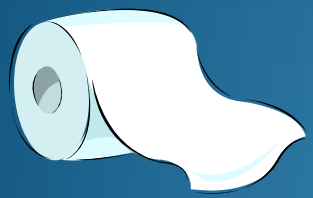
TP – It Stands for Total Phosphorus

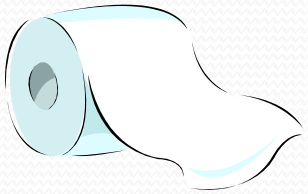


Methods of Analysis and its effect on Nature and Wastewater Treatment

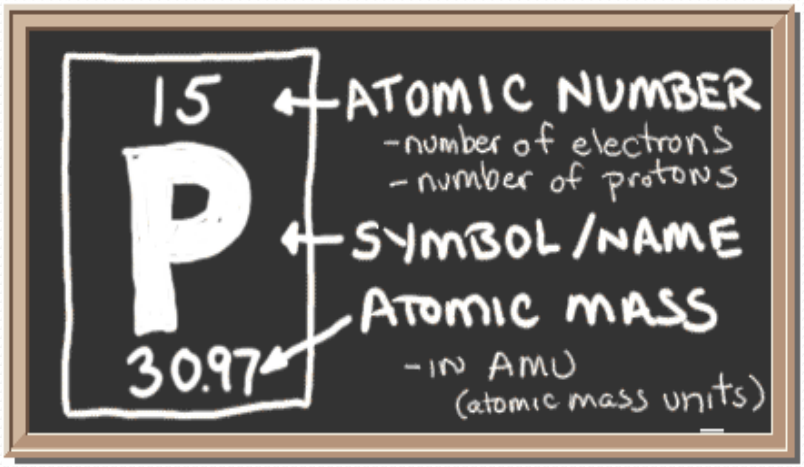
Cheryl Soltis-Muth, Supervising Chemist
NEORSD

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

What is Phosphorus?



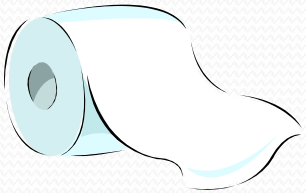
- Phosphorus (P) is a nutrient that is vital to human, animal, and plant growth.
- It's one of the most common substances found in nature.
- It's found in our water, our food, and our bodies.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

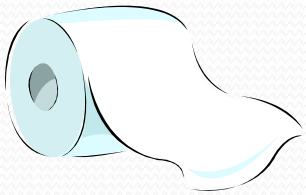
What is Phosphorus?

- It's a highly reactive, nonmetallic element existing in three allotropic forms, white (or sometimes yellow), red, and black. In its pure form, it is toxic.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Where does it come from?

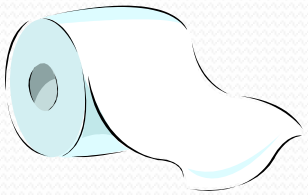


- Phosphorus occurs *naturally* at low levels in water, plants, and animals.
- Phosphorus occurs *unnaturally* in fertilizers (used in agriculture), cleaners (used in industry) and wastewater (from household sewage).
- Phosphorus is found in water, solids (detritus), and in the bodies of biological organisms.

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

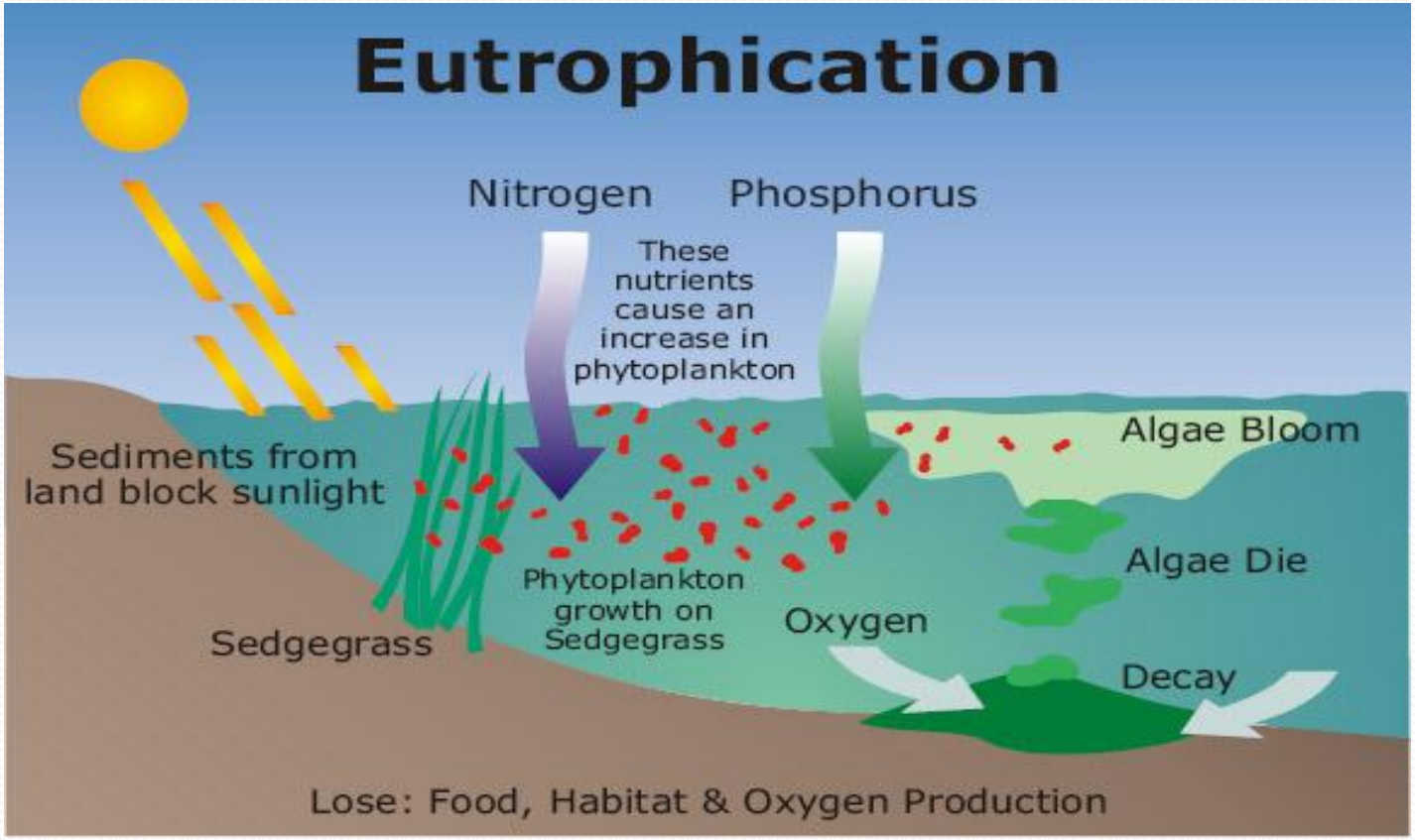
So why is it important?

- We need it to survive in low levels!
- However, high levels of phosphorus in nature can create *algal blooms* causing eutrophication or the premature “aging” of a water body.
- This process decreases sunlight and oxygen levels (hypoxia) thus affecting fish and other aquatic life.

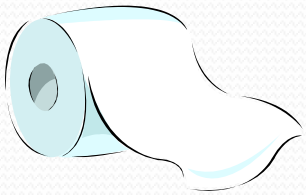


Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

So why is it important?



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment



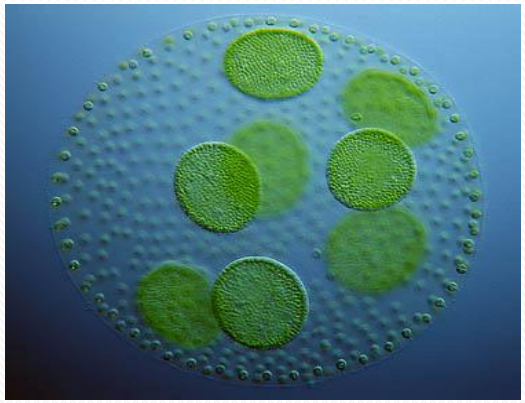
Algae – Lake Erie

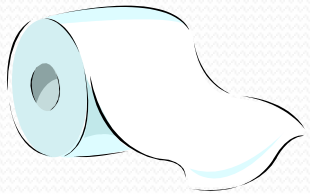
Algal Bloom - Pond

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Eutrophication

- Phosphorus is recycled so rapidly through biota, DRP concentrations as low as 0.005 mg/L are enough to maintain eutrophication in natural waterways.

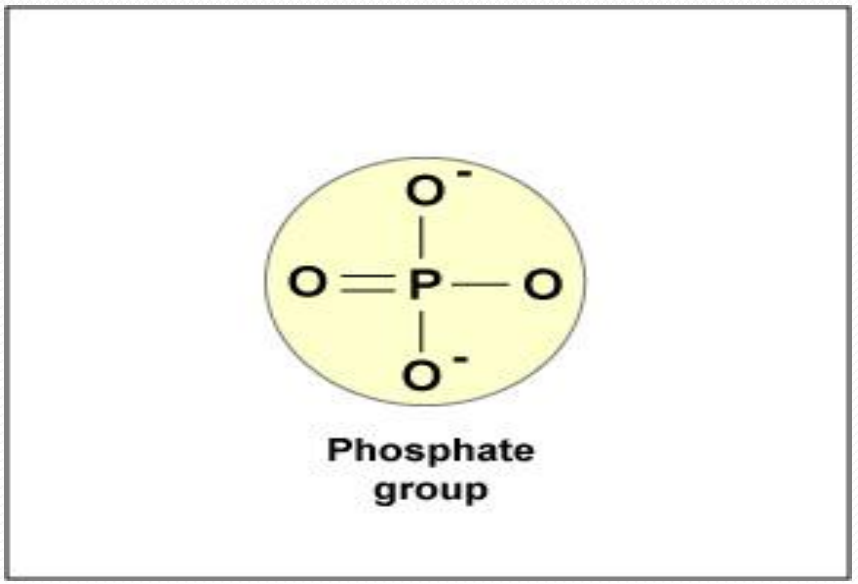




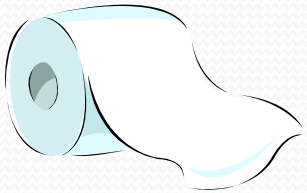
Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Forms of Phosphorus

- Phosphorus (P) occurs mostly as Phosphates (PO_4).

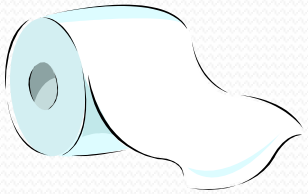


- These are classified as *Orthophosphates* (reactive phosphates), *Condensed Phosphates* (pyro, meta, and polyphosphates) and *Organic Phosphates*.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

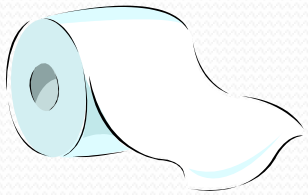
Orthophosphates



- Orthophosphates, also known as Reactive Phosphates, are a main constituent in fertilizers used for agriculture and residential purposes.
- Orthophosphates found in natural water provide a good estimation of the amount of phosphorus available for algae and plant growth. This is the form of phosphorus that is most readily utilized by biota.
- Orthophosphates can be carried into streams and lakes through run-off.

Condensed Phosphates

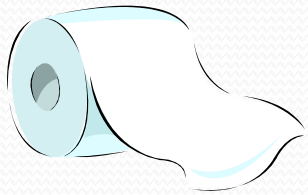
- Condensed (inorganic) phosphates are phosphorus compounds that contain salts and/or metals such as sodium, potassium, and calcium in various structures and chains.
- Condensed phosphates are used in industry and as food additives.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Did you know?

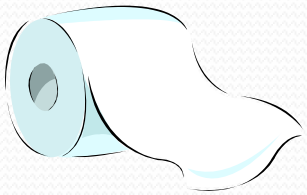
- Phosphoric acid was (and still is in dark varieties) added to pop to enhance flavor and fizz.
- However, phosphoric acid can leach calcium from bones and teeth.
- High levels of phosphorus in the body can cause premature aging and cancer.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Organic Phosphates

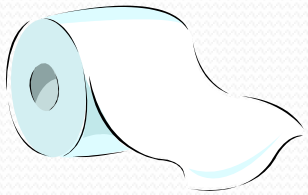
- Organic Phosphates are formed primarily by biological processes (ex: *ATP – Adenosine Triphosphate*). ATP is a chemical compound that breaks down to release energy in the body.
- Organic phosphates enter sewage via human waste and food residues.
- Organic phosphates can be formed from orthophosphates in biological treatment processes or by receiving water biota.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

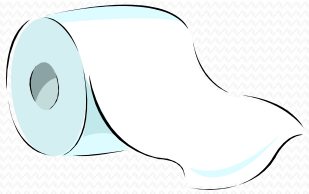
Phosphorus Analysis

- Collection, Preservation and Holding Times
- Ortho vs Total Phosphorus
- Dissolved Phosphorus
- Different Methods of Analysis
- Digestion of Total Phosphorus
- Quality Control (QC) samples
- Interferences



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Collection and Preservation

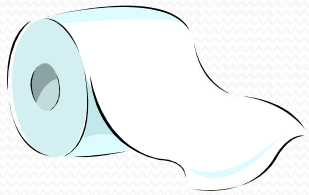


- Collection: Plastic or glass
- Hold Time: Total Phosphorus: 28 days
  Orthophosphate: 48 hours
- Preservation: Total Phosphorus: pH<2 H_2SO_4
  Orthophosphate: No chemical preservation
- Storage: Refrigerate, <6°C

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

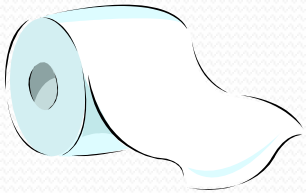
Orthophosphate vs. Total Phosphorus

- *Orthophosphate* (reactive) is analyzed directly on an unpreserved sample within 48 hours of sampling.
- *Total Phosphorus* (all forms) is analyzed on an acid preserved sample within 28 days of sampling following an acid digestion.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

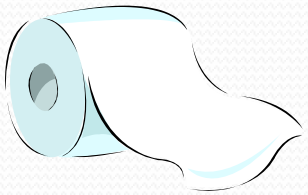
Dissolved Phosphorus



- *Dissolved Reactive Phosphorus* is when the sample is filtered through a 0.45-µm filter prior to analysis and analyzed within 48 hours of sampling.
  - NEW MUR – must be filtered in the field within 15 minutes of sampling.
- *Dissolved Total Phosphorus* is when the sample is filtered through a 0.45-µm filter prior to preservation. The sample is then digested and analyzed within 28 days of sampling.

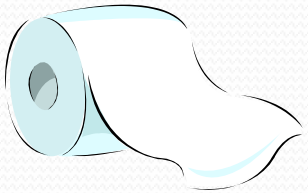
Phosphorus Methods

- Colorimetric EPA Method 365.2 – Manual Spectrophotometer
- Semi-Automated Colorimetric EPA Method 365.1 – Automated Spectrophotometer (Flow injection Analysis –FIA)
- Standard Methods 4500-P
- Ion Chromatography (IC) EPA Method 300.0
- Discrete Analyzers



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

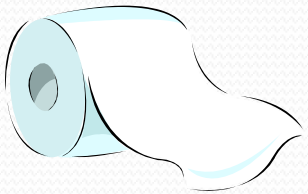
Discrete Analyzer



- A instrument that employs robotics and syringes to aspirate, dispense, and mix appropriate amounts of sample and reagents into reaction wells.
- The sample/reagent mixture then incubates in the reaction well for a pre-programmed time.
- A single aliquot of the mixture is then transferred to a cuvette for spectrophotometric analysis.
- Absorbance is plotted against ppm in a linear regression curve to calculate concentration.
- Analyzes orthophosphate and total phosphorus.

Discrete Analyzer

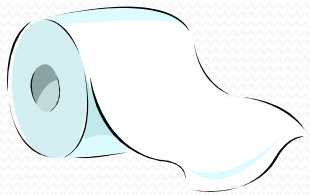
- Advantages:
  - Reduces manual labor
  - Reduces reagents
  - Reduces sample volume
  - Reduces waste
- Disadvantages:
  - EPA approval
  - Instrument cost



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Ion Chromatography

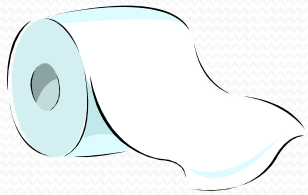
- Anions are separated based on their affinities toward the stationary phase in the column. A suppressor cartridge chemically suppresses the background conductance of the eluent (dilute CO_3/HCO_3 solution) and converts the anions into species of higher conductance.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

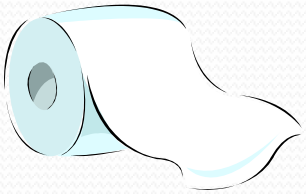
Ion Chromatography

- Using pressure and eluent, the sample is “pushed” through a stationary phase column. The anions are separated by size and then measured using a conductivity detector.
- The electronic signal is converted to peak area. Concentration is determined using a linear regression curve (plotting area vs. ppm).



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Ion Chromatography



Method A

Peak	Ret. Time	Ion	mg/L
1	1.17	F^-	2
2	1.73	Cl^-	20
3	2.02	NO_2^-	2
4	2.95	Br^-	2
5	3.20	NO_3^-	10
6	5.38	HPO_4^{2-}	2
7	6.92	SO_4^{2-}	60

Ion Chromatography

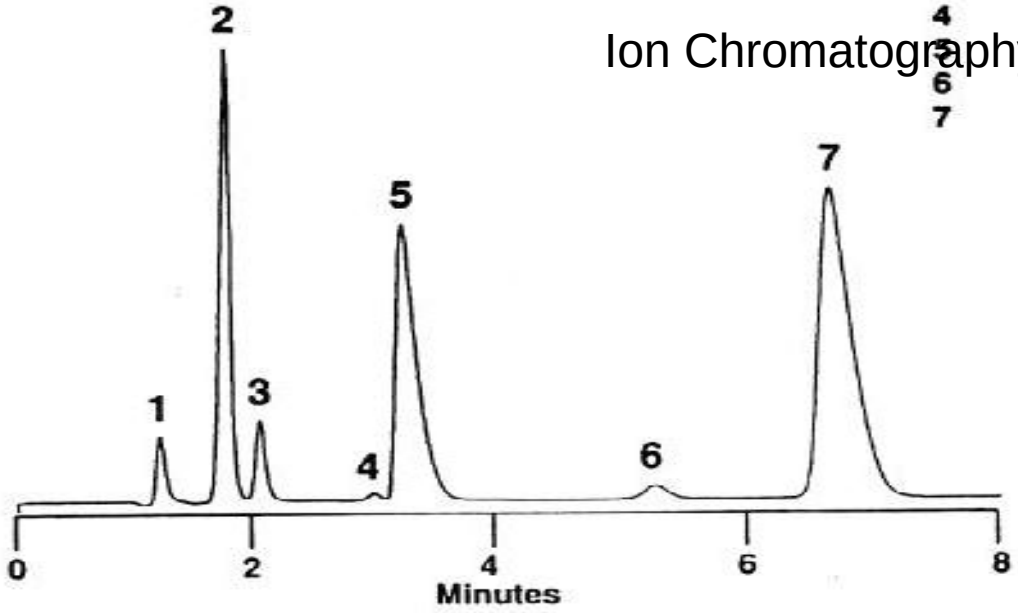
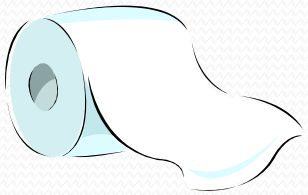


Figure 1. Chromatogram showing separation using the AS4A column

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Ion Chromatography

- Analyzes Reactive (Ortho) Phosphate only
- Linear Range 0.05-5 mg/L for Phosphate
- Calibrate monthly
- Minimum of 5 Standards covering the linear range
- ≥0.995 Correlation Coefficient
- Method Detection Limits (MDL) performed yearly



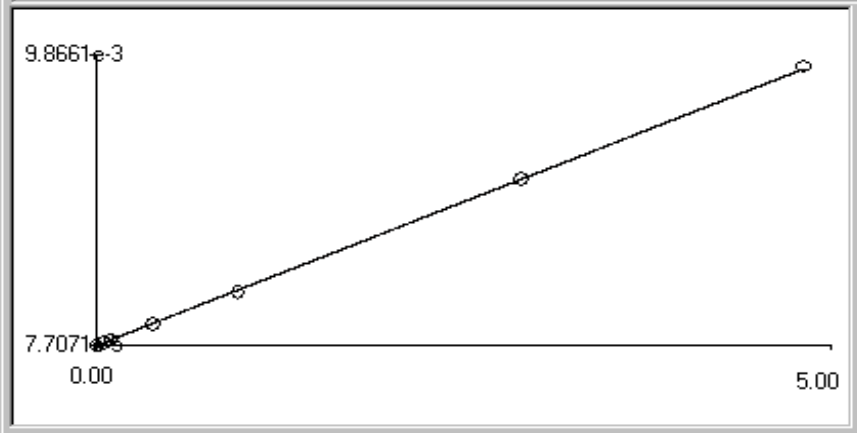
Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Linear Regression Curve

Calibration Results - Anions (Channel 1)

Fluoride | Chloride | Nitrite-N | Bromide | Nitrate-N | Phosphate-P | Sulfate

	Known Conc. (mg/L)	Rep.	Peak Area (V.min)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	5.00	1	9.87e-3	0.121	0.0	-1.0	☐	5.05	10/21/2008	10:59:01 AM
2	3.00	1	5.90e-3	0.0724	0.0	-0.2	☐	3.00	10/21/2008	11:05:39 AM
3	1.00	1	1.94e-3	0.0232	0.0	3.7	☐	0.961	10/21/2008	11:12:16 AM
4	0.400	1	8.11e-4	9.41e-3	0.0	4.5	☐	0.380	10/21/2008	11:18:54 AM
5	0.100	1	2.73e-4	2.88e-3	0.0	-1.9	☐	0.103	10/21/2008	11:25:31 AM
6	0.0500	1	1.73e-4	1.69e-3	0.0	-1.0	☐	0.0509	10/21/2008	11:32:08 AM
7	0.00	1	7.71e-5	5.76e-4			☐	1.67e-3	10/21/2008	11:38:45 AM

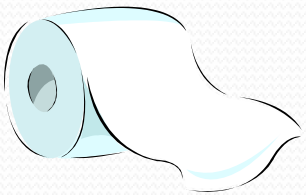


Area = 1.94e-3 * Conc + 7.39e-5
Conc = 515 * Area - 0.0381
Correlation Coefficient (r) = 0.99998

Weighting : 1/x

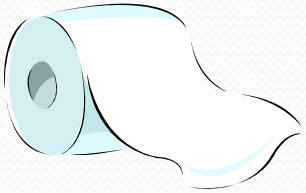
Settings

IC Analysis QC



- Initial Calibration Verification (**ICV**) and Initial Calibration Blank (**ICB**) analyzed daily
- Continuing Calibration Verification (**CCV**) and Continuing Calibration Blank (**CCB**) analyzed at the beginning, every 10 samples and at the end of the sequence
- Reporting Limit Check (**RLC**) analyzed daily for Drinking Water samples

IC Batch QC

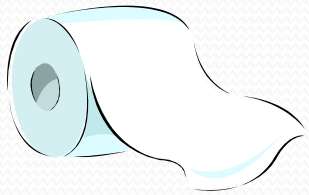


- Laboratory Control Blank (**LCB**) and Laboratory Control Sample (**LCS**) prepared fresh daily per batch of **20** samples
- Duplicate/Matrix Spike or MS/MSD per **10** samples
- Percent Recovery and Relative Percent Difference (RPD) are calculated
- Method or Laboratory established limits

IC Sample Preparation

- All samples and batch QC (LCB, LCS, Duplicates, MS/MSD) are filtered through a 0.45-µm syringe filter to remove all particulate.

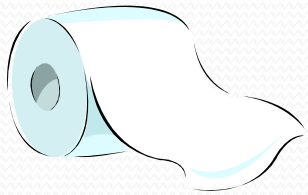
- Spike MS/MSD's appropriately within the analysis range.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

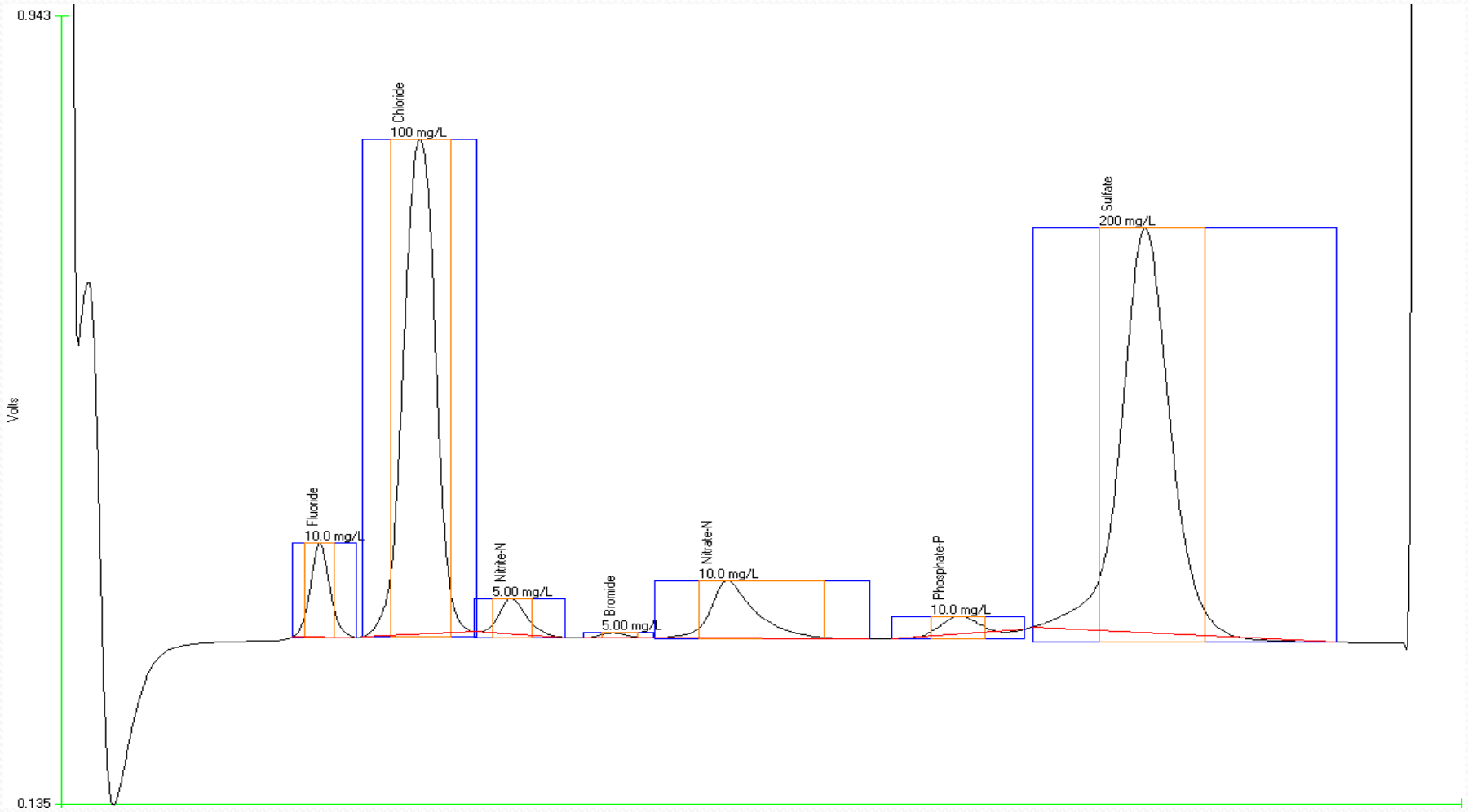
IC Interferences

- All solids must be filtered out. Any particulate in the system will cause problems and plug up the system.
- High concentrations of some ions will cause false readings of other ions. High sulfate concentration may interfere with phosphate.
- Peak shifting: as the column gets older, peaks may shift causing misidentification.



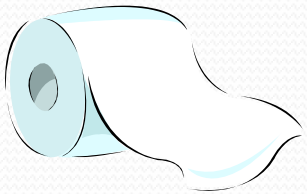
Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

IC Interferences



IC Advantages/Disadvantages

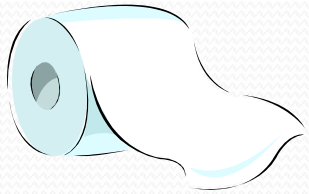
- The Good
  - Analyzes up to 7 anions in less than 15 minutes
  - Can be very stable
  - Can run overnight (load and go!)
  - No hazardous waste
  - Small sample volume needed
- The Bad
  - May have to do multiple dilutions per sample
  - Peak interferences (sulfate with phosphate)



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Phosphorus 365.1/365.2

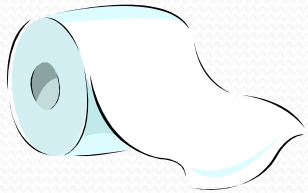
- Phosphorus is analyzed using colorimetric (spectrophotometric) analysis. This can be performed manually or automated.
- *Orthophosphate (Reactive Phosphorus)* is analyzed directly.
- *Total Phosphorus (as P)* is analyzed after going through an acid digestion to convert all forms of phosphorus to orthophosphate.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Method Summary

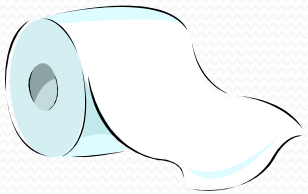
- Ammonium molybdate and antimony potassium tartrate react in an acid medium with phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to a blue-colored complex with ascorbic acid and read colorimetrically at 880-nm.



- This can be performed on a manual spectrophotometer or on an automated spectrophotometer.

Orthophosphate (Reactive)

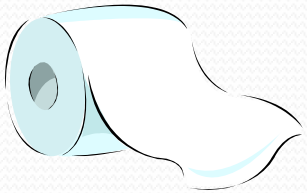
- Orthophosphate (reactive) is analyzed directly on an unpreserved sample within 48 hours of sampling.
- No preparation needed for Manual Spectrophotometer
- For Automated Spectrophotometer, samples must be filtered to remove solids
- Dissolved Reactive Phosphorus filtered through 0.45-µm syringe filter IN THE FIELD



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

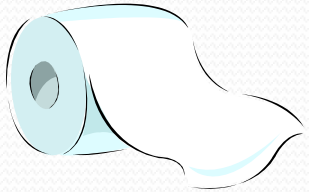
Orthophosphate (Reactive)

- Calibrate Daily
- Linear Range 0.01-2 mg/L
- Minimum of 5 Standards covering the linear range
- ≥0.995 Correlation Coefficient
- Method Detection Limits (MDL) performed yearly



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Analysis QC

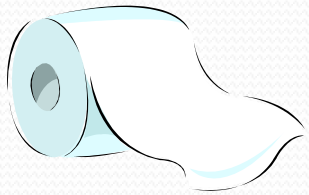


- Initial Calibration Verification (**ICV**) and Initial Calibration Blank (**ICB**) analyzed daily

- Continuing Calibration Verification (**CCV**) and Continuing Calibration Blank (**CCB**) analyzed at the beginning, every 10 samples and at the end of the sequence

Batch QC

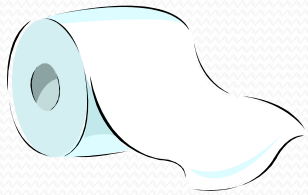
- Laboratory Control Blank (**LCB**) and Laboratory Control Sample (**LCS**) prepared fresh daily per batch of **20** samples
- Duplicate/Matrix Spike or MS/MSD per **10** samples
- Percent Recovery and Relative Percent Difference (RPD) are calculated
- Method or Laboratory established limits



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Total Phosphorus

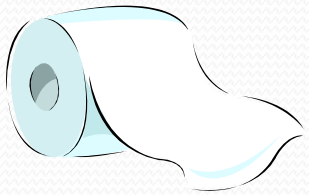
- **Method Summary: Total Phosphorus** analysis has two procedural steps:
  - *First* - convert all phosphorus forms to orthophosphate using acid hydrolysis.
  - *Second* - analyze orthophosphate colorimetrically, either manually or automated.



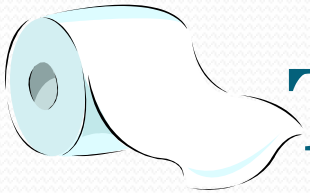
Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Total Phosphorus Digestion

- In the *acid hydrolysis step*, sulfuric acid and ammonium persulfate (peroxydisulfate) are added to a known volume of sample. It is then digested on a hotplate to near dryness. The sample is cooled and diluted back to the original volume. Sample is then filtered to remove any solids for Auto-Analysis.
- Alternatively, an autoclave may be used for digestion (30 min at 121°C, 15-20 psi) or hotblock (30 min at 150°C).



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment



Total Phosphorus Analysis

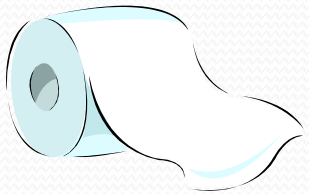
- In the *colorimetric step*, ammonium molybdate and antimony potassium tartrate react in an acid medium with phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to a blue-colored complex with ascorbic acid and read colorimetrically at 880-nm.
- The colorimetric step may be performed on a manual spectrophotometer or on an automated analyzer.

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Total Phosphorus

- Final results are derived by plotting *absorbance* (or *peak area* for auto-analysis) against *concentration* (mg/L) using a linear regression curve.

- This entails calibrating with a series of standards covering the linear range of the method.



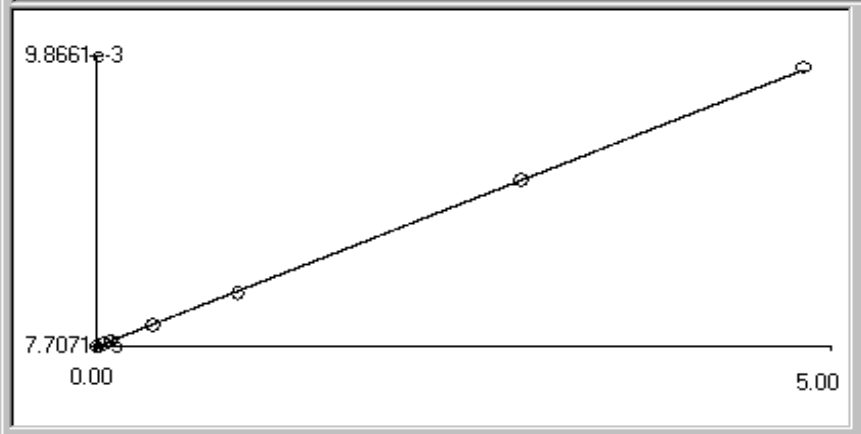
Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Linear Regression Curve

Calibration Results - Anions (Channel 1)

Fluoride | Chloride | Nitrite-N | Bromide | Nitrate-N | Phosphate-P | Sulfate

	Known Conc. (mg/L)	Rep.	Peak Area (V.min)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	5.00	1	9.87e-3	0.121	0.0	-1.0	☐	5.05	10/21/2008	10:59:01 AM
2	3.00	1	5.90e-3	0.0724	0.0	-0.2	☐	3.00	10/21/2008	11:05:39 AM
3	1.00	1	1.94e-3	0.0232	0.0	3.7	☐	0.961	10/21/2008	11:12:16 AM
4	0.400	1	8.11e-4	9.41e-3	0.0	4.5	☐	0.380	10/21/2008	11:18:54 AM
5	0.100	1	2.73e-4	2.88e-3	0.0	-1.9	☐	0.103	10/21/2008	11:25:31 AM
6	0.0500	1	1.73e-4	1.69e-3	0.0	-1.0	☐	0.0509	10/21/2008	11:32:08 AM
7	0.00	1	7.71e-5	5.76e-4			☐	1.67e-3	10/21/2008	11:38:45 AM



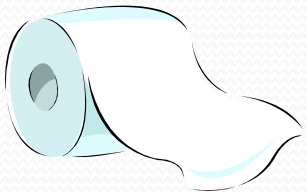
Area = 1.94e-3 * Conc + 7.39e-5
Conc = 515 * Area - 0.0381
Correlation Coefficient (r) = 0.99998

Weighting : 1/x

Settings

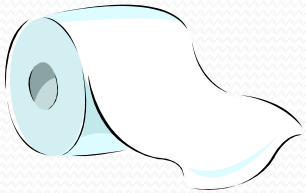
Total Phosphorus Analysis

- Calibrate Daily
- Linear Range 0.01-2 mg/L (ours 0.01-1 mg/L)
- Minimum of 5 Standards covering the linear range
- ≥0.995 Correlation Coefficient
- Method Detection Limits (MDL) performed yearly



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

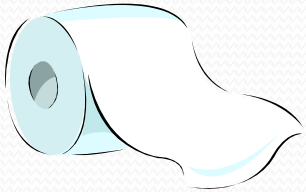
Analysis QC



- Initial Calibration Verification (**ICV**) and Initial Calibration Blank (**ICB**) analyzed daily

- Continuing Calibration Verification (**CCV**) and Continuing Calibration Blank (**CCB**) analyzed at the beginning, every 10 samples and at the end of the sequence

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

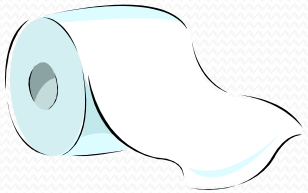


Batch QC

- Laboratory Control Blank (**LCB**) and Laboratory Control Sample (**LCS**) digested fresh daily per batch of **20** samples
- Duplicate/Matrix Spike or MS/MSD per every **10** samples
- Percent Recovery and Relative Percent Difference (RPD) are calculated
- Method or Laboratory established limits

Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

QC Failure

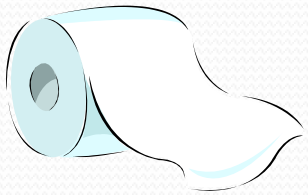


- Failure in meeting Calibration Criteria results in recalibrating the instrument.
- Failure in meeting Analysis QC criteria results in re-analyzing the initial or continuing QC. Repeated failure results in re-calibrating the instrument.
- Failure in meeting Batch QC may result in re-digestion and/or re-analysis of QC and samples.

Phosphorus Interferences

- As with any colorimetric analysis, *turbidity* (solids) can be a positive interference but can be removed with filtration. Filtration must occur prior to analysis, not prior to digestion (unless the sample is dissolved) on total phosphorus samples.

- Sample color may also interfere. Background correction can be performed in this case.

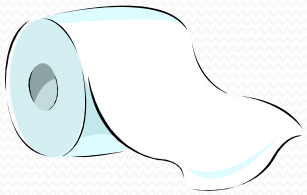


Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Phosphorus Interferences

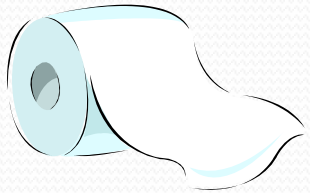
- High levels of arsenic can cause a positive interference if the concentrations are higher than the phosphorus concentration.

- High levels of iron may cause the precipitation of, and subsequently the loss of phosphorus.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Troubleshooting



- Contamination!! Contamination!! Contamination!!
- All glassware must be washed with hot water and phosphate free soap, rinsed with dilute hydrochloric acid and rinsed with copious amounts of de-ionized water.
- All instrument components and reagents must be phosphorus free.

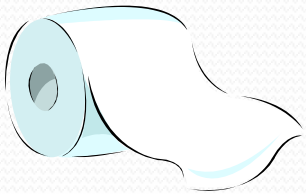
Troubleshooting

- Auto-Spectrophotometers: *Plugs* and *leaks* are the most common problems.
- Routine Maintenance helps prevent problems:

  -Changing Tubing

  -Cleaning/lubricating components

  -Removing Algae

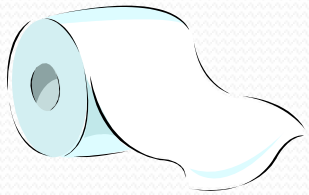


Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Treatment of Phosphorus

- Some of the Phosphorus entering the treatment plant is removed by primary (settling) and secondary treatment. The phosphorus remains in the solids.

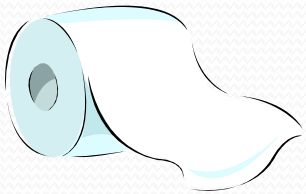
- Additional phosphorus is removed by adding Ferric Chloride, Ferrous Sulfate, Alum, or Lime during the waste treatment process.



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Treatment of Phosphorus

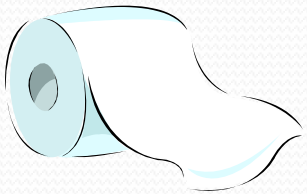
- Chemical removal
  - Ferric Chloride
    - $Fe^{3+} + (H_nPO4)^{3-n} \leftrightarrow FePO_4 + nH^+$
  - Aluminum Sulfate (Alum)
    - $Al^{3+} + (H_nPO4)^{3-n} \leftrightarrow AlPO_4 + nH^+$



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Future Concerns

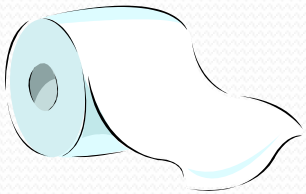
- Permit limits
- Point and non-point concerns
- Blue-green algae
- The Dead Zone



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

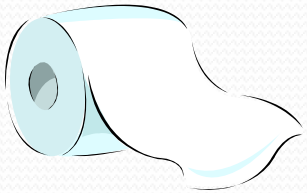
Phosphorus

Any Questions??



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment

Phosphorus



Special thanks to

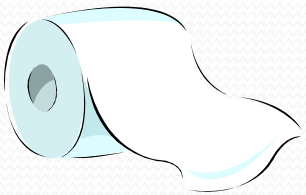
Leslie VanKuren

Northeast Ohio Regional Sewer District

Protecting Your Health and Environment

Phosphorus

Cheryl Soltis-Muth
Supervising Chemist
Northeast Ohio Regional Sewer District
4747 East 49th Street
Cuyahoga Heights, Ohio 44125
Office: 216-641-6000 X2501
Mobile: 216-925-3708
soltis-muthc@neorsd.org



Northeast Ohio Regional Sewer District
Protecting Your Health and Environment