UTILIZING ORP IN WASTEWATER TO IMPROVE PROCESS EFFICIENCY

ORP in Wastewater: *A Magic Wand?*

WHAT IS ORP WITH REGARD TO WASTEWATER?

- ORP Oxidation Reduction Potential
- Commonly Misunderstood Science
- In Wastewater often considered a mystery or “black magic”
- Trending versus an exact value
- Used in Biological Nutrient Removal
- Used in Chlorination or Dechlorination

ORP THEORY

Oxidation Reduction Potential:

- An indication of a solution's ability to oxidize or reduce another solution.
- Systems capacity to release or accept electrons from chemical reactions.
- Oxidizing systems are accepting electrons and
- Reducing systems are releasing electrons.
- Changes with intro of new "species" or change in concentration of existing species.

-or-

The sum of all the potentials in the water

ORP- POINTS OF CONFUSION

- ORP is an old test parameter, it predates the electronic DO meter
- Readings should not be taken as absolute values but ranges
- Those using ORP must become comfortable with ranges and relative values.
- Two meter, side by side will have different values.

- There are three reference electrodes, Ag/AgCl, Standard Hydrogen, and Calome.
  - ORP (E_C) +45mV = ORP ($E_{Ag/AgCl}$) +210mV = ORP (E_H)
  - Most wastewater probes are Ag/AgCl
  - Researchers often use the Standard Hydrogen probe and report values 210 mV higher

HOW IS ORP MEASURED?

Nernst Equation

$$E = E_0 + kT \log \frac{[\text{Oxidants}][H^+]}{[\text{Reductants}]}$$

PH EFFECT ON ORP

$$E = E_0 + kT \log \frac{[\text{Oxidants}][H^+]}{[\text{Reductants}]}$$

- E increases as $[H^+]$ increases {pH decreases}
- E decreases as $[H^+]$ decreases {pH increases}

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TEMPERATURE EFFECT ON ORP

$$E = E_0 + kT \log \frac{[\text{Oxidants}][H^+]}{[\text{Reductants}]}$$

- E increases as temperature increases.
- E decreases as temperature decreases.

ORP MEASUREMENTS

- ORP is not an exact measurement.
  - A pH of 7 is 7
  - A DO of 8mg/L is 8mg/L
  - But an ORP of -100mV is in the range of -50mV to -150mV

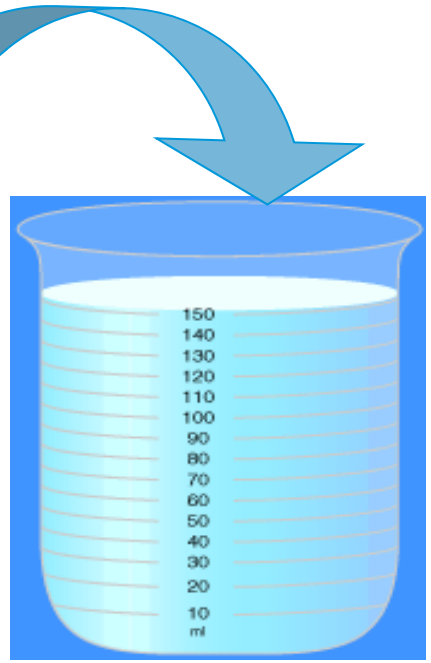
- The real strength of ORP is that it gives us usable operational data when DO is 0.0 mg/L
  - Biological activity does not stop when DO is zero, but it does change
  - ORP helps us determine what which bacteria are active and what the expected results should be

- ORP enlightens when DO = 0.0 mg/L

ORP THEORY

Example: Chlorination/Dechlorination

Add chlorine (strong oxidant) to wastewater effluent



ORP value moves in a positive direction (ie: 700mV)

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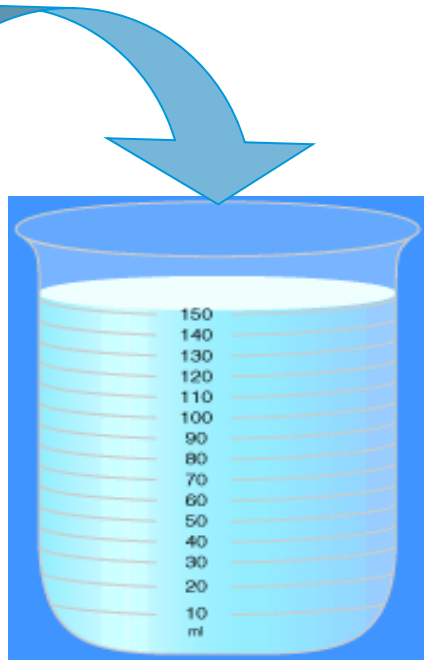
ORP THEORY

Example: Chlorination/Dechlorination

Add bisulfite (strong reductant) to wastewater effluent



ORP value moves in a negative direction (ie: 0mV)

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COLLECTION SYSTEM MONITORING

- Hydrogen Sulfide formation, beginning at about -50 mV
- Monitoring dosing of oxidizers such as nitrate solutions, permanganate, peroxide
- Monitoring fermentation potentials for phosphorus removal

ORP TO BIOLOGICAL NUTRIENT REMOVAL

Why is oxidation reduction potential important to BNR?

- ORP is a crystal ball: allowing operators to see what is happening in the system
- BNR microorganisms require certain environmental conditions that are best measured through ORP
- ORP is not an exact science – “Close Enough” is good enough
- ORP can be correlated to other parameters

ORP IN BNR

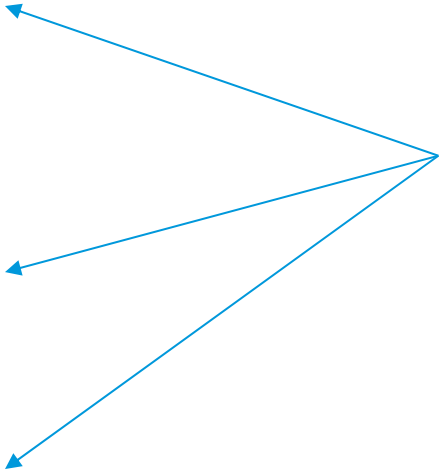
Biological Nutrient Removal

- Using microorganisms to remove nutrients from the wastewater
- In order for bacteria to respire need to donate an electron to a final electron acceptor.
- Combination of anaerobic, anoxic, and aerobic environments

Three Different Habitats

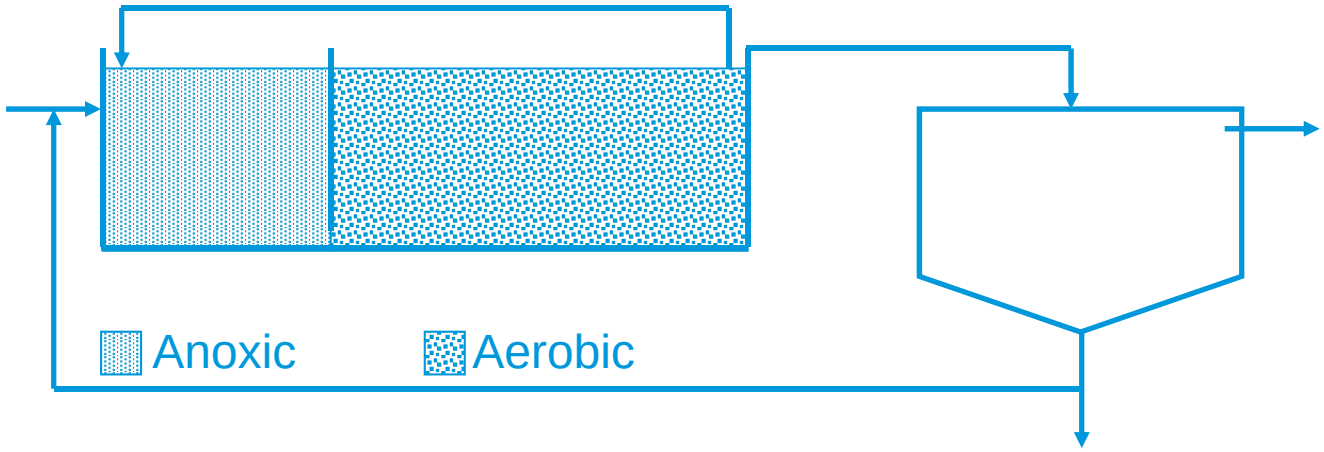
ORP IN BNR

- Anaerobic:
  - No oxygen, no nitrate
  - Sulfate present
- Anoxic
  - No oxygen
  - Nitrate Present
- Aerobic
  - Oxygen present



Electron Acceptors

ORP IN BNR
NITROGEN REMOVAL



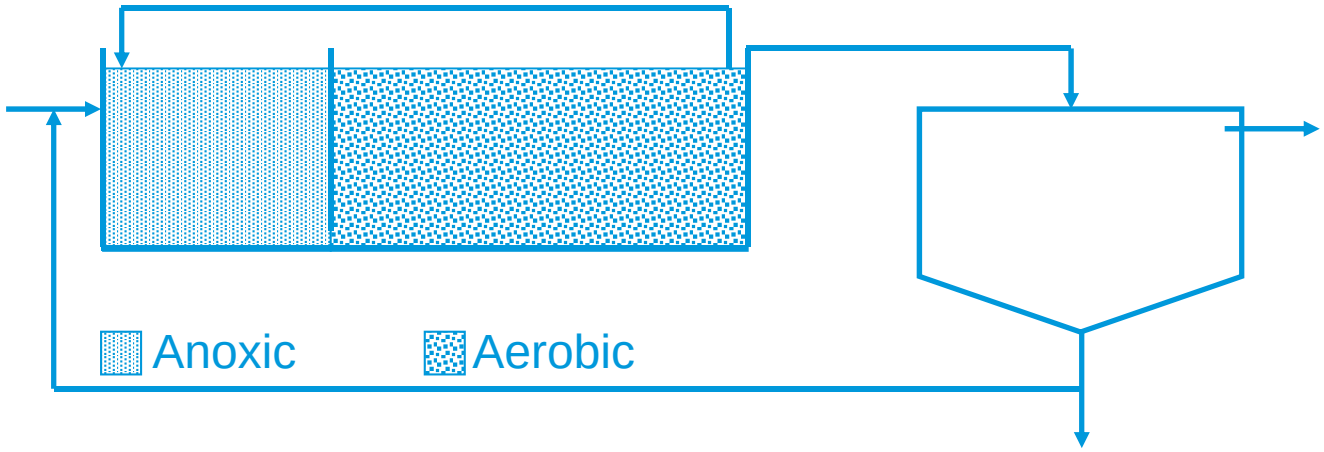
Aerobic zone: ammonia converted to nitrate in the presence of O_2

$$NH_3 \longrightarrow NO_2 \longrightarrow NO_3$$

Anoxic zone: nitrate converted to nitrogen gas without O_2

$$NO_3 \longrightarrow NO_2 \longrightarrow N_2$$

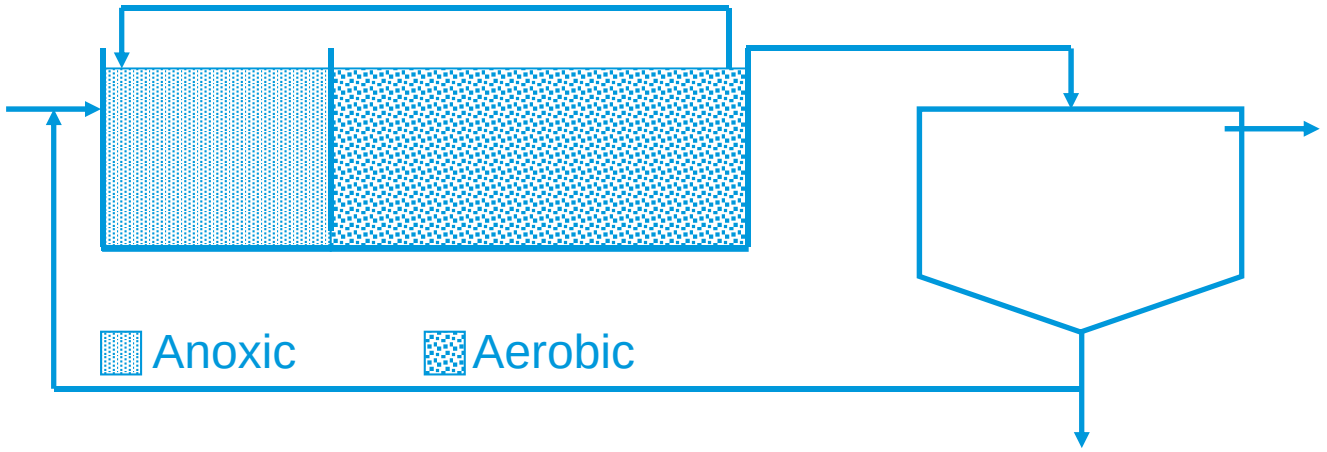
ORP IN BNR
NITROGEN REMOVAL



Can control DO concentrations in aerobic zone, but does that really tell you about denitrification?

What can you do to monitor/control anoxic zone? DO? Nitrate?

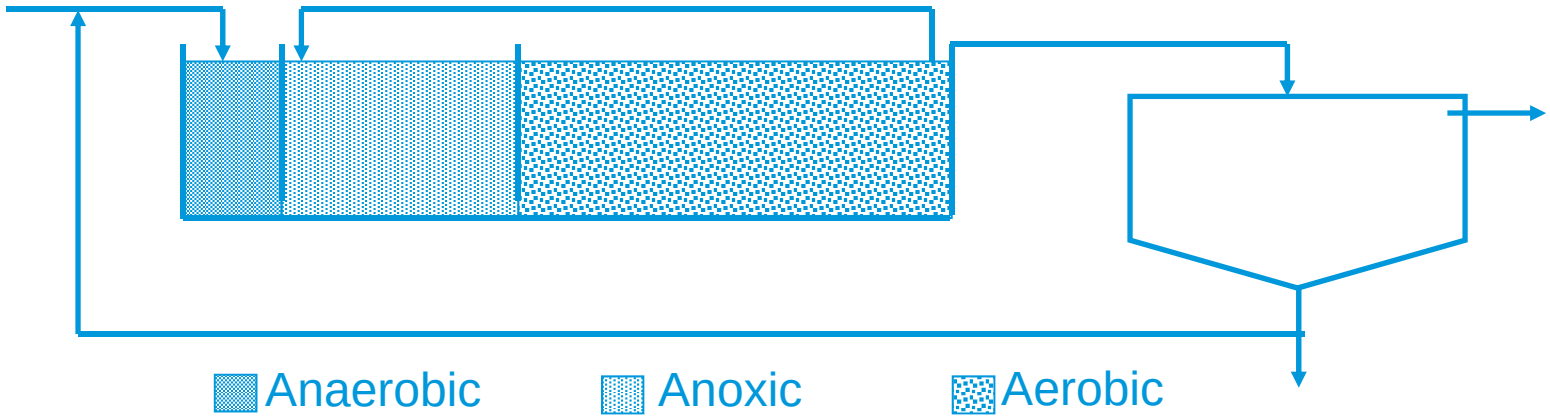
ORP IN BNR
NITROGEN REMOVAL



Aerobic zone: DO: 1.5-3mg/L; ORP: +100mV to +350 mV

Anoxic zone: DO < 0.3 mg/L ; ORP between –50mV & -150mV

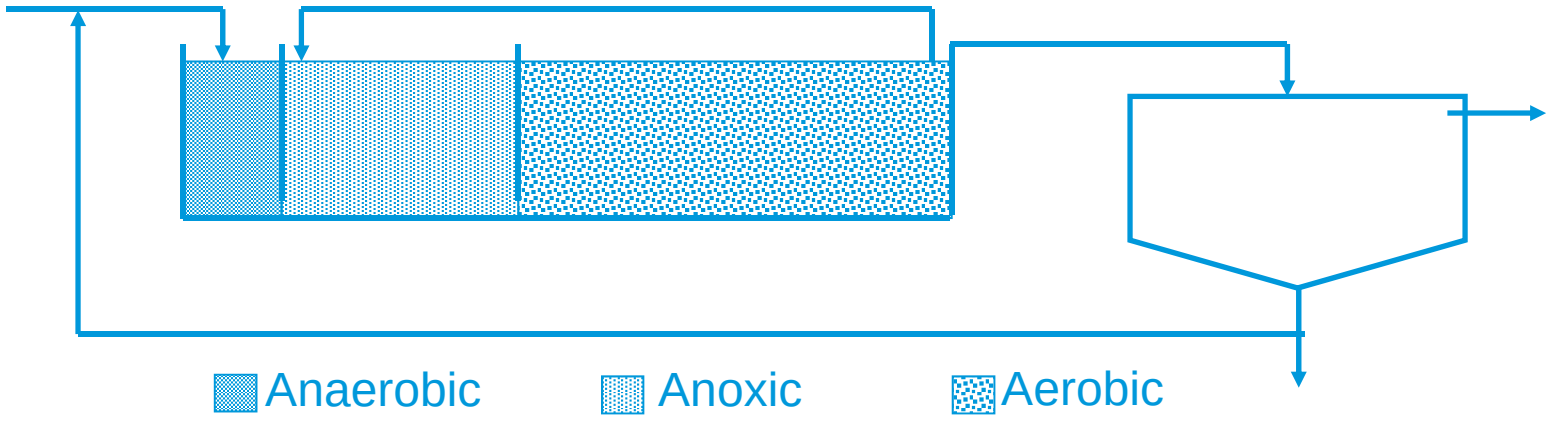
ORP IN BNR
PHOSPHOROUS REMOVAL



Anaerobic zone: organic phosphates broken down into orthophosphate (release)

Aerobic zone: orthophosphate assimilated into cellular material (luxury uptake)

ORP IN BNR
PHOSPHOROUS REMOVAL



How do you monitor/control anaerobic zone? DO? Phosphate?

ORP will respond to subtle changes in the anaerobic zone

Should see values < -100mV

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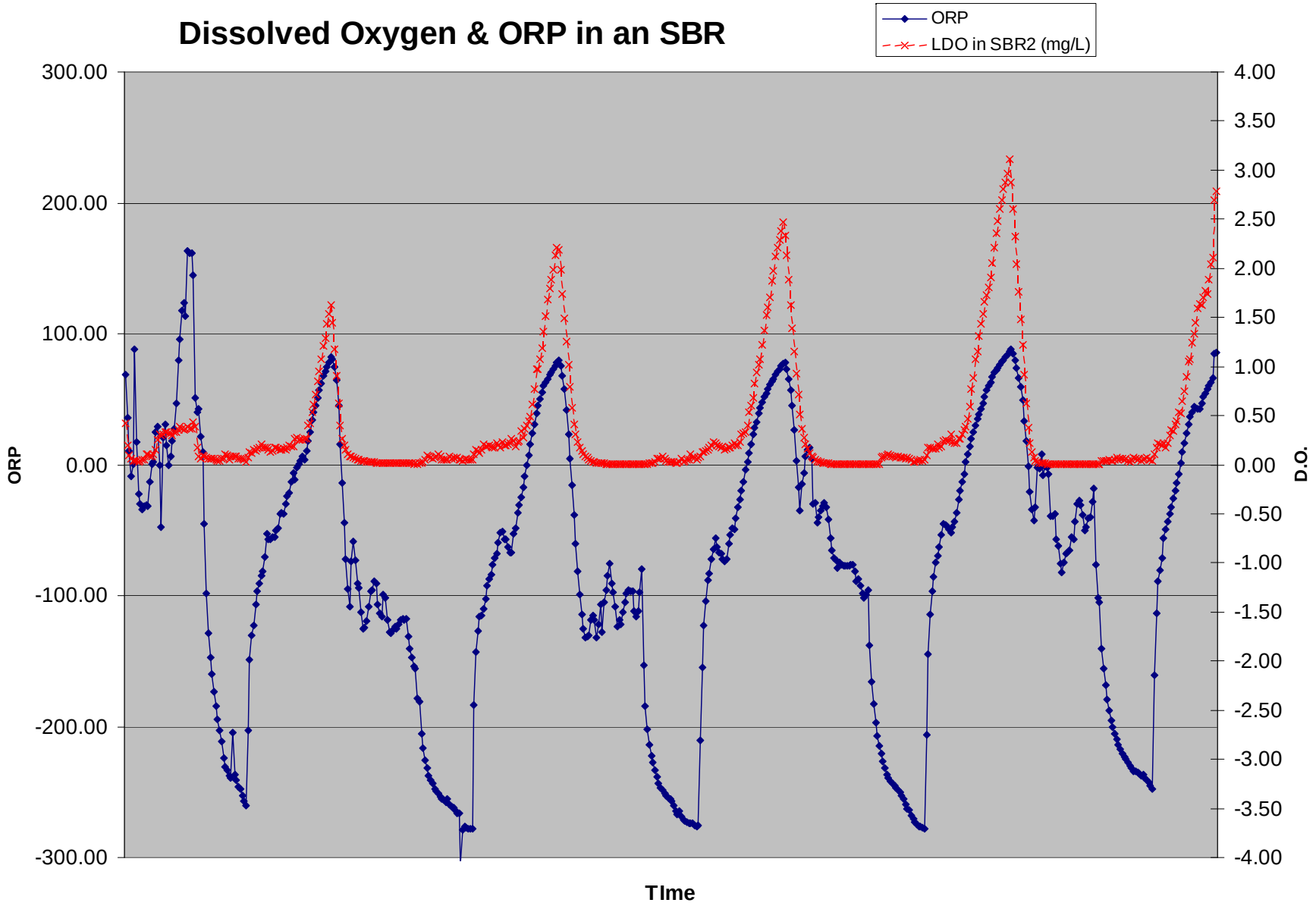
Dissolved Oxygen & ORP in an SBR



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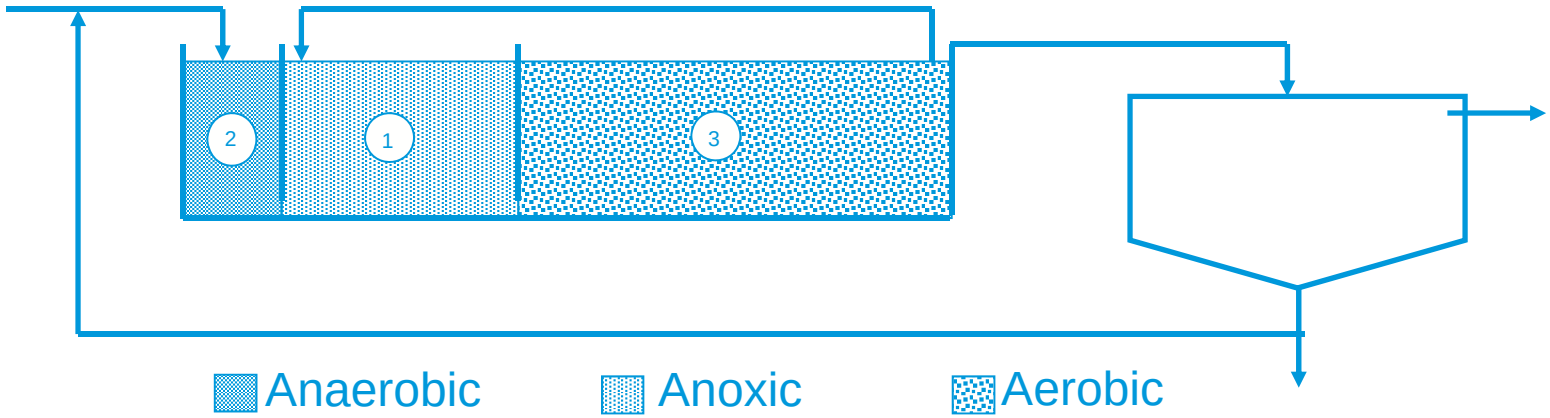
ORP IN BNR COMBINED REMOVAL

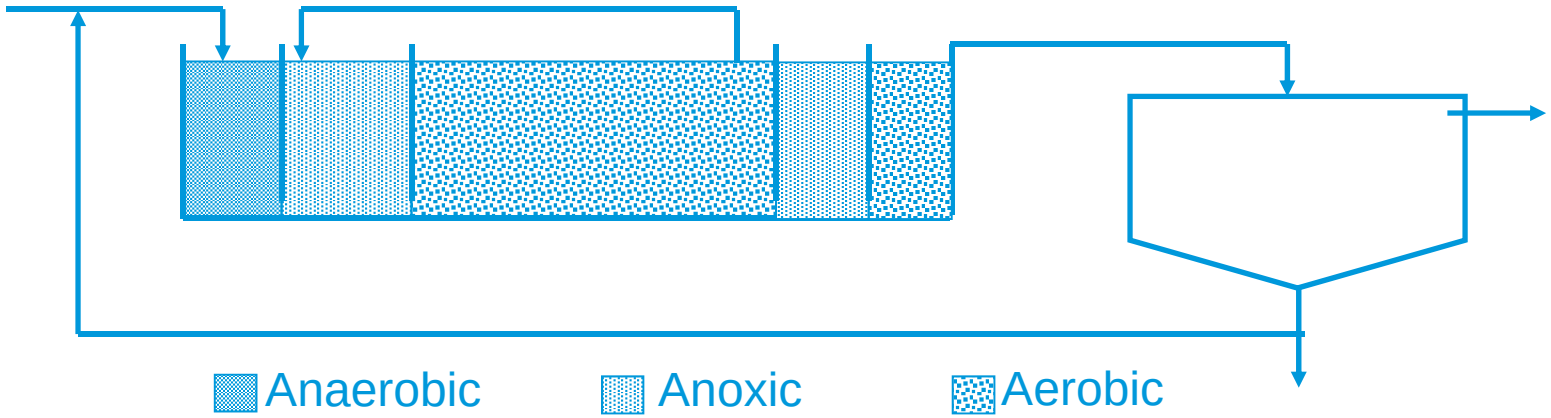


How & where to install ORP sensors?

General rules of thumb:

- Find a representative location
- Immerse sensor ¼ of the depth of the tank

ORP IN BNR
FIVE STAGE BARDENPHO



Pinery WWTP (Near Parker, CO: 2mgd, TP<0.05, TN<5.0)

Controlling first aeration at 80mV

Controlling first anoxic at -80mV

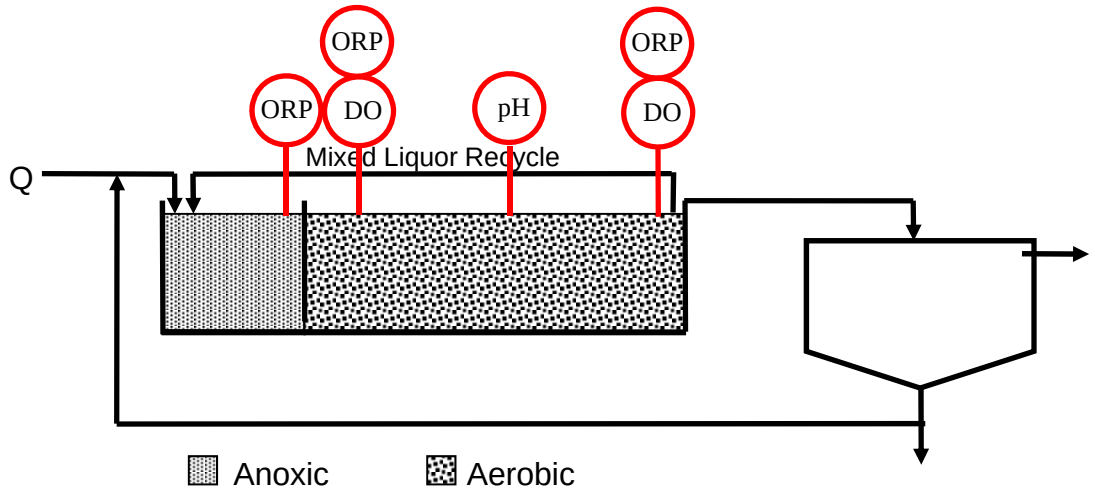
Monitoring anaerobic at -250mV

ORP IN BNR
COMBINED REMOVAL

- Portable ORP meter or Online system?

- In general, online process ORP sensor will give better data
  - "Better": more precise, trending, real-time values
  - Portable meter less sensitive to all potentials, good for spot checks, but +/- 10% compared to online is acceptable
  - Many online process systems can be configured to be "portable" datalogging systems

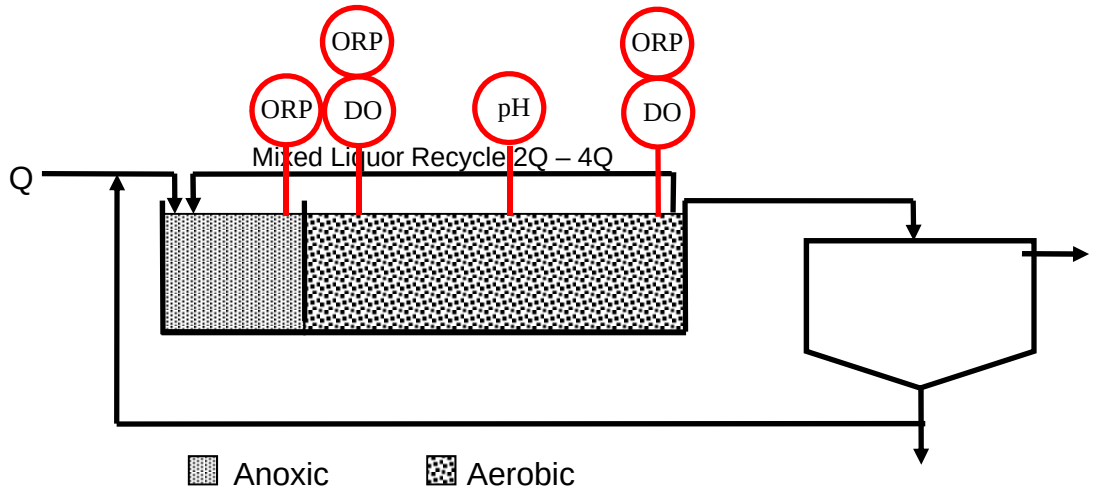
Modified Ludzack-Ettinger



Minimum

- DO in Aeration
  - –Monitor & manual DO control
  - –Automatic DO control with tapered aeration
  - –Ensure MLR does not contain too much oxygen

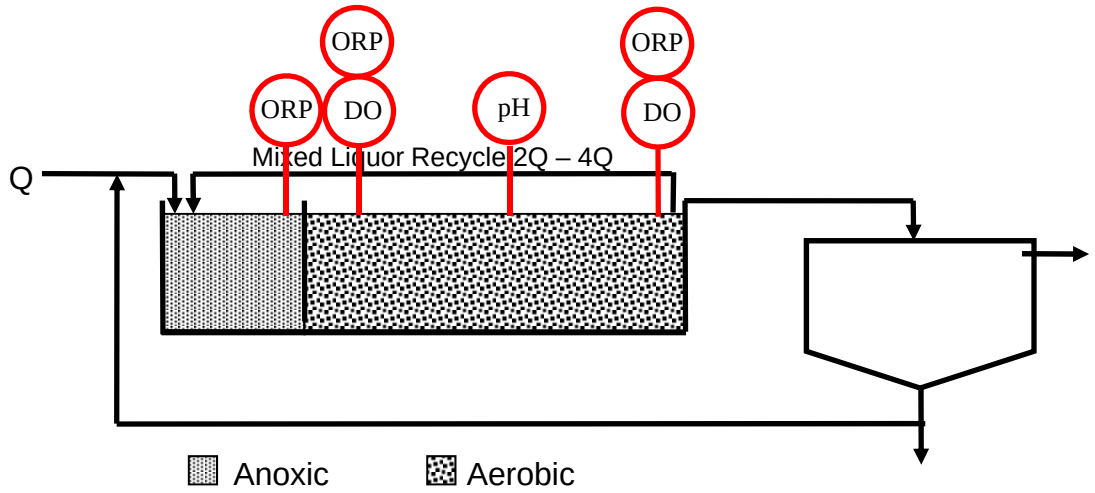
Modified Ludzack-Ettinger



Minimum

- ORP in Aerobic
  - Ensure aerobic conditions
  - Monitor oxidation of floc
  - Monitor Oxygen Demand…?

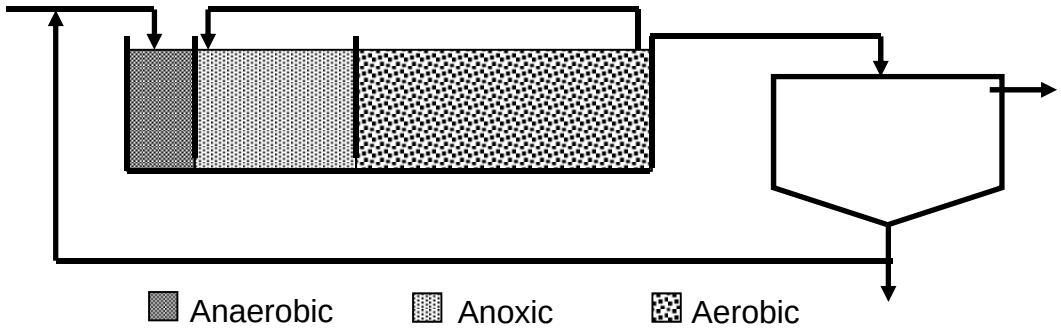
Modified Ludzack-Ettinger



Minimum

- pH in Aerobic
  - Watch for swings or changes
  - Possible indicator of alkalinity problems

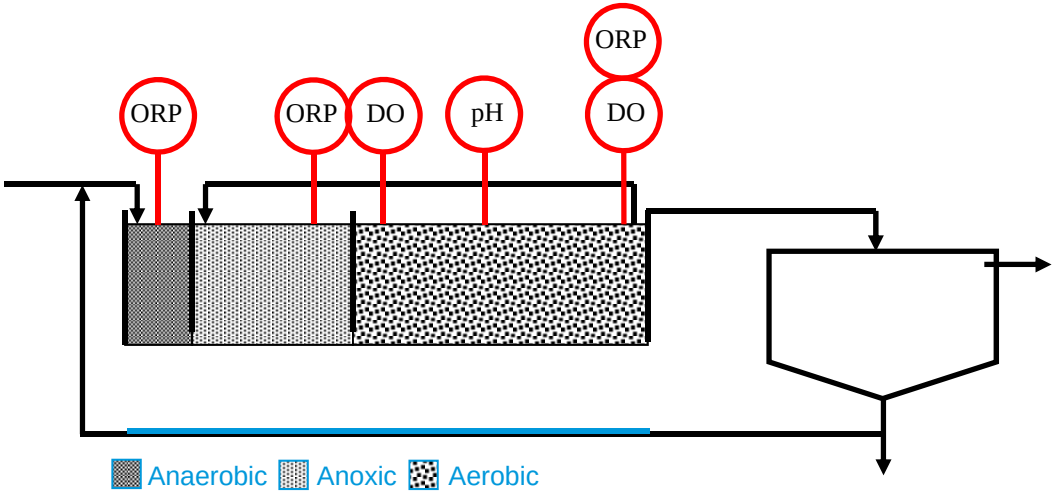
Three Stage Phoredox



Three Stage Phoredox

- Combined P and N removal
- MLE process with anaerobic zone

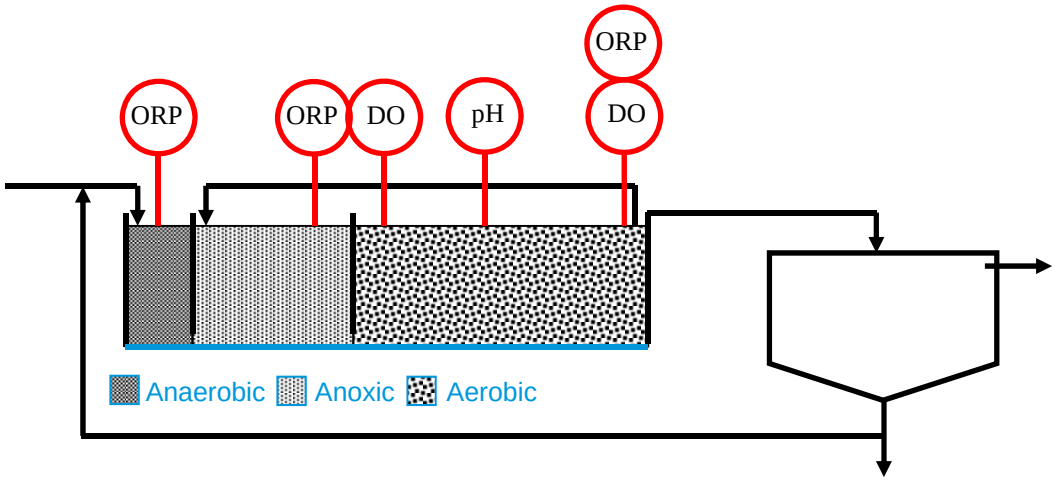
Three Stage Phoredox



Minimum

- ORP in Anaerobic
- Ensure anaerobic conditions
  - Watch for DO or NO_3
  - ORP should be less than –100mV
  - Low levels enhance fermentation & creation of VFAs
    - Turning mixer off in anaerobic

Three Stage Phoredox



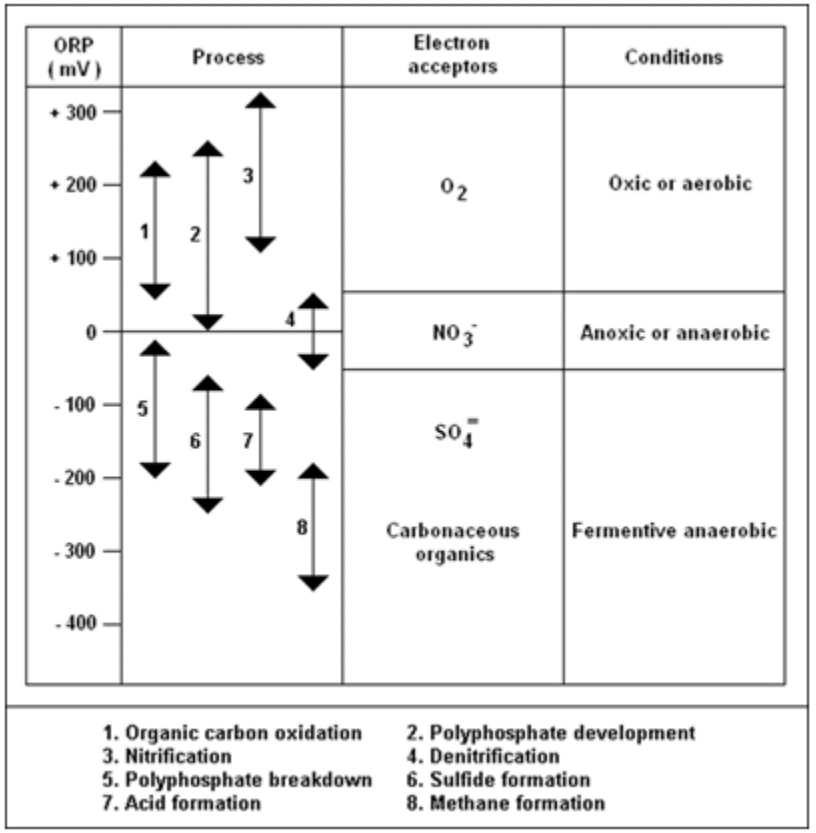
Minimum

- ORP in Anoxic
  - Same reason as MLE: control recycle, monitor anoxic
- ORP at end of Aeration
  - Help control tapered aeration
  - Correlate to NO_3 concentration

WBN1

ORP; PRACTITIONERS VALUES

- Ignore Positive Values use DO Meter
- Denit ~ -50 to -150 mV
- Fermentation Zone ~ -200 to -300 mV



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Slide 30

WBN1 The table on the right is the commonly seen table of ORP values which orginated with Gronasy. Nutient removal practitioners are pushing his #4 and #5 ranges lower.
Ward, Brett N, 7/25/2018

TIPS FOR USING ORP

Keep the sensor clean

- Check once a month, clean as necessary

Calibrate sensor every three months, or as necessary

- Use 200mV or 600mV calibration standard

Do not allow sensor to dry out

- Will dry out if left out of water >12 hrs

Do not allow sensors to freeze

QUESTIONS