

Phosphorus Removal

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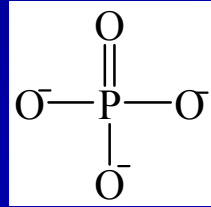
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Forms of P

- Note: it is phosphorus, not phosphorous!
- Almost all P is phosphate (PO_4^{3-})
 - Non-phosphate-P (e.g., C-P bond) is manmade (pesticides, nerve gas)
- So all P has same oxidation state
 - no oxidation reduction reactions
- Usually expressed as phosphate-P, but sometimes as phosphate
- 1 mg phosphate-P = $95/31 = 3.06$ mg phosphate

Types of Phosphates

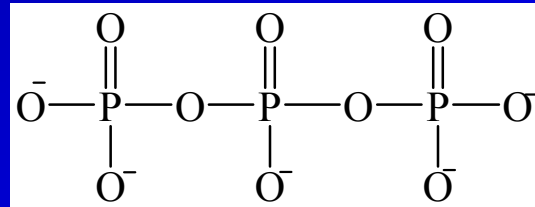
orthophosphate



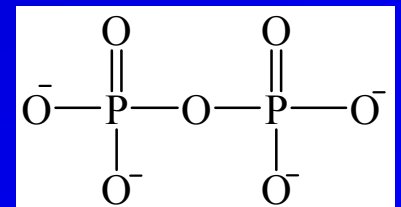
condensed phosphates

polyphosphates (linear)

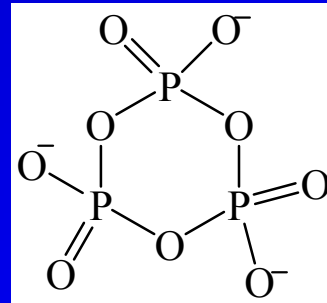
tripolyphosphate



pyrophosphate



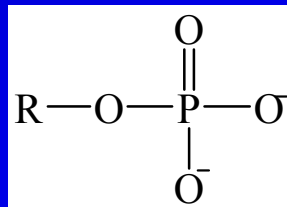
metaphosphates (cyclic)



trimetaphosphate

organic phosphates

R = organic



e.g., nucleotides, phospholipids,
sugar phosphates

Forms of P in Raw Sewage (mg/L P, approx.)

<u>old</u>	<u>now</u> *	
5	4	orthophosphate
3	0	tripolyphosphate (detergents)
1	0	pyrophosphate (breakdown of tripoly.)
1	1	organic phosphates
<u>0</u>	<u>1?</u>	hexametaphosphate (corrosion control)
10	5	total

* Phosphates voluntarily (mostly) removed from detergents.

P in Wastewater

- Phosphates added to water for
 - Corrosion (and scale) control in drinking water (sodium hexametaphosphate, ~ 1 mg/L)
 - industrial water softening
 - boiler waters
 - cleaning compounds
- In sewage
 - 1.2 lb/capita/yr from human and food waste

P in Secondary Effluent

- Usually now 3-4 mg/L
- Mostly orthophosphate
- <1 mg/L organic

2-3% of 20 mg/L = 0.4 to 0.6 mg/L P

Note: this means tertiary treatment (sand filter)
likely needed if limit is ≤ 0.5 mg/L

Methods of P Removal (Advanced Wastewater Treatment)

- Chemical Precipitation
- Biological
 - Assimilation
 - Enhanced Biological P Removal (EBPR)

Chemical Precipitation

- Precipitate with
 - lime - $\text{Ca}(\text{OH})_2$
 - alum - $\text{Al}_2(\text{SO}_4)_3$ – most common method
(or other aluminum compounds)
 - iron - FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$
- Add
 - before primary
 - in aeration tank
 - before secondary settling
 - separate unit process after secondary treatment
- Polymers may be added to enhance removal

Reactions Form Insoluble Phosphates

- Reaction with lime:



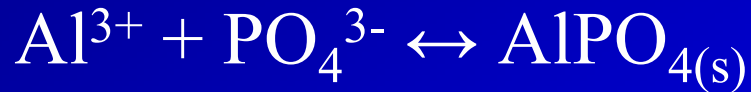
- But when add lime to water:



- So required dose of lime depends on alkalinity
 - once carbonate used up, get P removal

Aluminum and Iron

- Reactions:



- But in practice

- takes ~2 moles Al or Fe per mole P

- e.g., $\text{Al}^{3+} + 3\text{OH}^- \leftrightarrow \text{Al}(\text{OH})_{3(s)}$

Excess Sludge Production Example 1 (worst case? - from Metcalf & Eddy, 2003)

- Lime addition to primary treatment
- Assume

P: 10 mg/L \rightarrow 0.5 mg/L

Influent total suspended solids (TSS) = 220 mg/L

TSS removal: 60% \rightarrow 85%

Utilize 400 mg/L of $\text{Ca}(\text{OH})_2$

1000 m³/d flow (0.26 MGD)

80 mg/l Ca^{2+} , 10 mg/L Mg^{2+} , hardness 241 mg/L

Example 1 (cont.)

Sludge (dry weight) produced, kg/d

132 without lime

55 from additional TSS removed

51 $\text{Ca}_5(\text{PO}_4)_3\text{OH}$

24 $\text{Mg}(\text{OH})_2$

540 CaCO_3

802 total primary sludge

670 new sludge

615 new chemical sludge

236 kg/d typical sludge production assuming 1 ton/MG

$615/236 = 261\%$ increase

Example 2: Best Case?

- Alum addition after secondary treatment
- Same assumptions except
 - P: 3 mg/L \rightarrow 0.5 mg/L
 - Alum added at 1.7:1 molar ratio of Al:P
- Production of sludge (kg/d, dry weight):
 - 9.8 AlPO_4 sludge
 - 6.5 Al(OH)_3 sludge
 - 16.3 total chemical sludge
 - $16.3/236 = 7\%$ increase
 - Sludge aluminum content = 1.7%

Chemical Treatment

- Advantages
 - reliable
 - low levels of P in effluent possible
 - Retrofit for existing plant likely possible
- Disadvantages
 - cost of chemical feed system
 - cost of chemicals
 - substantial additional sludge production
 - chemical sludge reuse or disposal may be more difficult
 - may need to adjust pH
- Problem
 - digestion (especially anaerobic) may re-release P

Assimilation

- Cells are 2-3% P (dry weight)
- Removing sludge removes P
- Why doesn't P ↓ to 0?
 - Because C limiting, not P
- Could add C
 - Produce more sludge, so remove more P
 - 43 mg methanol/mg P removed
 - ~40 mg sludge produced/mg P removed
- Not practical!

How to Add C without Adding Organics?

- Use autotrophs – fix CO₂
- Which group?
 - Photoautotrophs
- Examples
 - Ponds with algae and/or plants (e.g., duckweed, water hyacinths)
 - Constructed wetlands (marshes)
 - Land treatment (grasses)

N or P Limiting?

- When P was high (10 mg/L), N was limiting
- Now?
 - Cell requirement for N:P \approx 5:1
 - Wastewater?
 - if 30:5 = 6:1; P-limited
 - if 20:5 = 4:1; N-limited
 - if 20:4 = 5:1; both

Enhanced Biological Phosphorus Removal

- Uptake beyond need for balanced growth
 - Originally called “luxury uptake” (wrong!)
- First noted:
 - 1959 in India
 - 1961 in USA
 - unintentional
 - conventional activated sludge, high loading

(activated sludge is most common aerobic wastewater treatment process)

Levin & Shapiro, 1965

- Pioneering work
- Gil Levin (the grad student)
 - later became president of Biospherics (now Spherix)
 - developed PhoStrip process

Early Findings for Activated Sludge

- For EBPR: must be anaerobic, then aerobic
 - P released under anaerobic conditions
 - P then taken up under aerobic conditions

e.g., 5 mg/L (influent) → 15 mg/L (anaerobic) → < 1 mg/L (aerobic)

- Biological removal or biologically mediated chemical precipitation?
 - ~1980 – largely agreed it was biological

Fuhs & Chen, 1975

- Studied P-removing sludge and found:
 - many bacteria could store P as polyphosphate
 - P storage uncommon in non-EBPR sludges
 - polyphosphate stored in granules
 - stain with Neisser stain
 - called “metachromatic” or “volutin” granules
- Granules:
 - decrease under anaerobic conditions
 - increase under aerobic conditions

Organisms

- Originally identified as *Acinetobacter sp.*
 - later turned out this was incorrect
- Now generically called “phosphate accumulating organisms” (PAOs)
 - Some competing organisms accumulate glycogen (GAOs) instead of P
- Pure cultures:
 - if fed acetate, show similar behavior for P release and uptake
 - cannot utilize glucose
- PAOs require oxygen for growth (aerobic)

Maximum P Accumulation

- Fuhs and Chen reported 20%
 - never reproduced
 - would not share their culture
- Generally accepted max: ~7%
 - Note: 7% P \approx 20% PO_4^{3-}

Summary of Initial Findings

- All plants removing P were conventional activated sludge with long plug flow reactors, high loadings; influent end apparently anaerobic, and P released
- P release occurs anaerobically if sufficient BOD present (fermentation products formed)
- Excess P uptake occurs when DO is present if P release occurred previously
- PAOs store P internally as polyphosphate
- Anaerobic/aerobic cycling is essential
- Anaerobic/aerobic cycle selects for PAOs, which are aerobes

Explanation?

Explanation of EBPR

- P storage is not “luxury uptake” of the nutrient
- It is energy storage
- Polyphosphate probably pre-dated ATP as energy carrier in early microbes (high energy bonds)
- Anaerobic conditions: PAOs release P from polyphosphate, utilizing the energy for uptake and storage of organics
- Aerobic conditions: PAOs utilize the stored organics, and take up P to produce the polyphosphate for energy storage

Selective Advantage of PAOs

- Under anaerobic conditions:
 - aerobes can't utilize BOD
 - anaerobes ferment BOD; little energy available
 - PAOs take up and store fermentation products
- Under aerobic conditions:
 - aerobes find little BOD left
 - anaerobes inactive
 - PAOs oxidize previously stored BOD
- PAOs selected for by anaerobic conditions:
 - produces fermentation products they need
 - limits competition from aerobes

Example of Energy Availability

- Glycolysis (fermentation):



- Krebs cycle (aerobic):

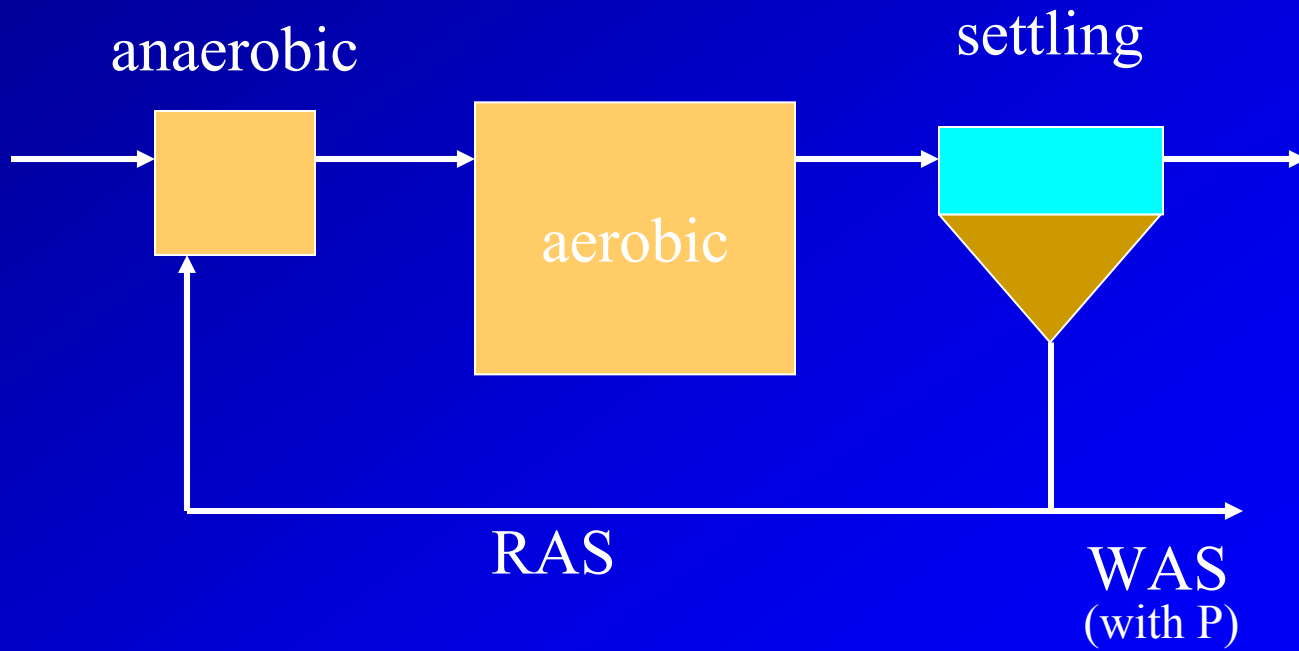


- Total: 22 moles ATP available from 1 mole glucose

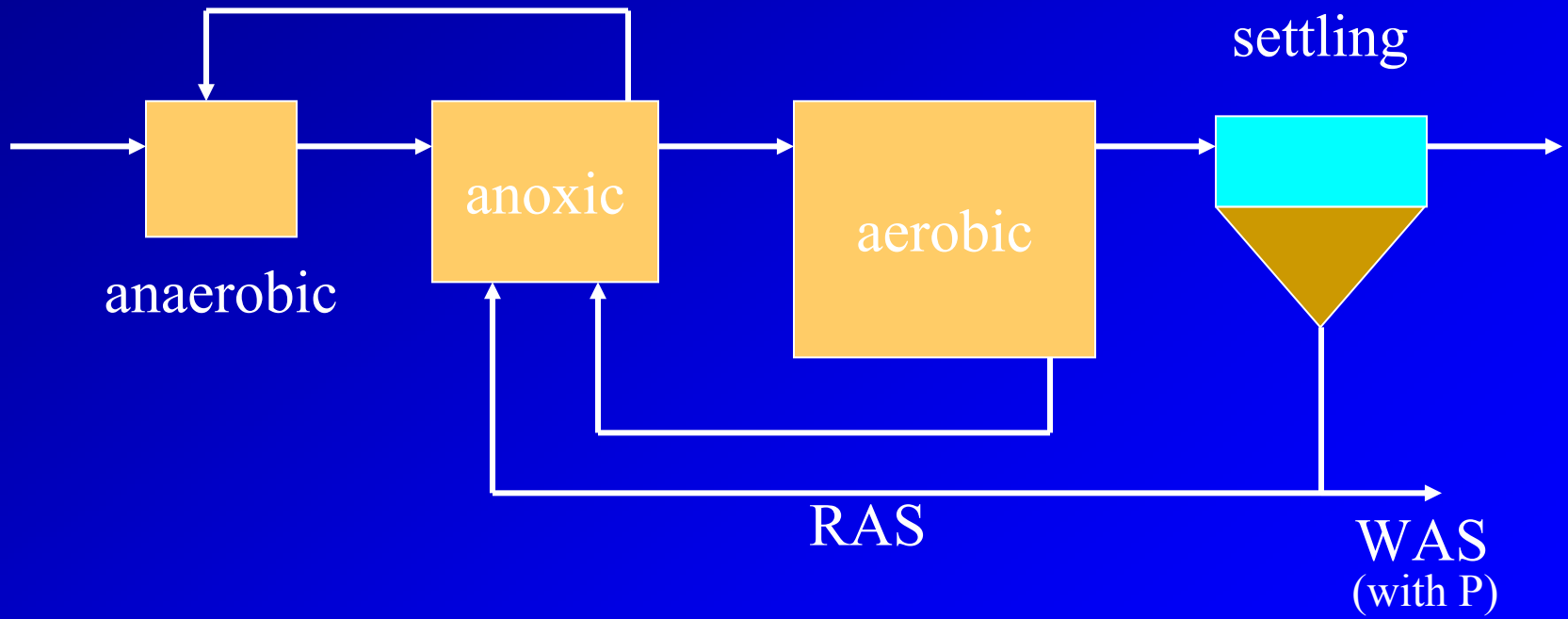
Major Processes

- A/OTM (A²/OTM for N and P removal)
- Bardenpho - J.L. Barnard - N (denitrification) and phosphorus removal
 - Phoredox
 - UCT
- PhoStripTM (may be practical as retrofit)
- Sequencing Batch Reactors (SBRs)
- Oxidation Ditch (e.g., OrbalTM; N and P removal)

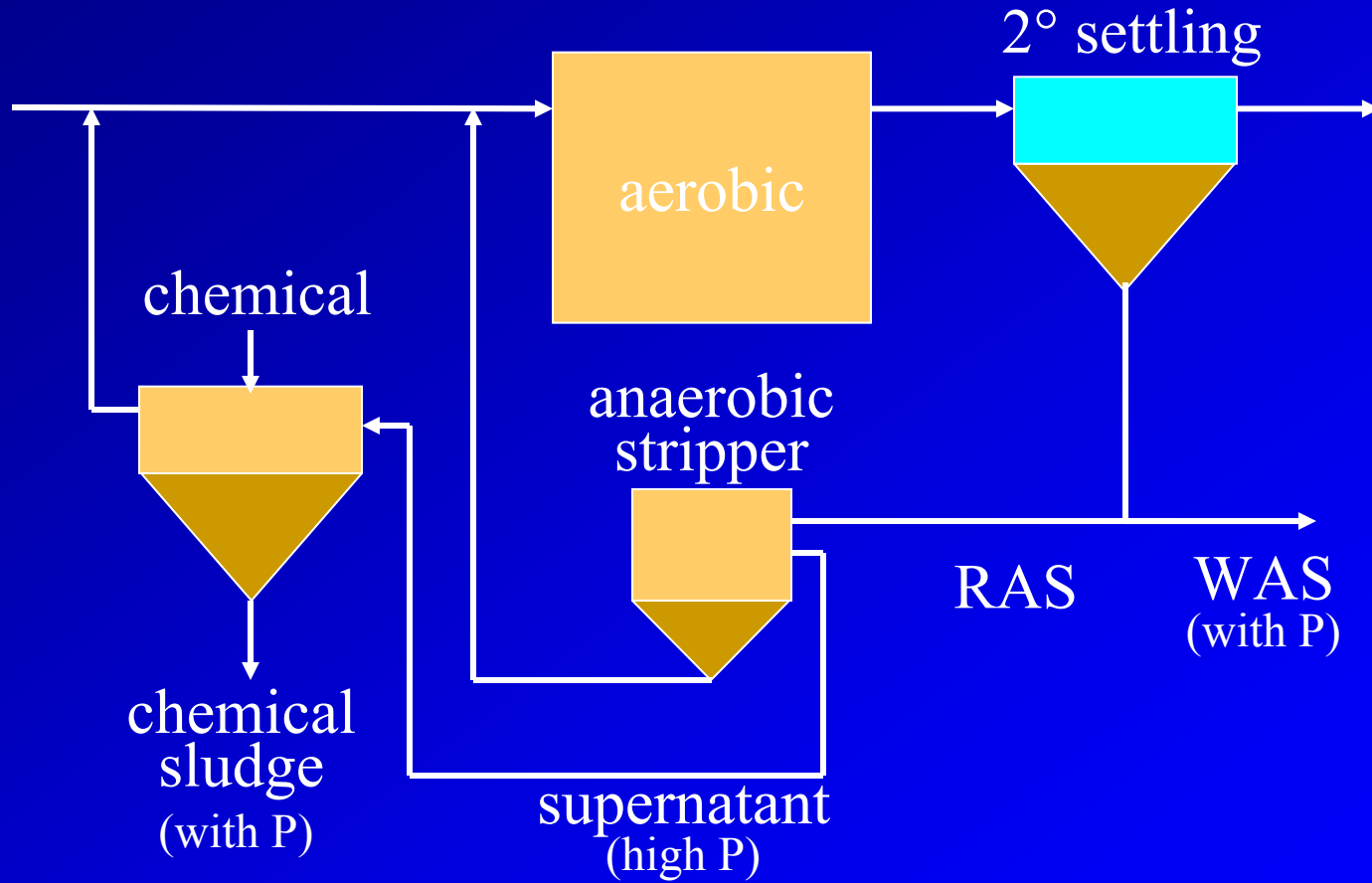
A/O



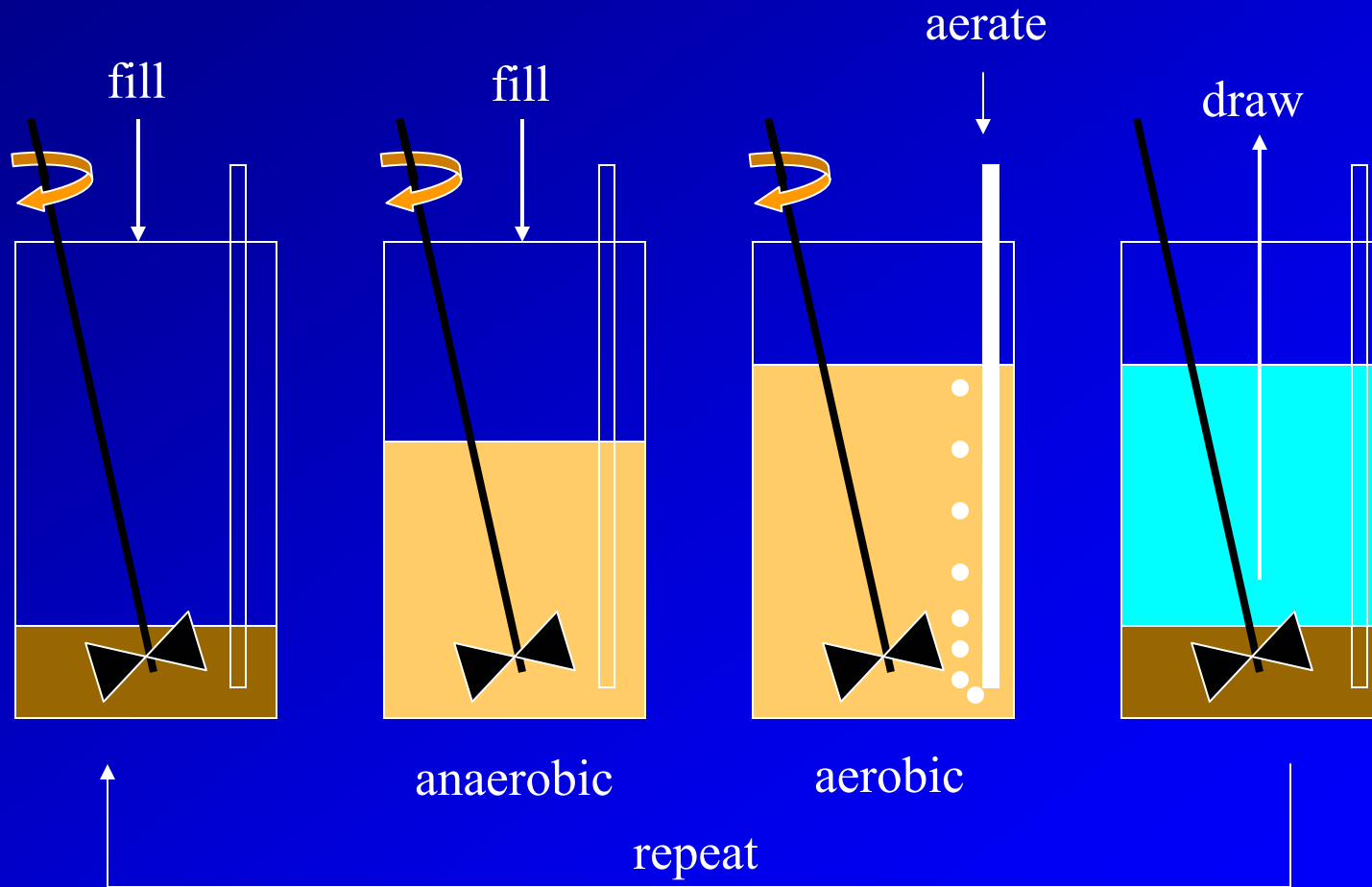
UCT



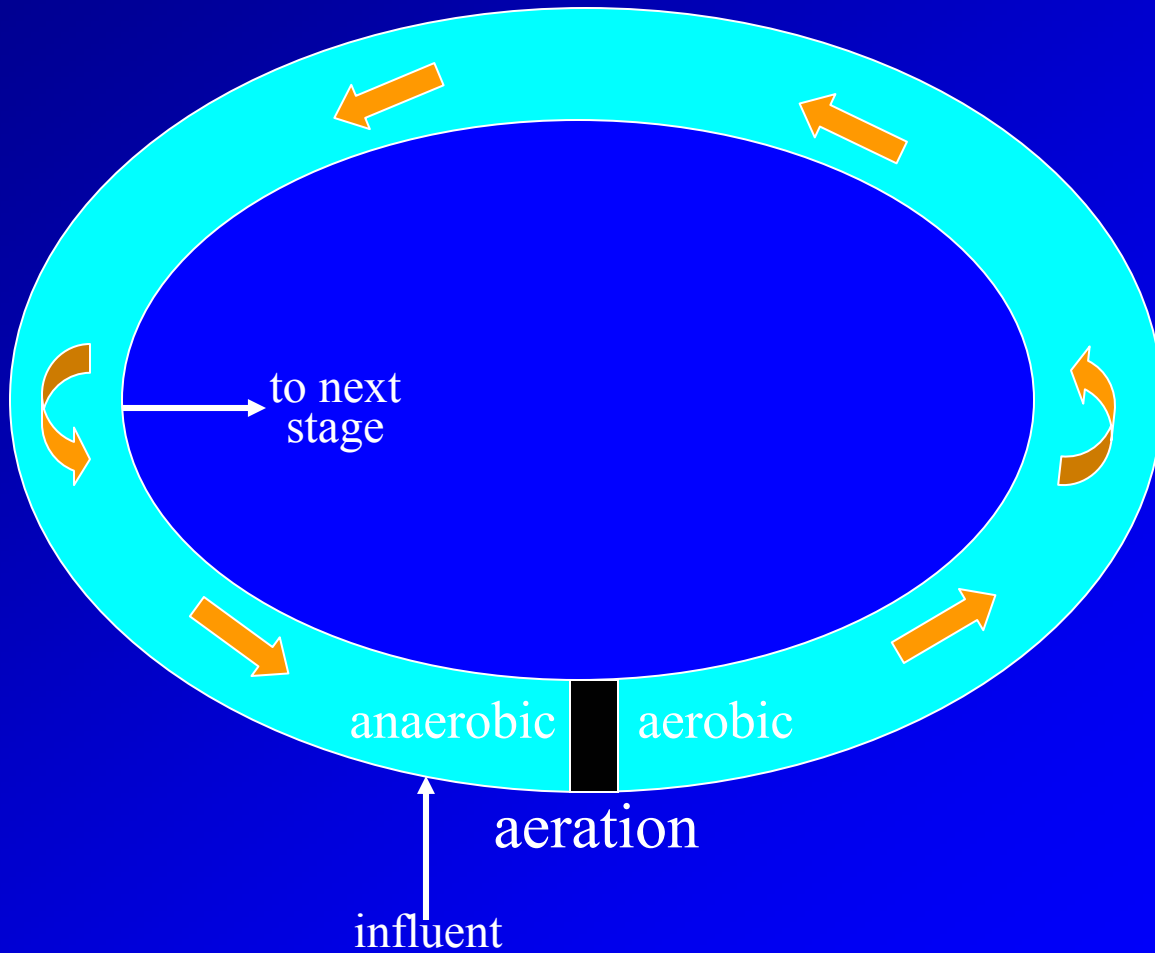
PhoStrip



SBR



Orbal



Advantages and Disadvantages

- Advantages
 - no (or less – PhoStrip) chemical costs
 - no (or less) chemical storage and handling
 - no (or less) chemical sludge disposal
- Disadvantages
 - not as reliable (initially – maybe it is now)
 - limitation – need enough BOD
 - may be difficult to get < 0.1 mg/L consistently
- Problem
 - digestion (especially anaerobic) releases P

Research/Information Needs

- Treatment Plants
 - Present influent/effluent P concentrations
 - Present treatment processes
 - Present sludge handling methods
 - Space limitations
 - Retrofit possibilities
- P Removal Process Reliability for NJ Plants
- Costs?