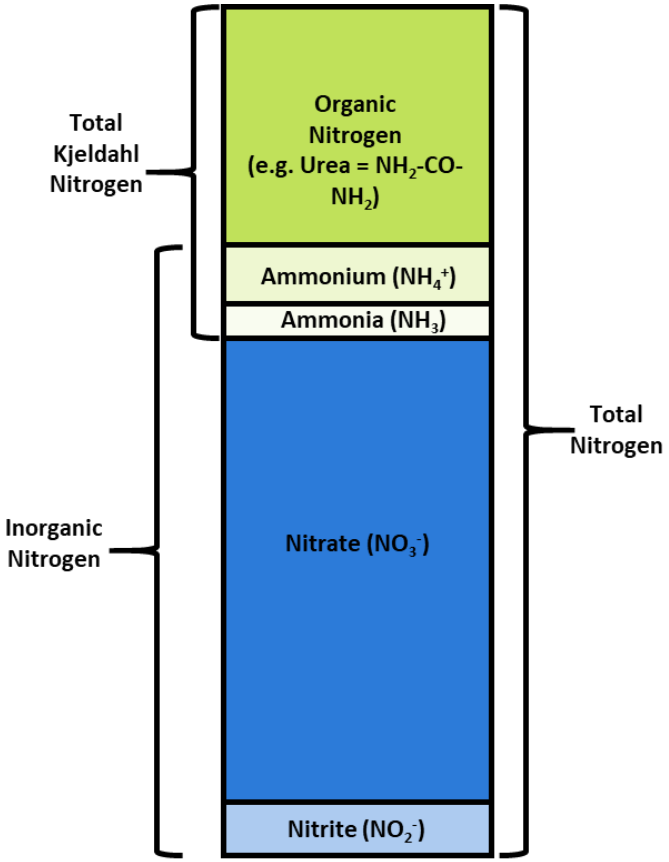
- Ammonia-Nitrogen (NH_3)– Ammonia, which is produced from the breakdown of nitrogen-containing compounds, is found naturally in waters. In excess, algal blooms may occur. Elevated ammonia levels are indicative of organic pollution. These elevated levels can cause stress on aquatic organisms, as well as damage to tissue and gills.

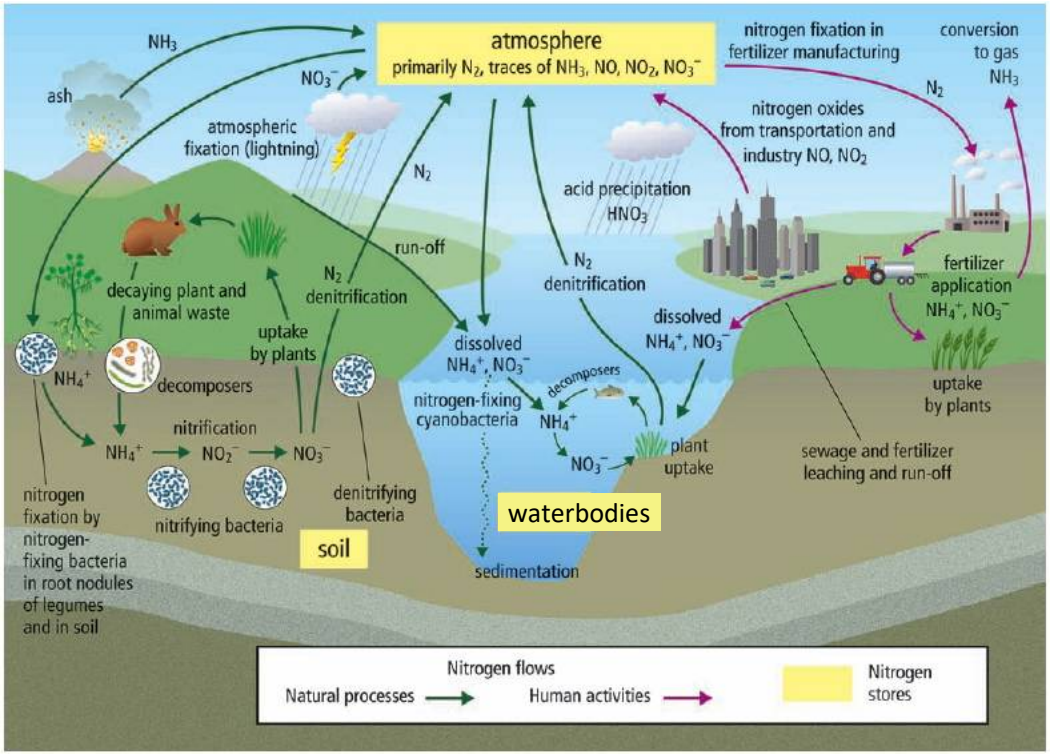
- Nitrate + Nitrite-Nitrogen - Elevated levels of nitrite and nitrate can produce nitrite toxicity in fish (“brown blood disease”) and methemoglobinemia (“blue baby syndrome”) in infants by reducing the oxygen-carrying capacity of blood. In surface water, high levels of nitrates can lead to excessive growth of aquatic plants. High levels of nitrates are also indicative of human-caused pollution.

The Nitrogen Cycle

TN=TKN + NO3- + NO2-

Sources: Fertilizers, WWTP, Sewage





Water Quality Monitoring: Conventional Parameters

- Chloride - Chloride is one of the major inorganic ions in water and wastewater. It is an essential element for maintaining normal physiological functions in all organisms. Elevated chloride concentrations can adversely affect survival, growth, and/or reproduction of aquatic organisms.

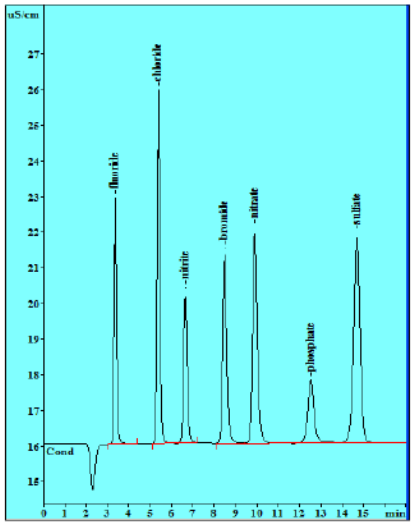
- Sulfate - Sulfate is essential for plant growth, and low levels (under 0.5 mg/L) can be detrimental to algal growth. Excessive levels of sulfate can form strong acids and change the pH of the water. Excessively high levels may be toxic to cattle and other animals. Sulfate can also affect drinking water quality.

Nutrients - Chloride, Nitrite, Nitrate, Sulfate by Ion Chromatography (IC)

Theory of IC-What is chromatography? chroma *(Greek - colour)* graphein *(write)*

- Historically chromatography was a separation of a color in its elements.
- Today chromatography stands for a wide range of physicochemical separation processes in which elements of a sample are separated, detected, identified and quantified.

Anions = Ions having a negative charge



Fluoride (F^-)
Chloride (Cl^-)
Nitrite (NO_2^-)
Bromide (Br^-)
Nitrate (NO_3^-)
Phosphate (PO_4^{-3})
Sulfate (SO_4^{-2})

Increasing size/ charge ratio of ions

Nutrients (Chloride, Nitrite, Nitrate, Sulfate) by Ion Chromatography

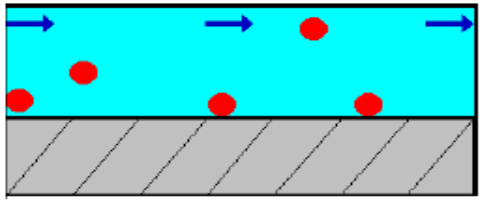
Ingredients for IC

Eluent, Pump, Sample Injection, Separation, Detector

- The mobile phase (eluent) is pumped through the system with a constant flow
- The sample is injected into it
- The mobile phase carries the sample through the static phase (separator) where the sample is split up into its component ions
- In the detector single components are recognized by a change in conductivity

Physical Chemistry of Chromatography

- components are separated by interaction with a stationary and a mobile phase



mobile phase liquid

stationary phase solid → *LSC*

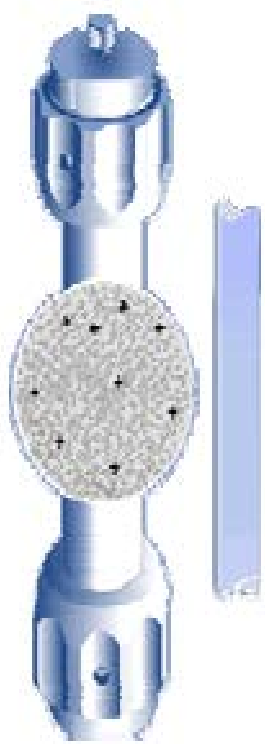
(HPLC - IC)

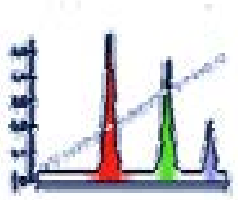
Nutrients (Chloride, Nitrite, Nitrate, Sulfate) by Ion Chromatography

I Column (separation column)
The separation of a sample takes place in the stationary phase inside the column. As it passes through the stationary phase, each ion will be retained for a certain amount of time before passing through to the detector. This time is called **retention time**. For proper identification and quantification, each ion should have a unique retention time .

Columns are accessories and can not be serviced. Sometimes they can be regenerated according to the manufacturers instructions.

i-Columns are an important part of intelligent IC technology, using an integral column chip to provide:
- traceability of the column
- monitoring options
- warning messages to protect the column
- availability of column properties
- customer tailored column handling



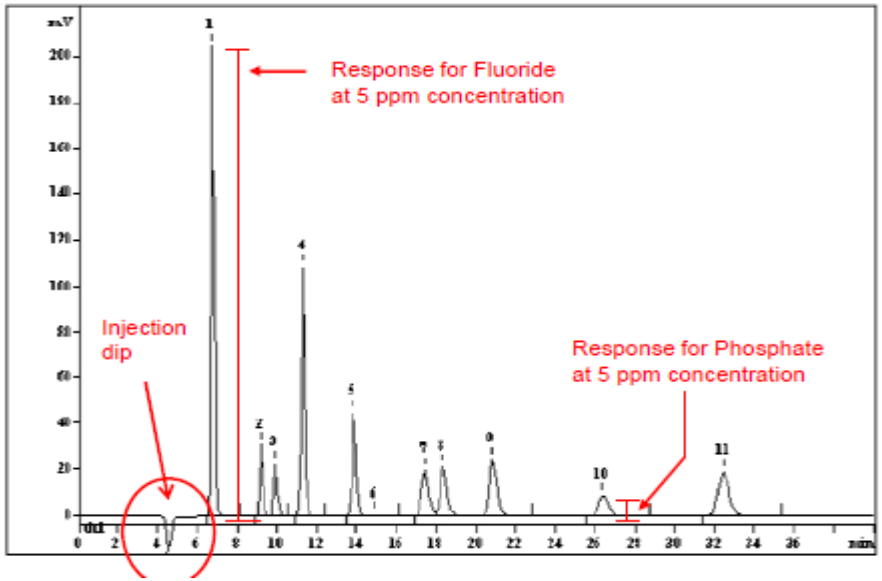


Nutrients (Chloride, Nitrite, Nitrate, Sulfate) by Ion Chromatography

Features of the chromatogram:

• The **injection dip** is a drop in conductivity caused by the water carrying sample passing through the detector as the sample ions are retained by the column. It is an indicator that a sample injection has been made.

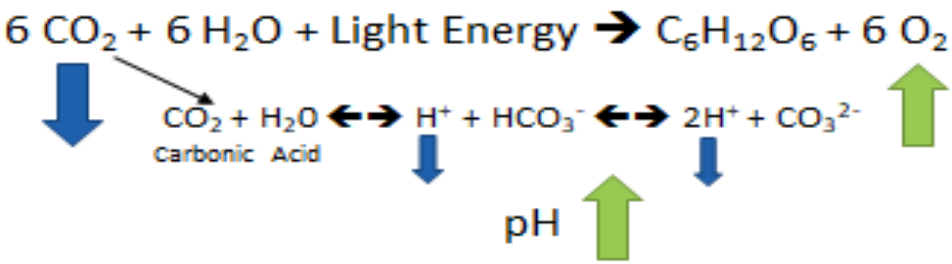
• Each ion has a different **relative conductivity**; this means some ions will have a much higher response than others at the same concentration (as shown below).



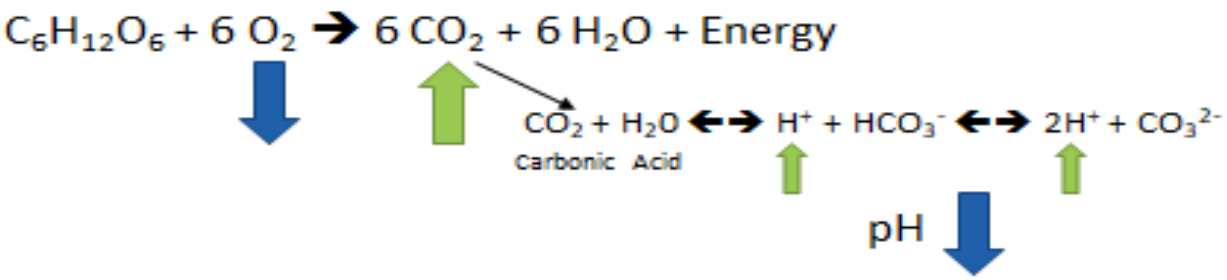
Water Quality Monitoring: Conventional Parameters

- Chlorophyll-*a*/Pheophytin-*a* - Chlorophyll-*a* is an indicator of algal biomass in a water body. Increased concentrations indicate potential eutrophication or nutrient loading. Diurnal shifts in DO and pH resulting from increased photosynthesis and respiration can cause stress to aquatic organisms.

Photosynthesis

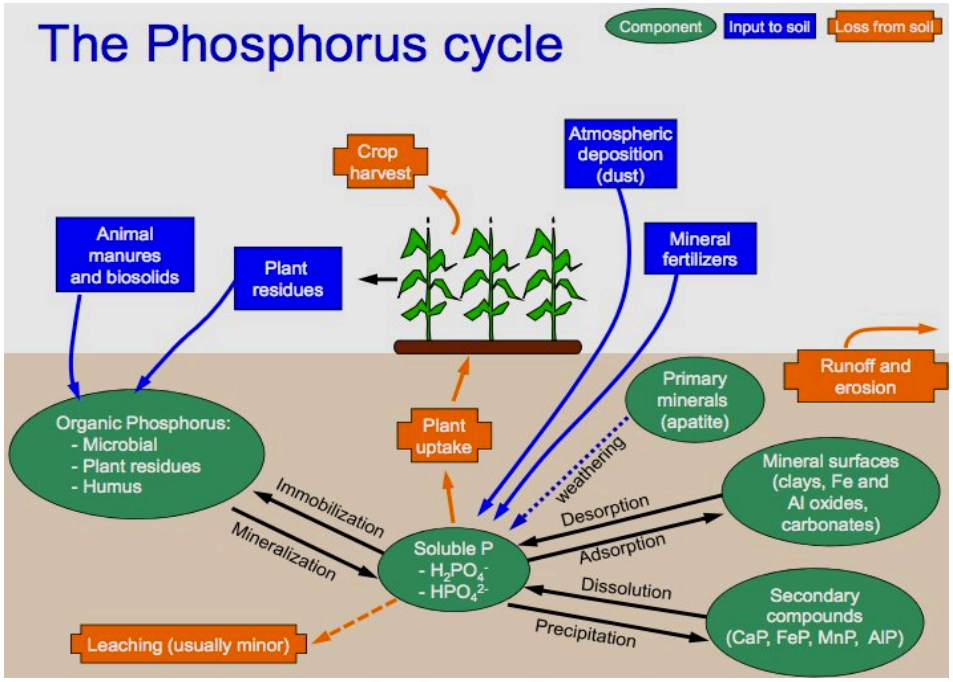


Respiration



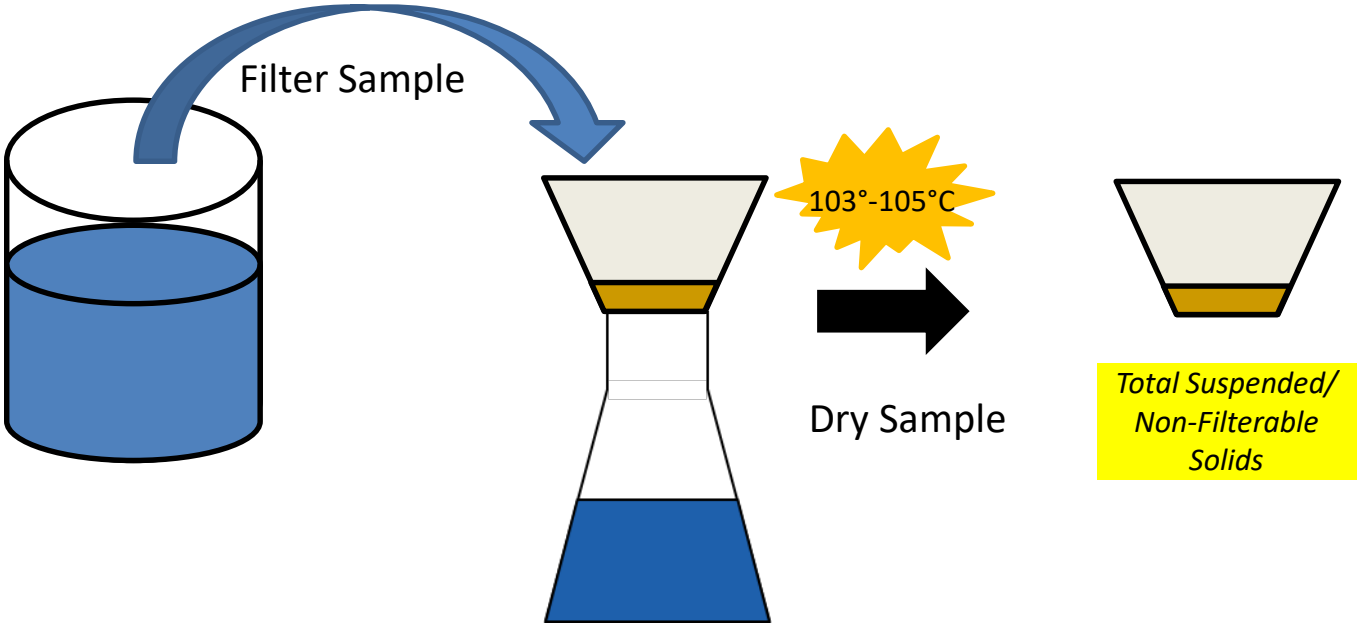
Water Quality Monitoring: Conventional Parameters

- Total Phosphorous (TP) -Phosphorus is essential to the growth of organisms, and is considered a growth-limiting nutrient. Elevated levels in water may stimulate the growth of photosynthetic aquatic macro and microorganisms. Elevated phosphorus levels contribute to eutrophication and may cause algal blooms.



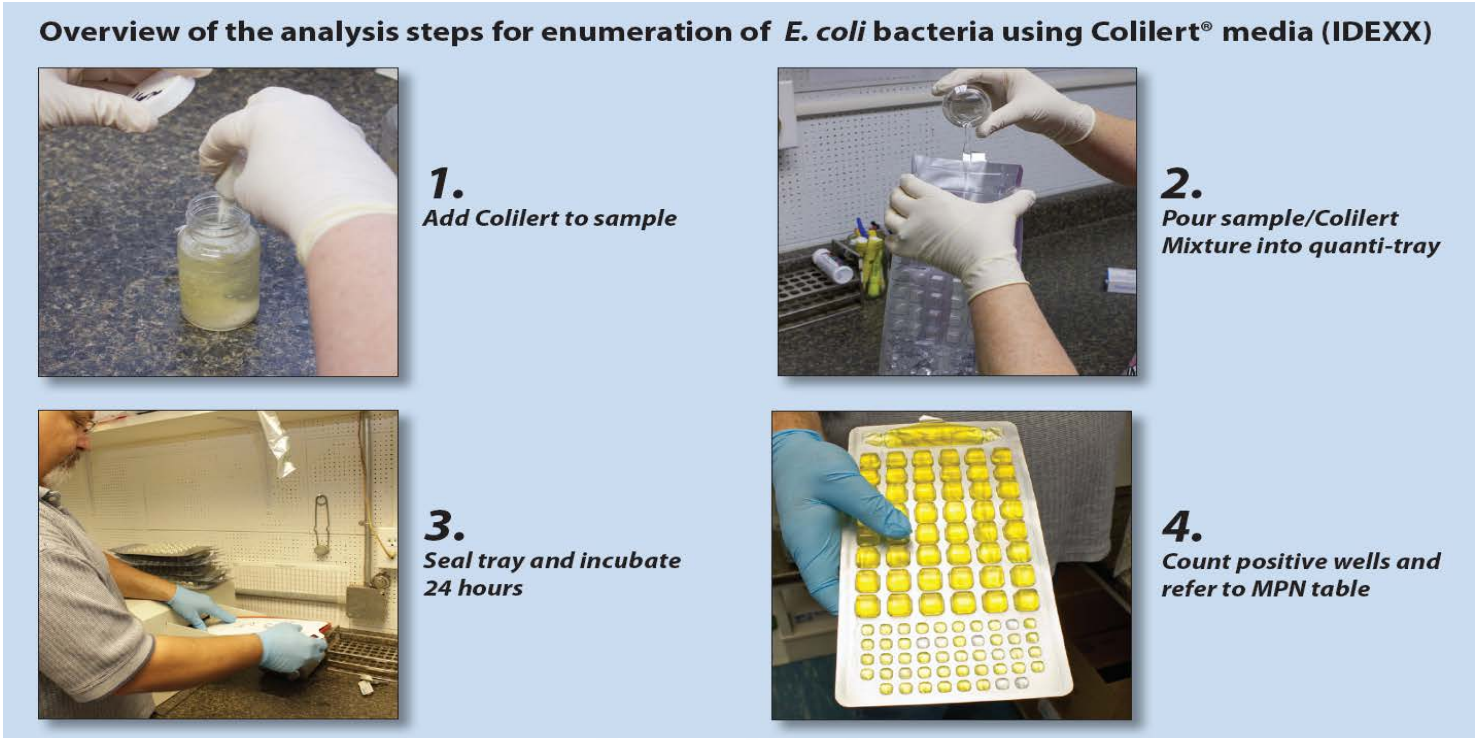
Water Quality Monitoring: Conventional Parameters

- Total Suspended Solids (TSS) – TSS is a measure of the total suspended particles in water (Non-Filterable Solids). High levels of TSS increase the turbidity of the water, reducing light penetration which subsequently decreases oxygen production by plants.

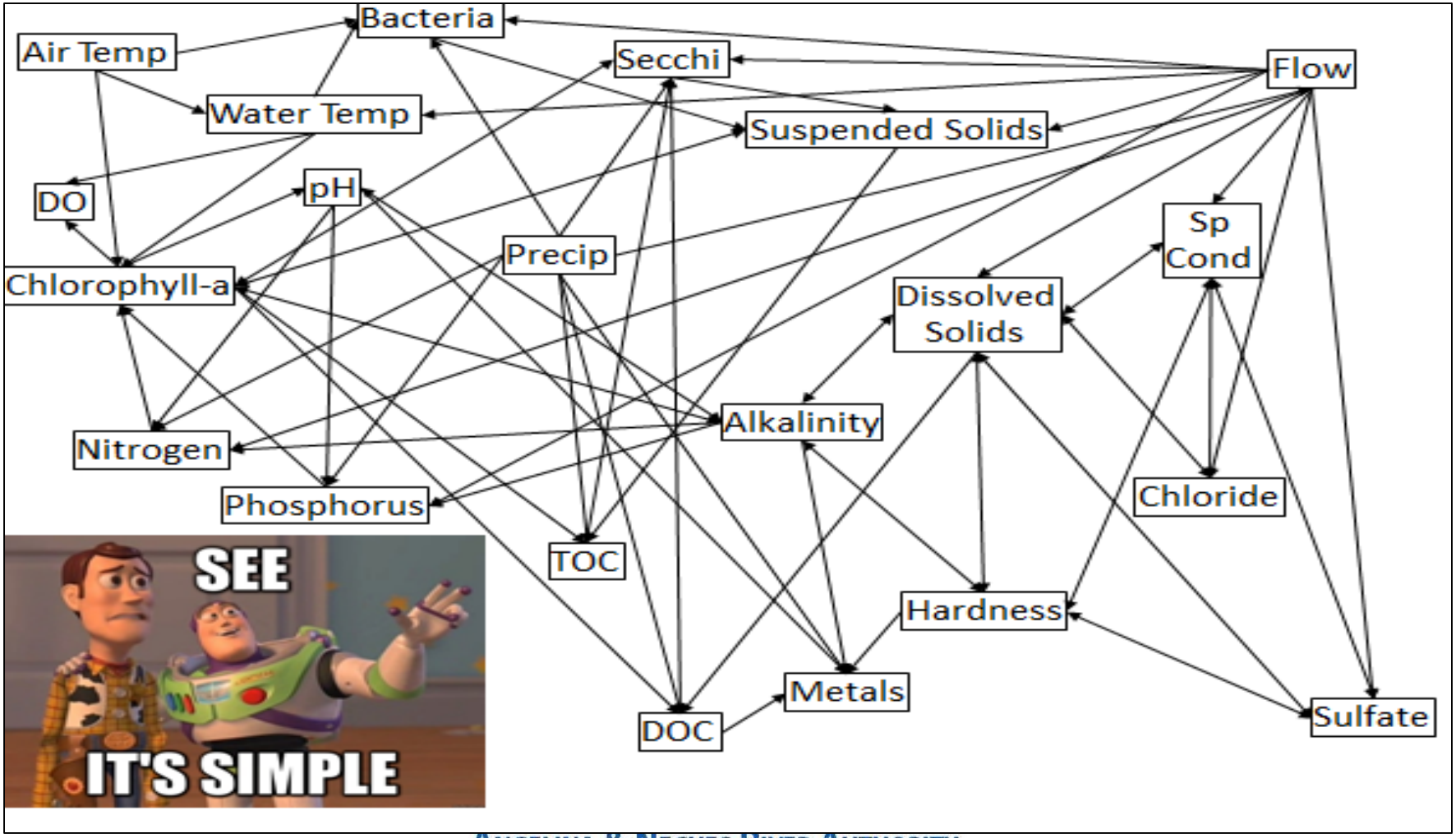


Water Quality Monitoring: Bacterial Parameter

- *Escherichia coli* (*E. coli*) - *E. coli* is an indicator of fecal contamination. Fecal contamination is a health concern to the general public, and its presence indicates a risk for contact recreation. The presence of *E. coli* in the water indicates that pathogenic organisms may be present.



Water Quality Monitoring: It's all Related



Questions?

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References and Resources:

- Surface Water Quality Monitoring Procedures, Volume 1: Physical and Chemical Monitoring Methods(https://www.tceq.texas.gov/assets/public/comm_exec/pubs/rg/rg415/rg-415.pdf)

- Water Quality: What We Collect and Why, A. Kilpatrick, Trinity River Authority (https://www.tceq.texas.gov/assets/public/waterquality/swqm/monitor/training/swqmworkshop30/Wed_Kilpatrick.pdf)

- Metrohm Training and Installation-850/881/882 IC- Basic IC Theory and Flow Path