NUTRIENTS AND NUTRIENT ANALYSIS

Ted Simmons
Regional Sales Manager
(970) 531-4322

OVERVIEW OF HACH COMPANY

- **Began in 1947 in Ames, IA**
- **1999: Acquired by Danaher Corporation**
- **Manufacturer of industrial and municipal water analysis solutions**
  - process and laboratory instruments
  - chemistries
  - service and software
- **Innovation leader**
  - 527 patents, 130 patent families
  - strong investment in R&D and acquired technologies

- **OUR MISSION**
  Ensure water quality for people around the world.

- **OUR VISION**
  We make water analysis better—faster, simpler, greener and more informative—via unsurpassed customer partnerships, the most knowledgeable experts, and reliable, easy-to-use products.

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OVERVIEW OF HACH COMPANY

- **70+ RSM's**
  - Regional Sales Managers
- **25+ CAM - KAM – ADM – TSS - CSS**
  - CAM - Corporate Account Managers
  - KAM - Key Account Managers
  - ADM - Application Development Managers
  - TSS - Technical Sales Specialist
  - CSS - Complex Sales Specialist
- **100+ Field Service Technicians**
  - Field Service Partnerships
  - Startups, Commissioning and Training
- **41+ Technical Support Representatives**
  - Global Customer Support
- **12+ Bench Service Technicians**
  - Two service centers for repair and certification

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Nitrogen and Phosphorus

- N & P discharged into Surface Waters
- Algae consume N & P and reproduce rapidly
- Bacteria eat algae and deplete oxygen levels
- Low DO kills fish, shellfish, invertebrates

- May increase toxicity of water due to ammonia

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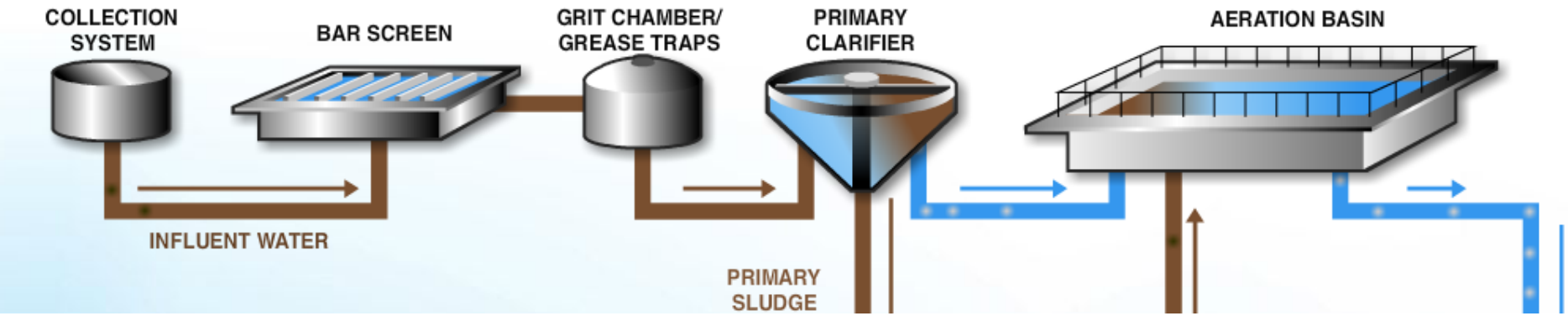
HOW CAN WE REMOVE N AND P?

- Chemical Removal
- Ion Exchange
- Air Stripping (NH_3)
- Biological Nutrient Removal (BNR)



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NUTRIENT REMOVAL

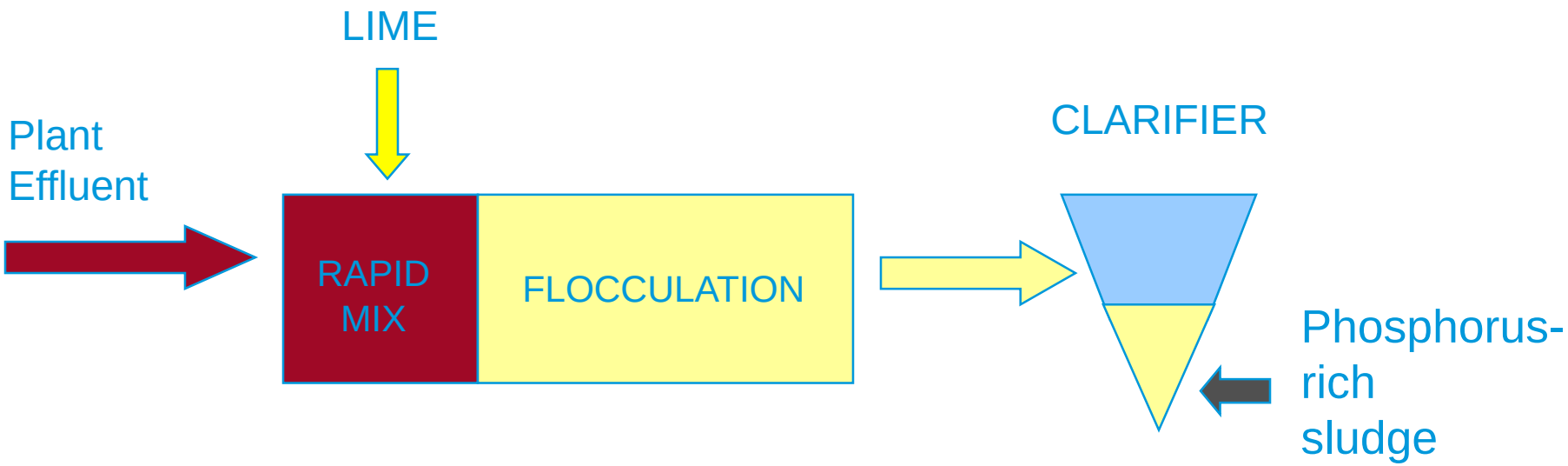
- CHEMICAL treatment processes
  - Flocculation & sedimentation (for Phosphorus)
    - Lime, Alum (Aluminum Sulfate)

- BIOLOGICAL treatment processes
  - 'Luxury uptake' with chemical addition (for Phosphorus)
  - Nitrification and Denitrification (for Ammonia)

CHEMICAL PHOSPHORUS REMOVAL

Chemical Precipitation

- Lime ($Ca(OH)_2$) or Alum is added to the effluent
- Chemicals bind phosphorous and cause it to settle out into a final clarifier and it's pumped out



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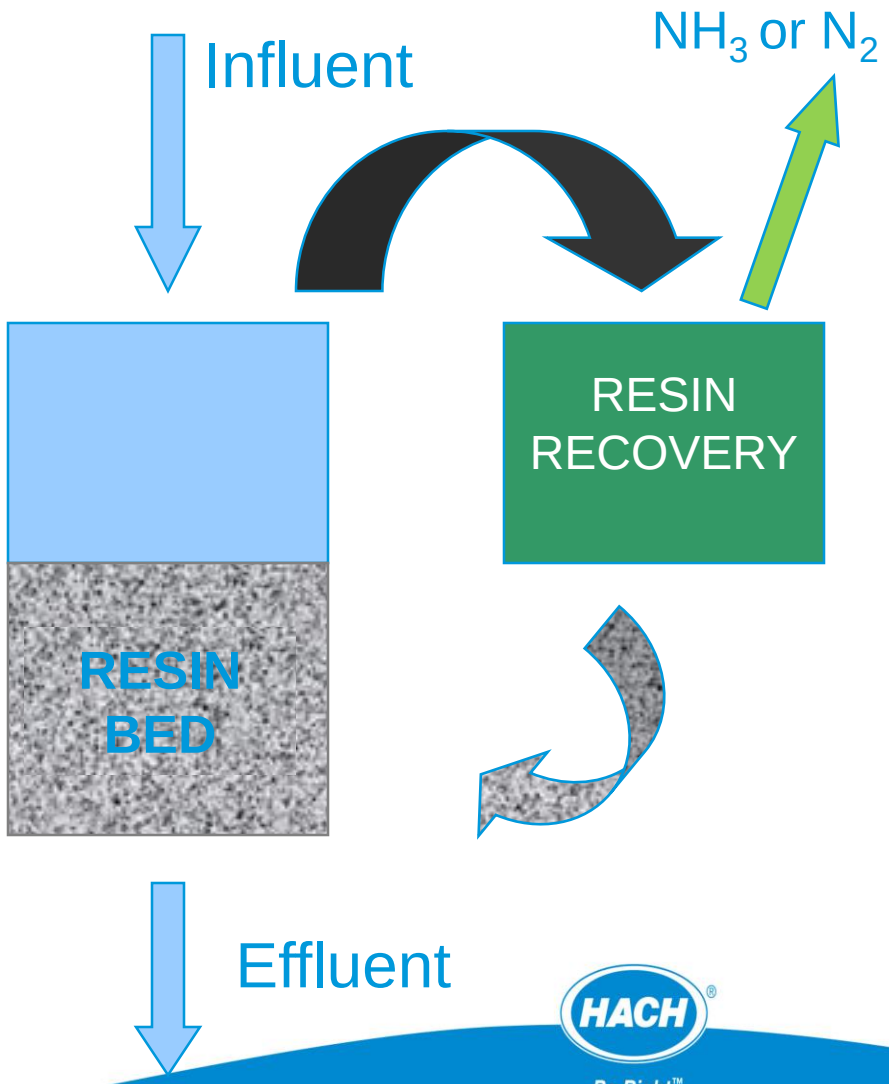
ION EXCHANGE

Nitrogen removal process involves passing ammonia-laden wastewater downward through a series of columns packed with natural or synthetic ion exchange resin.



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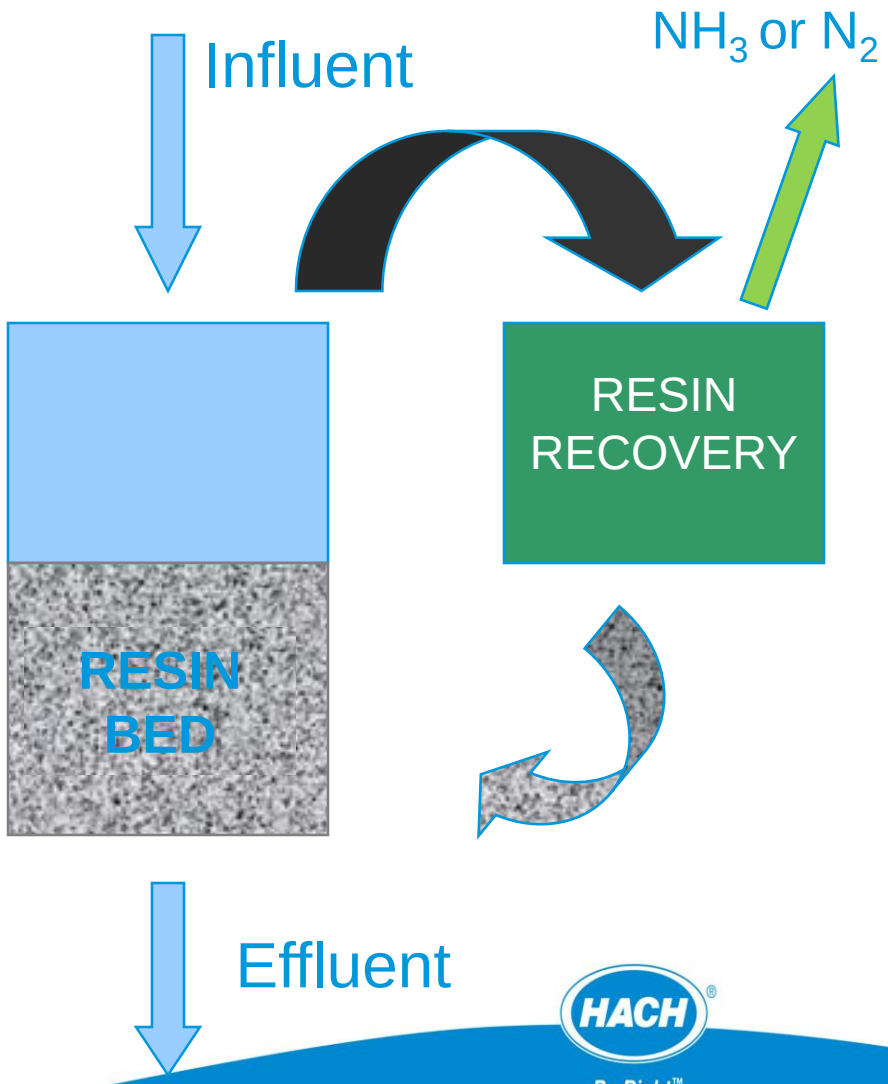
ION EXCHANGE

- Ammonium ion adheres to or is adsorbed by the resin. When the resin loses its ammonium ion adsorptive capacity, it is removed from the treatment scheme and washed with lime water.
- This step converts the captured ammonium ions to ammonia gas



AMMONIA STRIPPING

- Ammonium (NH_4) is converted to ammonia gas (NH_3) by raising pH levels
  - 10.5 to 11.0 pH
- Blowers force fresh air through ammonia and water mixture
- Ammonia gas is ‘stripped’ from the water droplets

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NUTRIENT REMOVAL: TAKE HOME MESSAGES

- Biological nutrient removal is simple: all systems use anaerobic, anoxic, and aerobic zones
- Instrumentation is critical to operating a nutrient removal system
- Understanding levels of nutrients can help optimize the process and save money

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NITROGEN
LAB MEASUREMENT AND TESTING

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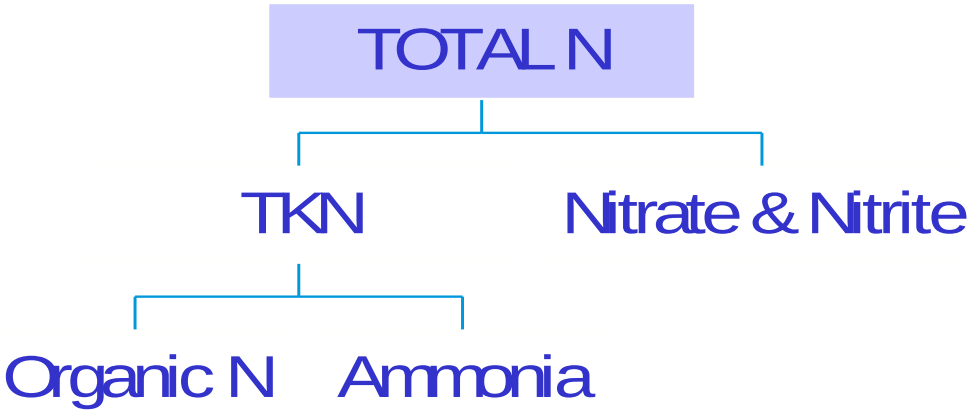
NITROGEN: WHY MONITOR?

- Why monitored in municipal wastewater?
  - Regulatory purposes
  - Plant efficiency
- Why monitor in industrial wastewater?
  - Regulatory purposes
  - Process efficiency
  - Must “fertilize” the microorganisms

FORMS OF NITROGEN

- Inorganic Nitrogen
  - Ammonia, NH_3
  - Ammonium, NH_4^+
  - Nitrate, NO_3^-
  - Nitrite, NO_2^-
  - Nitrogen gas, N_2



- Organic Nitrogen
  - Organic nitrogen is found in living organ
    - Proteins
    - Peptides
    - Nucleic acids (DNA, RNA)
    - Urea
  - Also found in decaying dead organisms

NITROGEN MEASUREMENT

- Inorganic nitrogen changes forms by the processes of nitrification and denitrification.

- Nitrification:
  - Ammonia → Nitrite → Nitrate

- Denitrification:
  - Nitrate → Nitrite → Nitrogen Gas

AMMONIA (NH3) / AMMONIUM (NH4+)

- Why Test?
  - WW Process Control: An excellent indication of the performance of aeration basin's ability to oxidize ammonia to nitrite/nitrate (typically looking at the removal of ammonia) – many nitrogen compounds take longer to oxidize than many organics and some facilities control their aeration basins based on ammonia oxidation
  - Required on WW Permits: Ammonia is a common regulated parameter on NPDES permits
  - Ammonia (NH_3) can be toxic to aquatic life.
- Occurs naturally due to breakdown of organic nitrogen compounds in water.
- Which species is predominate in WW?
  - Depends on pH and temp of water

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

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LAB METHODS FOR ANALYSIS

Ammonia Nitrogen (NH_3-N)

- Nessler Method* (with distillation)
- Salicylate
- Salicylate TNTplus*
- NH_4^+ Ion Selective Electrode
- NH_3 – Gas Sensing Electrode*

*EPA Approved or Accepted

Traditional Methodology

- Distillation
  - Specialty glassware: preparation, clean-up
  - Time consuming: At least 20 minute distillation
- Ammonia determination by titration, ISE, or Colorimetry
  - May contain mercury (Nessler Method)
  - ISE upkeep is very labor intensive

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TNT+ CHEMISTRY

- Barcoded vials
  - Automatically detects correct method
- Pre-measured reagent
  - Just add sample
- 10 Measurements
  - Eliminates outliers and improves results

Ammonia Method

- Reduced volumes may eliminate need for distillation
- Only 0.5 mL sample required
- ~ 15 minute total analysis time, minimal “hands-on” time
- Does not contain mercury
  - Represents savings of over $800/year based on running one test & blank 5 days a week (68% cost savings)

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SELECTING THE RIGHT AMMONIA METHOD FOR YOUR LAB

Both Colorimetric and ISE methods are typically approved

- How many samples are you running?
- How much time do you spend testing for ammonia?
  - Creating standards, Calibration of probe, Changing membranes
- What resources do you have available – lab techs and operators?
- Process control or compliance monitoring?

Individual facility needs are important to consider when selecting the right measurement method!

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NITRATE (NO3-)

- Present naturally in surface and ground waters
- Essential nutrient for plants
- End step of the nitrification process

  $NH_3 \Leftrightarrow NO_2^- \Leftrightarrow NO_3^-$

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METHODS FOR NITRATE ANALYSIS

- Nitrate Nitrogen (NO_3-N)
  - Ion Selective Electrode*
  - Chromotropic Acid
  - Cadmium Reduction
  - UV absorbance
  - Dimethylphenol TNTplus

*EPA Approved or Accepted

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METHODS FOR NITRITE ANALYSIS

- Intermediate step of the nitrification process

  $NH_3 \Leftrightarrow NO_2^- \Leftrightarrow NO_3^-$

- Nitrite is not highly stable
  - Tends to be either oxidized to nitrate or reduced to ammonia

- Nitrite Nitrogen
  - Diazotization*
  - Ferrous Sulfate

*EPA Approved or Accepted

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METHODS FOR TKN ANALYSIS

Total Kjeldahl Nitrogen

- Ammonia plus organic nitrogen
- Typically all nitrogen in influent
- Digestion converts “all” organic to ammonia
- Nessler method to measure ammonia

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TOTAL KJELDAHL-NITROGEN (TKN)

Traditional TKN methods can be:

- **Labor intensive**
  - Up to several hour digestion time
  - Glassware prep/cleanup
- **Dangerous**
  - High temperature digestion
  - High volumes of concentrated acids
  - Hazardous waste generating (mercury catalyst)
- **Costly**
  - $20k+ for semi-automated system
  - $50/test for outsourcing

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NEW SIMPLIFIED TKN METHOD

$$s\text{-}TKN = Total\ N - (NO_3^-\text{-}N + NO_2^-\text{-}N)$$

Everything needed to measure TKN in one box

- Eliminates the use of hazardous mercury
- Reduces operating expenses with costs under $4 per test— annual savings of over $550 compared to outsourcing TKN on a monthly basis
- Minimizes training and equipment requirements by offering a test that anyone can perform
- Takes ~ 1 hour total analysis time with minimal hands-on time
- 3 Tests in one: TKN, TN, and NO_3^- + NO_2^-

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LAB METHODS FOR ANALYSIS

Total Nitrogen

- All nitrogen present
  - Ammonia + Nitrate + Nitrite + Organic Nitrogen
- Digestion with an alkaline persulfate soln
  - Oxidizes everything to nitrate
  - Measured with chromotropic acid method

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WHY IS PHOSPHORUS IMPORTANT?

- Essential to the growth of organisms
- Limiting factor for photosynthesis
- Excess quantities can cause eutrophication

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PHOSPHORUS MEASUREMENT

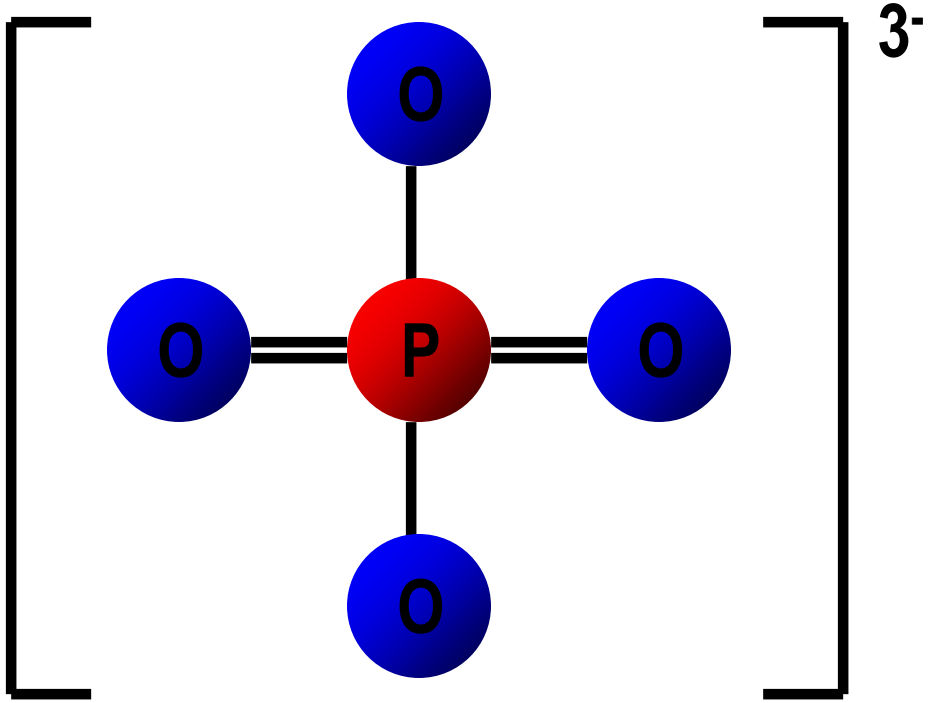
- Phosphorus is a nutrient, essential to growth.

- Phosphorus occurs in natural waters and wastewaters primarily in the form of phosphate.
  - Orthophosphate
  - Condensed phosphate
  - Organic phosphate
  - *Only orthophosphate (reactive) can be measured directly*

HOW DOES PHOSPHORUS OCCUR?

The chemical formula for the phosphate ion is PO_4^{3-}

- Orthophosphate
- Reactive phosphate



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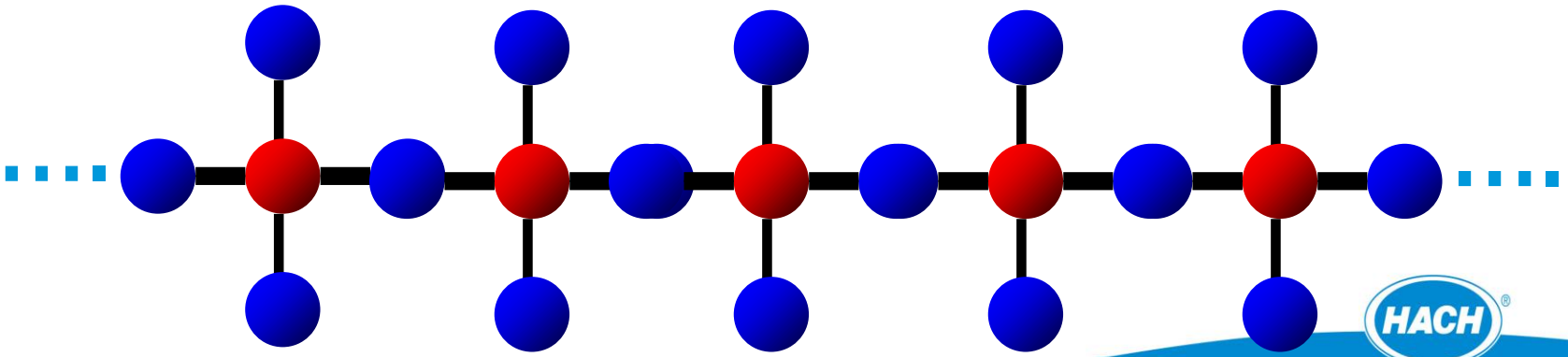
HOW DOES PHOSPHORUS OCCUR?

- Condensed phosphate
  - Metaphosphate
  - polyphosphate
  - pyrophosphate



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LAB METHODS FOR ANALYSIS

- Orthophosphate
  - Ascorbic Acid (PhosVer3)*
    - 0 – 2.50 mg/L PO_4^{3-}
    - “Blue method”
  - Molybdovanadate
    - 0 – 45.0 mg/L PO_4^{3-}
    - “Yellow method”

*EPA Approved or Accepted

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LAB METHODS FOR ANALYSIS

- Total Phosphorus
  - Sum of Ortho, Condensed & Organic
  - Acid persulfate lab method*
    - Digests everything to orthophosphate

* EPA Approved or Accepted

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ANALYSIS OF TOTAL PHOSPHORUS

1. Requires Acid or Persulfate Digestion
   - Boil the sample with acid for 30 minutes to break the condensed phosphate chains into orthophosphate
   - Hot plate or Test N Tubes
2. Neutralize with hydroxide and perform the most suitable orthophosphate test
3. Perform an orthophosphate test on an undigested portion of sample
4. **Final Results:** Subtract the orthophosphate results (undigested) from those of the digested sample.

Digested – Undigested =

mg/L Condensed Phosphate

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ULR PHOSPHORUS PROCEDURE

- The detection limit for the LR TNT+ method is 50 µg/L, which may be too high for some state's nutrient standards plans to limit surface water eutrophication.

- Ultra Low Range Total & Reactive Phosphorus
  - Concentration range is 10 to 500 µg/L PO_4-P.

- Instrumentation:
  - DR3900, or DR6000
  - TNT 843: TNT+ phosphorus reagents
  - DRB200 Digital Reactor Block for TNT+
  - 5-cm semi micro cuvette, PN LZP341

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ULR PHOSPHORUS TEST

Range:10 to 500 µg/L PO_4- P

- Application note with procedures available - Lit # 2097
- User entered calibration is required
  - Hach supplies you with all information for this calibration curve.

- Approved for Reporting?
  - Although same Ascorbic Acid chemistry…different sample cell path length
  - Must check with your state regulator

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ASKING THE RIGHT QUESTIONS

Results help answer fundamental questions:

- Regulations or Permits
  - Am I in compliance?
- Process control
  - Is my plant operating correctly?
  - Is it time for preventative maintenance?
- Problems and Troubleshooting
  - What is wrong with my system?
  - How can I fix it?

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ADDITIONAL SLIDES

REGULATORY DEFINITIONS

EPA METHOD APPROVALS
EPA REFERENCE METHOD: 365.2

Hach Method 8048 **Reactive Phosphorus (Orthophosphate)**

PhosVer 3 (Ascorbic Acid) Method (Also TNT+ Method 10209)

USEPA Accepted Method for reporting wastewater analyses – (Standard Methods 4500 P-E)

- EPA Letter dated March 1, 1999

Hach Method 8190 **Total Phosphorus**

PhosVer 3 (Ascorbic Acid Method) with Acid Persulfate Digestion Method (Also TNT+ Method 10210)

USEPA Approved for Reporting Wastewater Analyses (Standard Methods 4500 P-E)

- EPA Letter dated March 1, 1999

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DEFINITIONS – USEPA APPROVED

USEPA Approved Methods:

The USEPA has evaluated and approved new technological methods developed by Hach Company. The methods have undergone a nation-wide inter-laboratory validation study that was submitted to the EPA for approval. All USEPA-Approved methods are cited in the Federal Register and compiled in the Code of Federal Regulations at 40 CFR 136 and CFR 141.

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DEFINITIONS – USEPA ACCEPTED

***USEPA-Accepted Methods*:**

The USEPA has reviewed Hach methods and accepted them for use in compliance monitoring. These methods are defined by USEPA as **Acceptable** versions of previously approved methods. These methods are generally not published in the *Federal Register* or in the *Code of Federal Regulations*. The USEPA documents Acceptance in a formal letter to Hach Company. A facsimile of the USEPA-Acceptance letter is available upon request.

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DEFINITIONS: USEPA EQUIVALENT

Hach Equivalent Methods:

All USEPA-Approved methods have specification criteria built into their procedural steps. When an approved or accepted EPA method has been packaged by Hach from the EPA reference method as a test method that meets or exceeds these specification criteria, these methods are deemed to be equivalent for use in EPA compliance monitoring. EPA does not normally review "Equivalent Methods" or issue equivalence letters of packaged reference methods. Hach maintains the formulation, procedure, and analytical data demonstrating equivalency and is available to end users and regulatory authorities upon request.

EPA LETTER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 11 1999

OFFICE OF WATER

David Gustafson
Coordinator of Regulatory Affairs
Hach Company
PO Box 389
Loveland Colorado 80539-0389

Dear Mr. Gustafson:

We are pleased to inform you that in the judgement of the Analytical Methods Staff (AMS), Hach Method 8190 [version 1.0, August 1998] for determination of total phosphorus (ATP case No. N95-0015) and Hach Method 8048 [version 1.0, August 1998] determination of orthophosphate (ATP case No. N95-0014) are acceptable versions of EPA Method 365.2, approved at 40 *Code of Federal Regulations* (CFR) part 136 for use in National Pollution Discharge Elimination System (NPDES) compliance monitoring.

AMS and the Office of Ground Water and Drinking Water (OGWDW) also have determined that Hach Method 8048 [version 1.0, August 1998] for determination of orthophosphate (ATP case No. D95-0011) is an acceptable version of EPA Method 365.1, approved at 40 CFR part 141 National Primary Drinking Water Regulation (NPDWR) compliance monitoring.

We appreciate Hach's continued interest in the development of environmental compliance monitoring methods. If you have any questions regarding this determination or review of your applications, please contact Maria Gomez-Taylor (AMS) at 202/260-1639 or Herb Brass (OGWDW) at 513/569-7936 at your convenience.

Sincerely,

William A. Telliard, Director
Analytical Methods Staff
Engineering and Analysis Division (4303)

for Herbert J. Brass
Team Leader, Analytical Methods
Office of Ground Water and Drinking Water
(MS 140- Cincinnati)

cc: USEPA Regional Administrators (all Regions)
Quality Assurance Managers (all Regions)
Water Management Division Directors (all Regions)
Maria Gomez-Taylor, USEPA, EAD
James Westrick, USEPA, TSC

Notice of Equivalency of TNT Plus® 843 and 844 Test Vials for Regulatory Compliance Reporting

To Users of the TNT Plus 843 and 844 Phosphorus Test Vials for Regulatory Reporting:

This document and its attachments are being provided as verification of equivalency when using Hach TNT Plus 843 and 844 Phosphorus Test Vials for regulatory reporting purposes. Hach TNT Plus 843 and 844 phosphorus test vials are formulated to the standards of the EPA accepted Hach TNT® 8048 and 8190 phosphorus test vials and meet all of the performance criteria of EPA Method 365.2 and Standard Method 4500-P E for wastewater.

The U.S. Environmental Protection Agency requires that supporting data of an equivalent method (minor modification or re-packaging of a EPA approved method) used for compliance reporting purposes be available for inspection. The attached side-by-side comparative study provides verification of equivalence to the EPA approved method for phosphorus, and may be used for discussions with your regulatory compliance officer.

Questions regarding this document and its accompanying side-by-side study should be directed to Dr. Gary B. Jackson, Hach Director of Regulatory Affairs.

PHOSPHOROUS AND NUTRIENT REMOVAL

For Reporting and Process Control

Thank You