By
Greg Paul -- *Op2Myz, LLC*

Personal History to Get to This Point

1.5 yrs. Greeley Co

31 yrs. LaCrosse

3.2 yrs. QLF

0.8 yrs. Op2Myz, LLC

Tested &/or Observed since 2011- **41 BNR SYSTEMS** – While With QLF & Op2Myz, LLC

- 5 States - WI/MN/IL/AR/VA
- WWTP flows ranged from 20,000 gpd to 40 MGD

Tested &/or Observed since 2011

12 TYPES OF BNR SYSTEMS

- AO/Modified AO/Modified AO with separate fermenter
- Orbital Ditch NO separate AN zone
- Oxidation Ditch with separate AN zone
- FluidDyne SBR
- A2O/A2O with separate fermenters
- 5 Stage Bardenpho
- Johannesburg
- 2 Oxidation Ditches run in series with separate AN & AX zones
- One unknown unique design.

What We'll Attempt to Cover

1. What is ORP?
2. What do you use to measure ORP?
3. How does an ORP meter work?
4. What maintenance does an ORP meter require?

What We'll Attempt to Cover

5. What is the ORP measurement used for?
6. How is ORP used in biological nutrient removal?
7. Case Studies/Bench Work

ORP

What is it?

Multiple Choice

(A) Optional Retirement Program

(B) Office of River Protection

(C) Off Road Parking

(D) Oxidation-Reduction Potential

(E) Objective Rally Point

(F) Office of Radiation Programs

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1. What is ORP?

WARNING!!!

I'm going to repeat myself on purpose

My experience and understanding is we learn through repetition.

VERY SIMPLY- It is a measurement of an positive/negative electrons in a liquid

Simple Examples of Oxidation

- Slow - iron rusting, or a slice of apple turning brown,
- FAST - fire

NOTE:

WHEN YOU OXIDIZE YOU ALSO REDUCE

Cut it apart…..
to figure it out……

- Oxidation
- Reduction
- Potential

Definition of Oxidation

The process or result of **oxidizing** from Dictionary.com

- *Define oxidize*
  - to convert (an element) into an oxide; **combine with oxygen.**
  - to remove electrons from (an atom or molecule), thereby increasing the valence. (valence - chemical bond)
  - **VALENCE – chemical bond (EX. Paint sticks good or not) - *[GLUE]***

Definition of Reduction

- *Define (Reduce) in Chemistry* from Dictionary.com
  - –to change (a compound) so that the val ence of the **positive element is lower**.

Definition of Potential

As an adjective

Possible <u>but not yet actual</u>

British Dictionary

Put it All Together

- ORP meter assigns a numeric value to a liquid's ability to;
- *Accept electrons denoting an increased the valence (chemical) bond **[GLUE]** The liquid will have more of a positive charge.*

OR

- *Donate electrons denoting a decreased the valence (chemical) bond. The liquid will have less positive charge to it, i.e. more of a negative charge.*

THE CASSINO

- In the OXIDATION-REDUCTION react there are GAINS and LOSSES
- When atoms or molecules pick up extra electrons, it loses the electrical energy that makes it "hungry" for more electrons.

ODDS/ENDS……

Something Like This….

- When you want to join pieces of irons together to make brace for holding up a roof, you?
  - Use a glue, tape or welding to join the iron?
  - The VERY RAPID oxidizing force of the welder creates the conditions to fuse the iron pieces creating a very STRONG bond.

Something Like This….

- When you want to chemically transform soluble BOD, phosphorus and nitrogen into solids so you can remove them from wastewater what do you use?
  - Do you use a helium gas, hydrogen gas or oxygen to transform them to solids?
  - The oxidizing force of oxygen in the water creates the conditions for microbes to grow using up the BOD, N and P removing them from the water

Similar….with a Different Twist

- When you want to chemically transform BOD to Volatile fatty acids or even convert organic solids to VFAs what do you use?
  - Do you use a oxygen or a condition with NO oxygen to do the chemical transformation?
  - NO Oxygen---In this case it is the exact opposite of oxidizing. It is call reducing. Think if it as the BOD or solids being REDUCED to more basic chemically elements, VFAs

Oxidation-Reduction Potential Info from WEF MOP 37

- **O**xidation-**R**eduction **P**otential is a measurement of the ABILITY of a solution to **accept** or **donate** ELECTRONS.

+ **Positive ORP** Value indicates the ability to **ACCEPT** electrons in an oxidative environment (oxygen present)

- **Negative ORP** Value indicates the ability to **DONATE** electrons in a reductive environment (no oxygen available)

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I'm ready to **ACCEPT** electrons. There is lots of room in my dump truck and I'm ready for them

(+) Positive ORP
the Ability to ACCEPT Electrons
(Aerobic Zone)

Oxidation Potential

I've have lots of electrons ready to **DONATE** to whoever can use them, where do you want them dumped

(-) Negative ORP
the Ability to
DONATE Electrons
(Anaerobic Zone)

Reduction Potential

Again

- Oxidization Potential
  - Ability to;

  Pull/suck/take away/remove electrons
- Reduction Potential
  - Ability to;

  Push/blow/gave away/donate electrons

From Robert's Hot Tubs!!!

- "Oxidation-Reduction" is used with a hyphen because the two chemical reactions are really "joined at the hip" - one cannot occur without the other also occurring.
- From http://www.rhtubs.com/ORP.htm

Last One from Hach Website

- Oxidation-Reduction Potential (ORP or Redox Potential) measures an aqueous system's capacity to either release or accept electrons from chemical reactions.
- When a system tends to accept electrons, it is an oxidizing system.
- When it tends to release electrons, it is a reducing system. A system's reduction potential may change upon introduction of a new species or when the concentration of an existing species changes.

Agenda

1. What is ORP?
2. **What do you use to measure ORP?**
3. How does an ORP meter work?
4. What maintenance does an ORP meter require?
5. What is the ORP measurement used for?
6. How is ORP used in biological nutrient removal?
7. Case Studies/Bench Work

2. What do you use to measure ORP?

ORP Meter

- Stationary, portable and handheld/pen style
- Hach, Insite, ABB, Oakton, YSI units and Others

The meter used depends on what are you looking for?

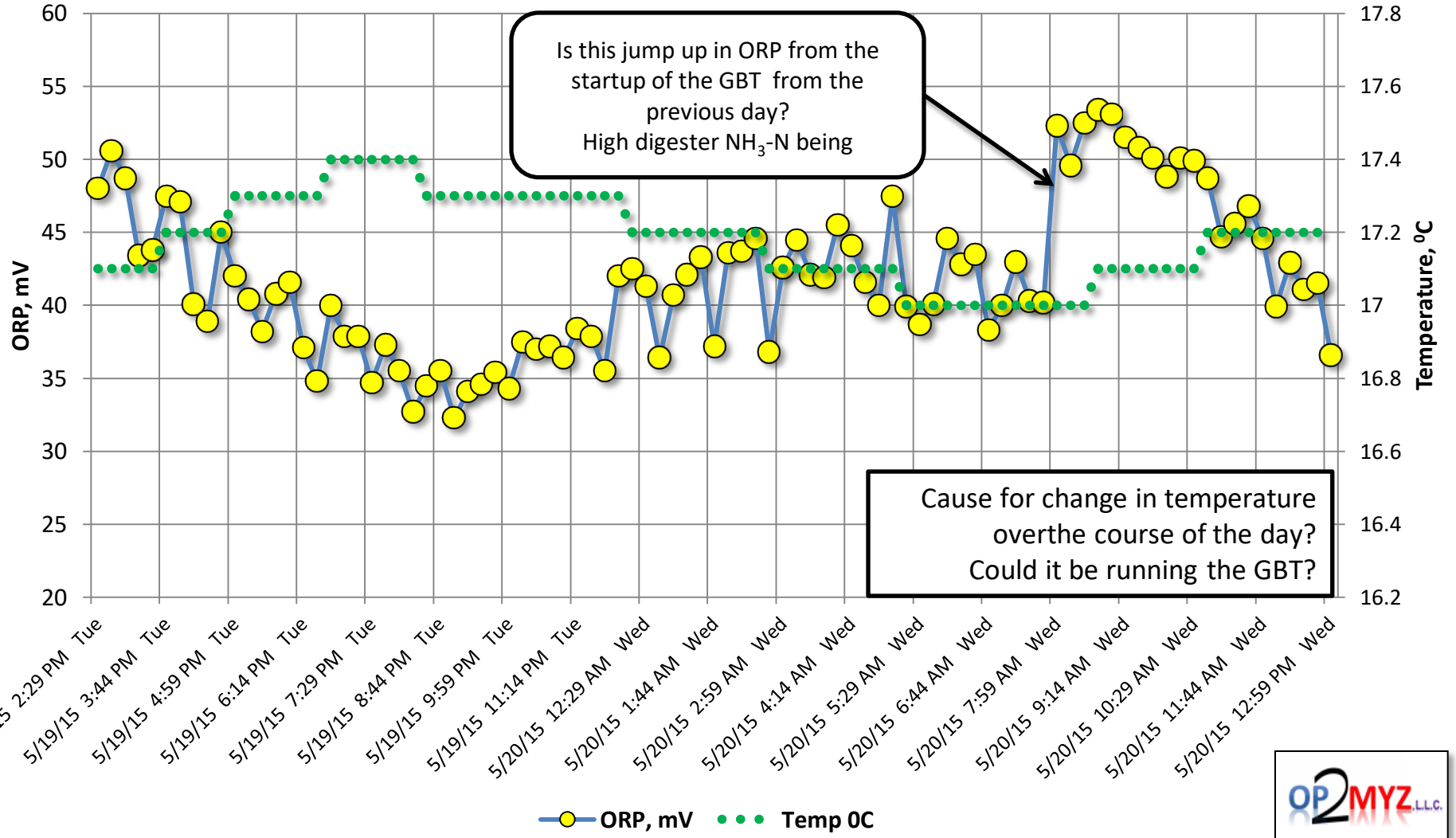
- Trends
- Surveys
- One time measurement?

Realtime & Trends

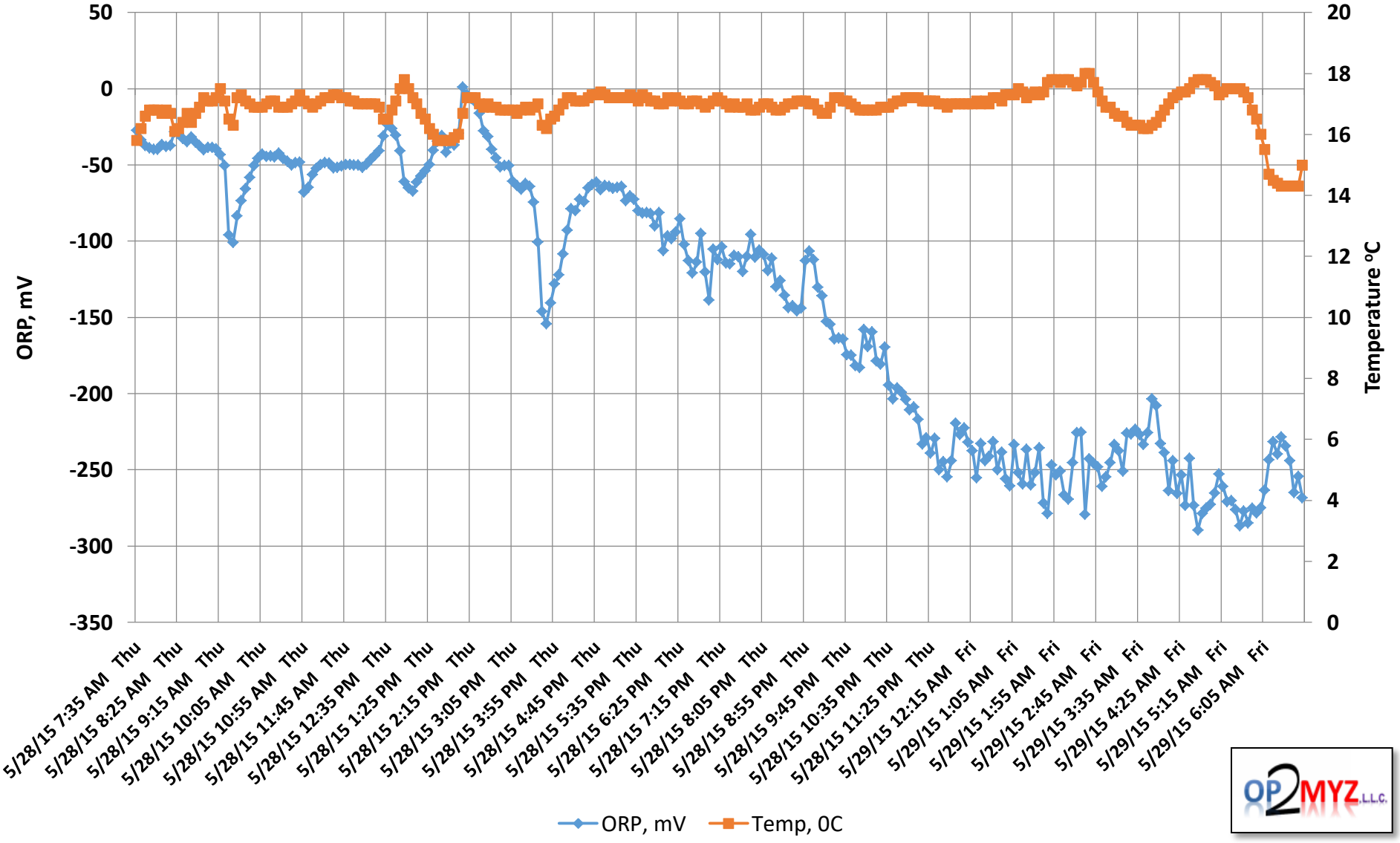
Inline measurement is the best method for constant ORP measurement

- **Gives continuous trend – Invaluable!!**
- **No waiting for achieving probe equilibrium**

Menomonie WWTP - RAS ORP (from Wet-Well)



Menomonie – Influent ORP

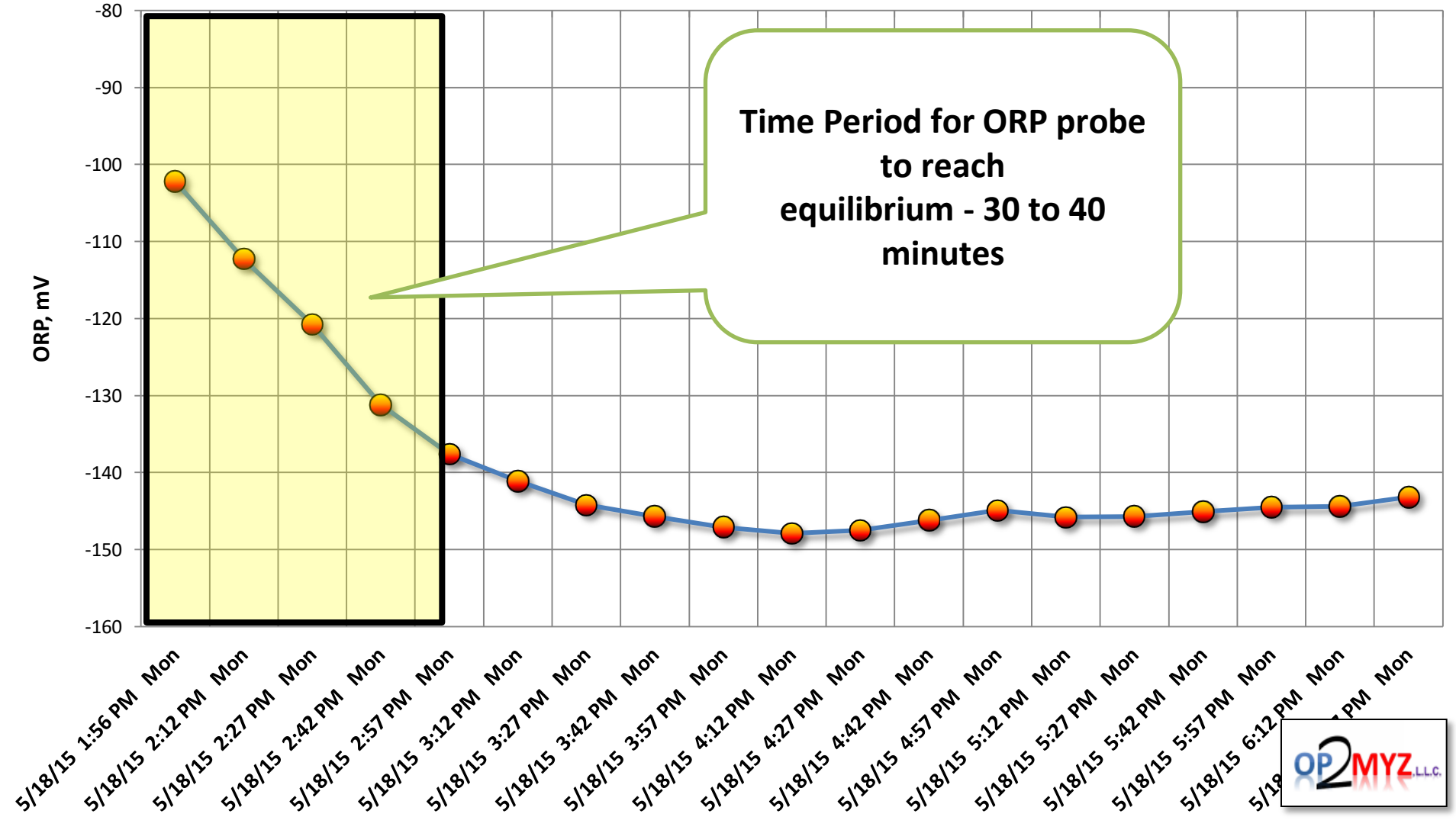


What is Used to Measure ORP

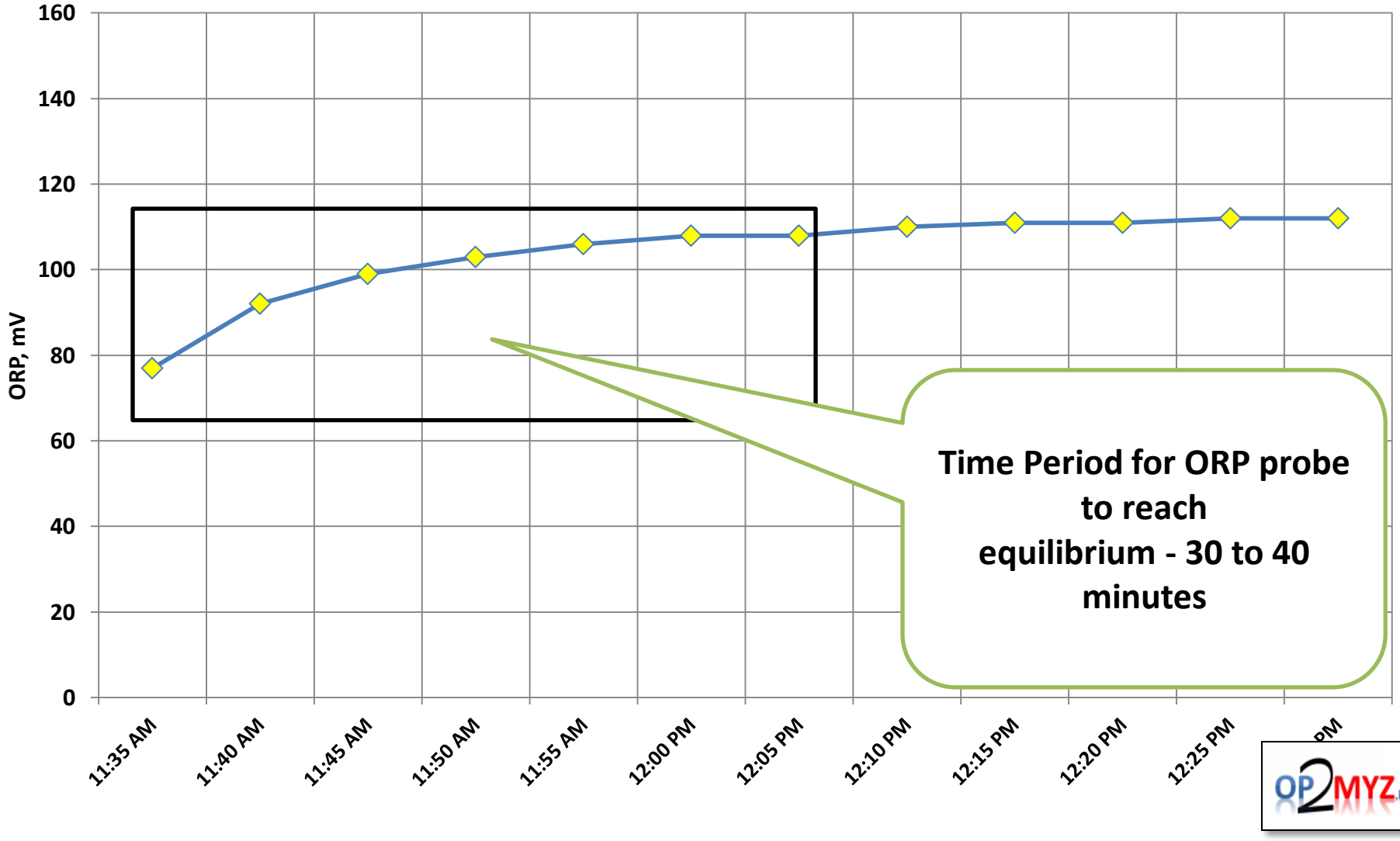
Portable – measuring In situ

- Need to let probe stabilize to reach equilibrium.
  - **May be as long as 30-45 minutes. Once equilibrium is reached in a solution with a specific level next reading it does not take very long.**
  - **Every time you switch to a solution with a significantly different ORP level you need to wait for the equilibrium to be achieved.**
- **Good economical method for surveying various WWTP locations**

Menomonie WWTP
AN-2 Zone ORP (5-18-15), mV



Medford WWTP AB-1 - ORP, mV



What is Used to Measure ORP

Handheld/Pen Style

- Equilibrium issue as above
- Ok for surveying various WWTP locations
- Stirring sample while reading

Types of Probes

- Gel filled – electrolyte has a limited life the electrons within the gel get used up
- Refillable ORP Probes – probe life is longer not depended on electrolyte running out.
- Rugged vs. lab bench style

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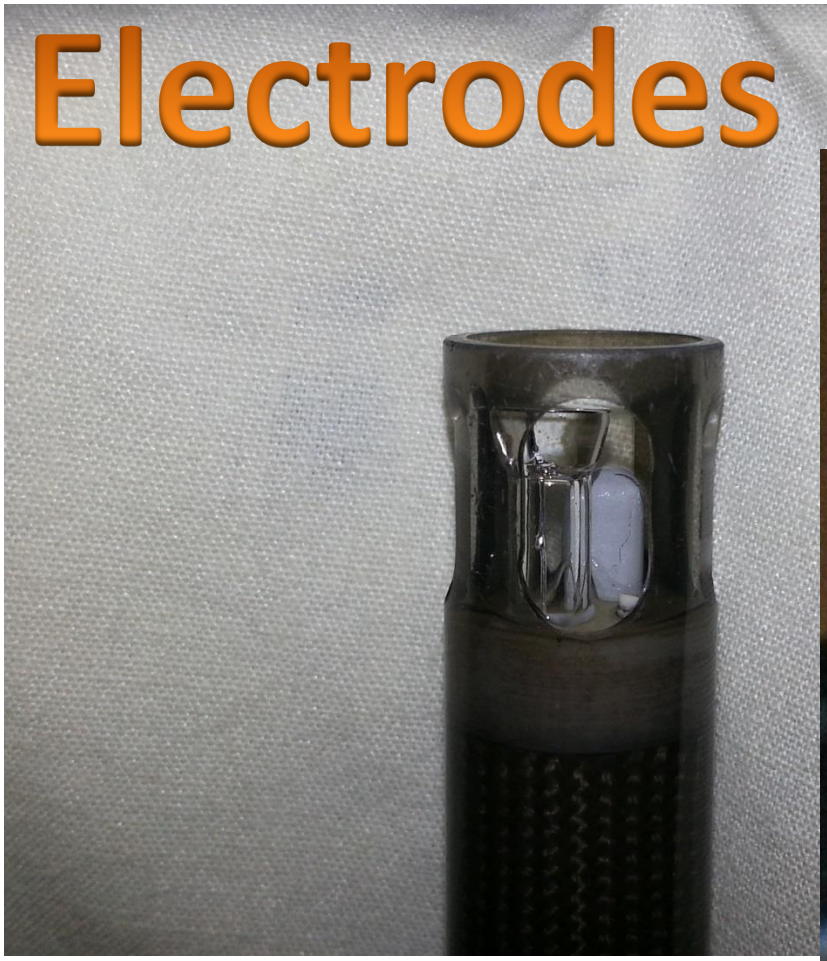
3. How does an ORP meter work?

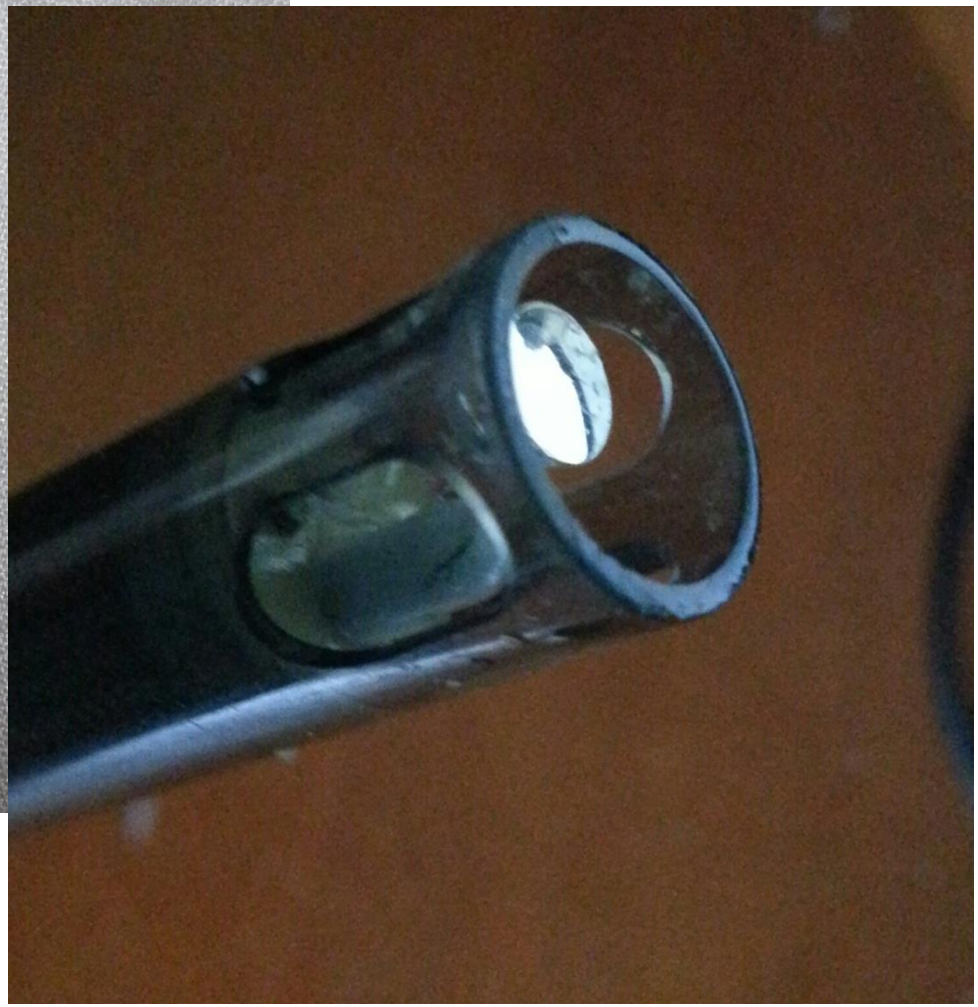
- I have NO clue!!
- Just Kidding…..I'm new to this stuff too…so bear with me….

From Robert's Hot Tubs!!!

- Really a millivolt meter, measuring the voltage across two electrodes (poles).
  - A reference electrode constructed of silver wire (negative pole)
  - A measuring electrode constructed of a platinum band (positive pole),
  - With the wastewater between Negative/Positive Poles

Reference & Platinum Electrodes





From Robert's Hot Tubs!!!

- The reference electrode
  - Surrounded by salt (electrolyte) solution that produces tiny voltage.
  - Voltage produced by the reference electrode is constant and stable
- It provides a reference against which the voltage generated by the platinum measuring electrode and the oxidizers in the water may be compared.
- The difference in voltage between the two electrodes is what is actually measured by the meter.

From Robert's Hot Tubs!!!

- ORP electrodes are almost always combination electrodes, both electrodes are housed in one body - so it appears that it is just one "probe."
- Meter's circuitry very sensitive so it can measure the very tiny voltages generated by the circuit.

FYI

%$##*!@@#$

FROM YSI - TIPS, CAUTIONS AND LIMITATIONS

- ORP sensors can show a **slow response** in environmental water if the platinum button of the probe has been **contaminated** with extraneous material. Common contaminants include hard water deposits, **oil/grease, or other organic matter.**

FYI

%$##*!@@#$

FROM HACH - INTRODUCTION TO OXIDATION REDUCTION POTENTIAL MEASUREMENT

- ORP measurement readings occur slowly compared to pH measurements. While a pH value can be obtained within seconds, a stable ORP value **can take up to several minutes**, if not hours, to reach the final equilibrium due to the type of reactions and their reaction rates. Example Linden

Learn how to use ORP Meters correctly – Read O&M manual that comes with unit – **BUT** keep in mind the tips from above

WEF Manual of Practice No. 37
ORP Meter Information

Principle of Operations

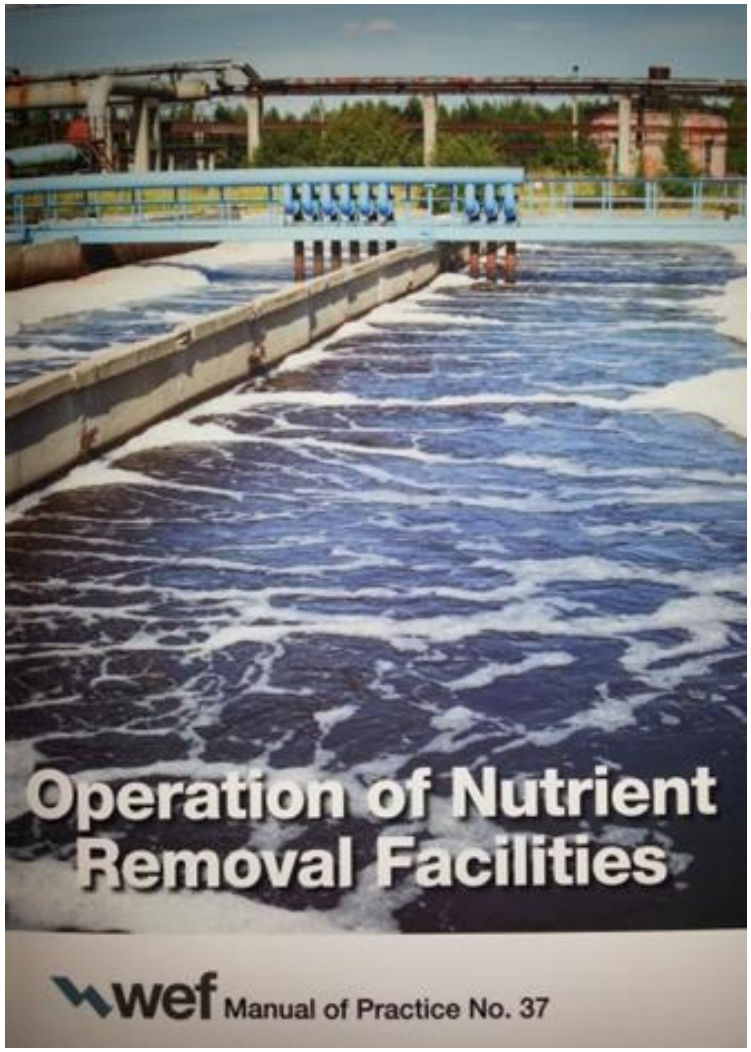
Installation

Concerns

Drifting & Fouling

Accuracy & Repeatability

Cleaning & Maintenance Requirements



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4. What maintenance does an ORP meter require?

- Each manufacturer has it's own methods and procedures
- **IMPORTANT – STORE PROBE TIP IN 3M KCL**
- Generally
  - Keep platinum electrode clean and free of foreign material, grease, films, etc
  - Clean with mild detergent or ORP probe cleaning solution.

Maintenance

- If refillable – change out electrolyte periodically
- Using mild acid (to remove hard water deposits) or a chlorine solution on probes
- FOLLOW ALL the manufacturer's recommendations for maintenance and operation

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5. What is the ORP measurement used for?

- Disinfection Control -
  - "ORP is the only practical method we have to electronically monitor sanitizer effectiveness" from http://www.rhtubs.com/ORP.htm
  - Pools/Hot tubs
  - Wastewater disinfection control
- Ethanol fermentation
- Biological Nutrient Removal

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6. How is ORP used in biological nutrient removal?

- Aerobic – nitrification
- Anoxic – Denitrification
- Anaerobic - Fermentation

What Happens When You Do This?

Now you have to guess how anaerobic or anoxic your zones are….

This what you do when you don't use ORP in a BPR or BNR System

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WWTP 101

- Clean water and Treat Solids
- How?
- Create Environments – by design & operation

What Does ORP Have to Do with BPR/BNR?

- Basics of BPR/BNR
- Apply the ORP measurements to BPR/BNR operations

Basics BPR/BNR

- What's BPR/BNR?
- Goal – Getting PAOs to Grow
- Creating environments
  - Cycling between aerobic/anaerobic
  - VFAs
- Anaerobic (AN)

Basics BPR/BNR

- BNR-Nitrogen Removal
- Goal – Get Denitrifying organisms to Grow
  - –Cycling between aerobic/anoxic
  - –BOD
- Anoxic (AX)

LooKING INSIDE THE TANK
ORP in a TANK – AN or AX

- Result of numerous things
  - 1st - Weighed Average of Liquids into TANK
    - Inf. Flow gpm X ORP = A
    - RAS Flow gpm X ORP = B
    - Weighed Average =
    - (A + B) / (Inf. Flow gpm + RAS Flow gpm)
  - Detention
  - Solids concentration
  - Available nutrition

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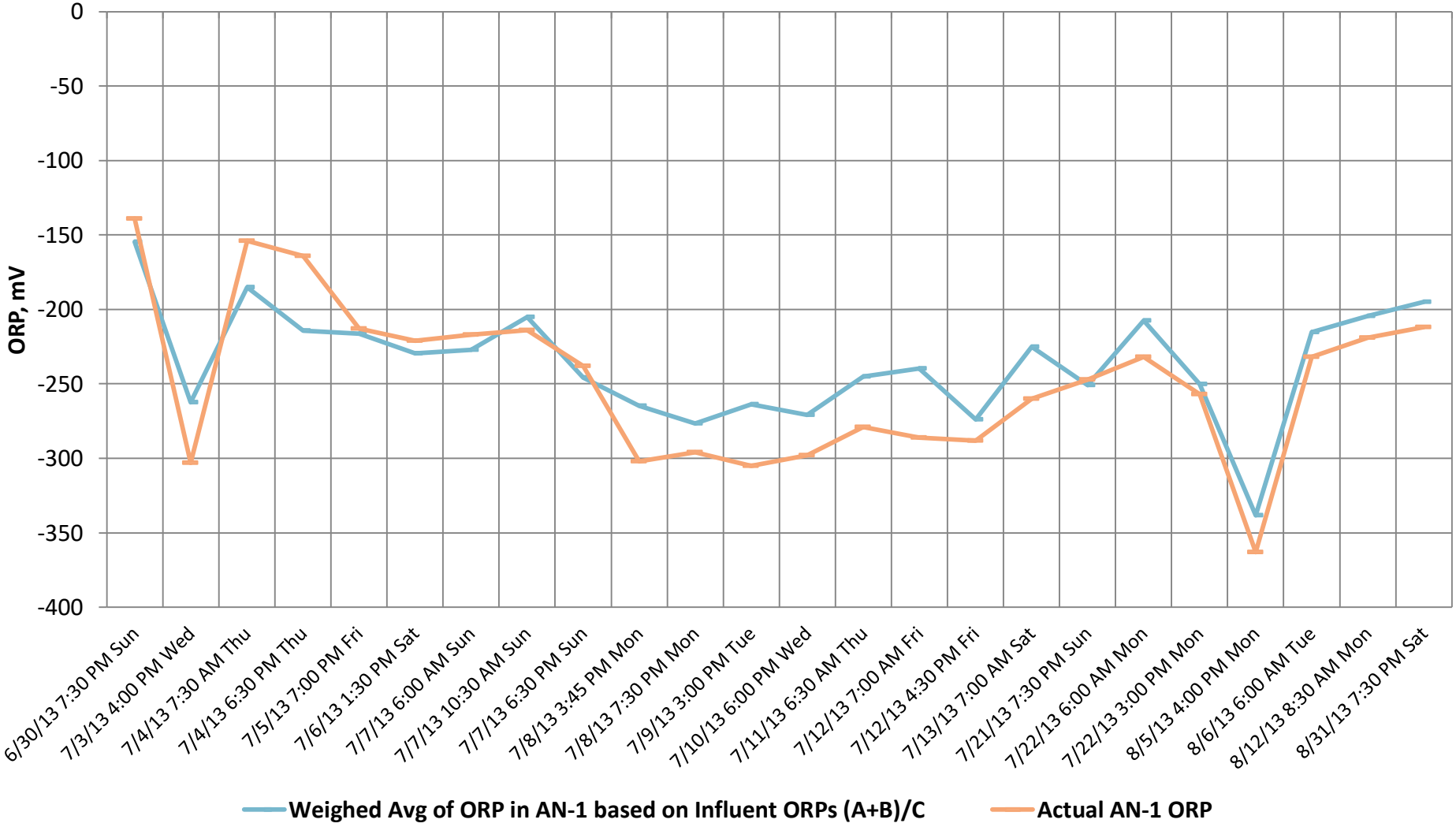
Weighed Avg vs Actual - ORP



How Does the Biology Affect the Chemistry of ORP?

Florida Rural Water Associate	ORP, mV		YSI	ORP, mV		Hach	ORP, mV
Organic Carbon Oxidation	+50 to +225		cBOD degradation with free molecular oxygen	+50 to +250			
Polyphosphate Development	0 to +250		Biological phosphorus removal	+25 to 250			
Nitrification	+100 to +350		Nitrification	+100 to +350			
Denitrification	-50 to +50		Denitrification	-50 to +50			
Polyphosphate Breakdown	-25 to -200		Biological phosphorus release	-100 to -250			
Sulfide Formation	-50 to -250		Sulfide(H_2S) formation	-50 to -250			
Acid Formation	-100 to -225		Acid formation (fermentation)	-100 to -225		Reduction of sulfate	+100 to -200
Methane Formation	-200 to -350		Methane production	-175 to -400		Development of methane	-150 to -280

WEF WE&T Jan '13	ORP, mV		WEF MOP-30	ORP, mV		MPCA-Biological Nutrient Removal	ORP, mV
Carbon oxidation (cBOD stabilization)	+50 to +200					Aerobic (oxic)	+50 to +200
Polyphosphate accumulation	+50 to +250						
Nitrification	+150 to +350						
Denitrification	-50 to +50					Anoxic - little or no oxygen, just nitrates	+50 to -200
Polyphosphate release	-40 to -175						
Sulfide(H2S) formation	-50 to -250						
Acid formation (fermentation)	-40 to -200		Acid-forming bacteria proliferate	-300		Anaerobic - No nitrate, no oxygen present	Less than -300
Methane production	-200 to -400		Methanogenesis onset which can adversely affect VFA	Less Than -600			

PUSHING THE BUTTONS

What Makes an AN Zone Anaerobic?

Low ORP – The stronger potential to donate electrons the better the anaerobic zone.

Horror Story with Acid Bath – dripping the Victim.

Strong the Acid the quicker & more complete the melt

In AN-the quicker & more complete the conversion of BOD &/or solids to VFA s

- High BOD
- High HRT - bench trial
- Lower RAS
- Control mixing on/off – increase SRT
- Final Clarifier Secondary P-Release

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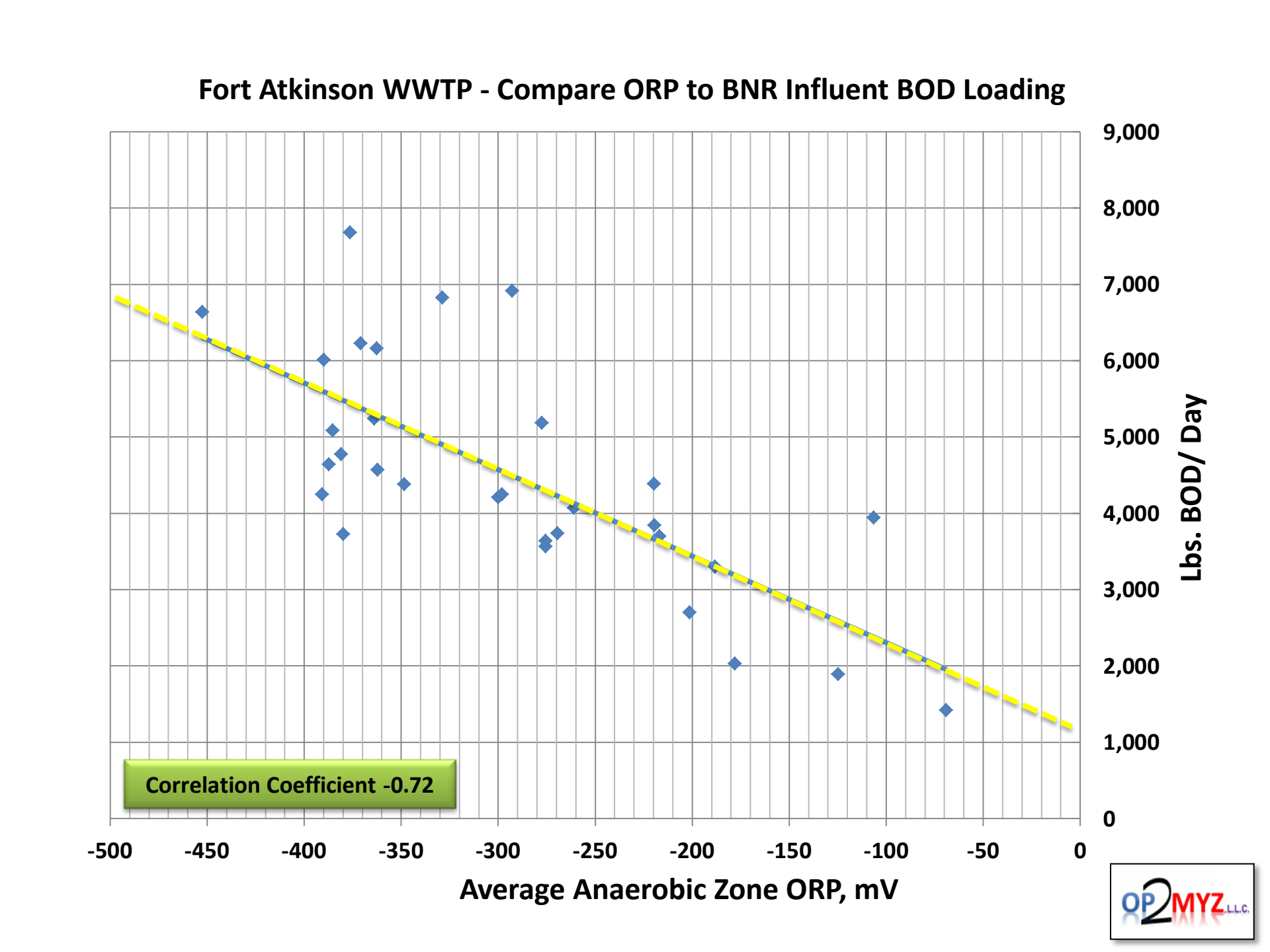
Fort Atkinson WWTP - Compare ORP to BNR Influent BOD Loading
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
Lbs. BOD/ Day
-500
-450
-400
-350
-300
-250
-200
-150
-100
-50
0
Average Anaerobic Zone ORP, mV
Correlation Coefficient -0.72
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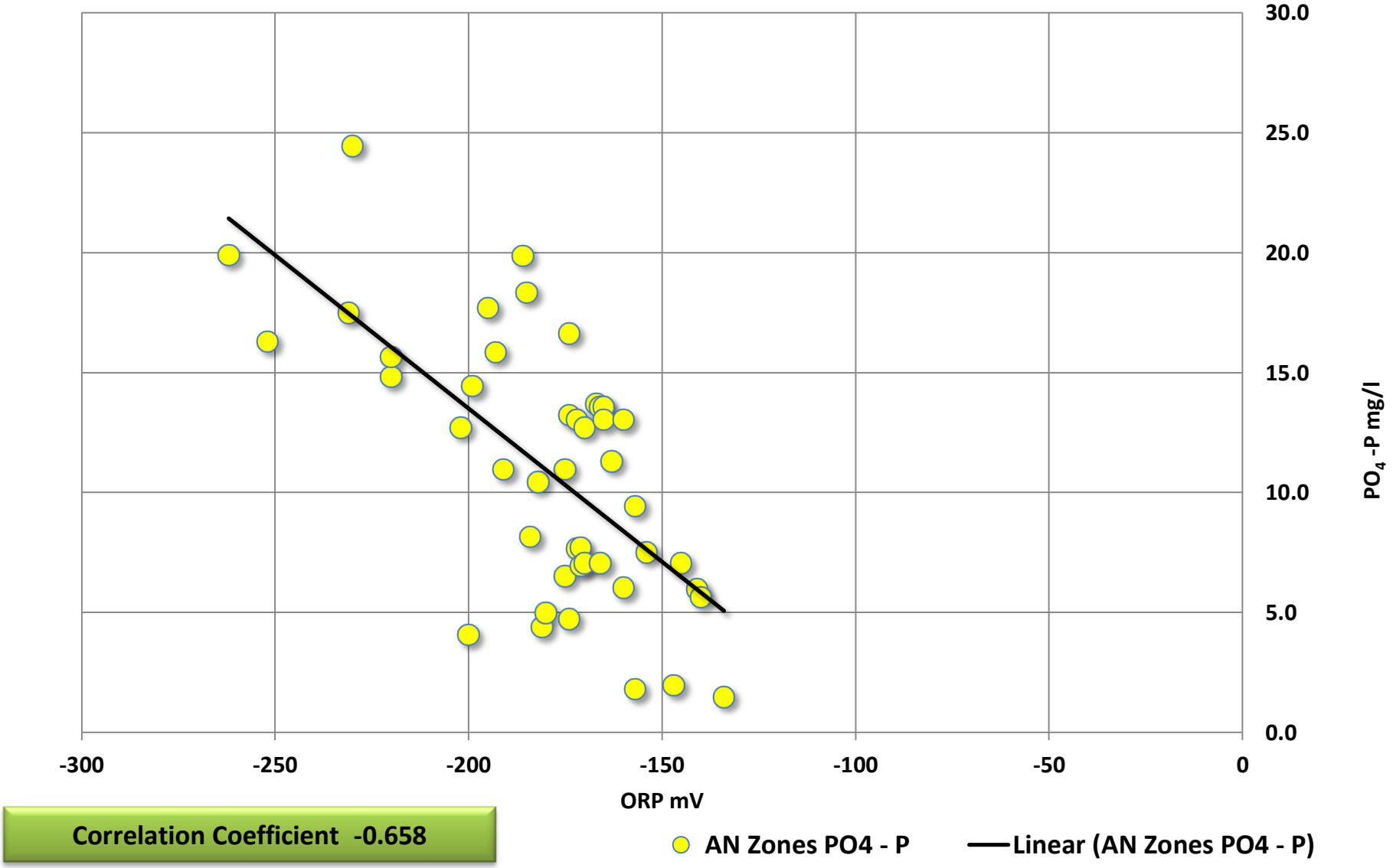
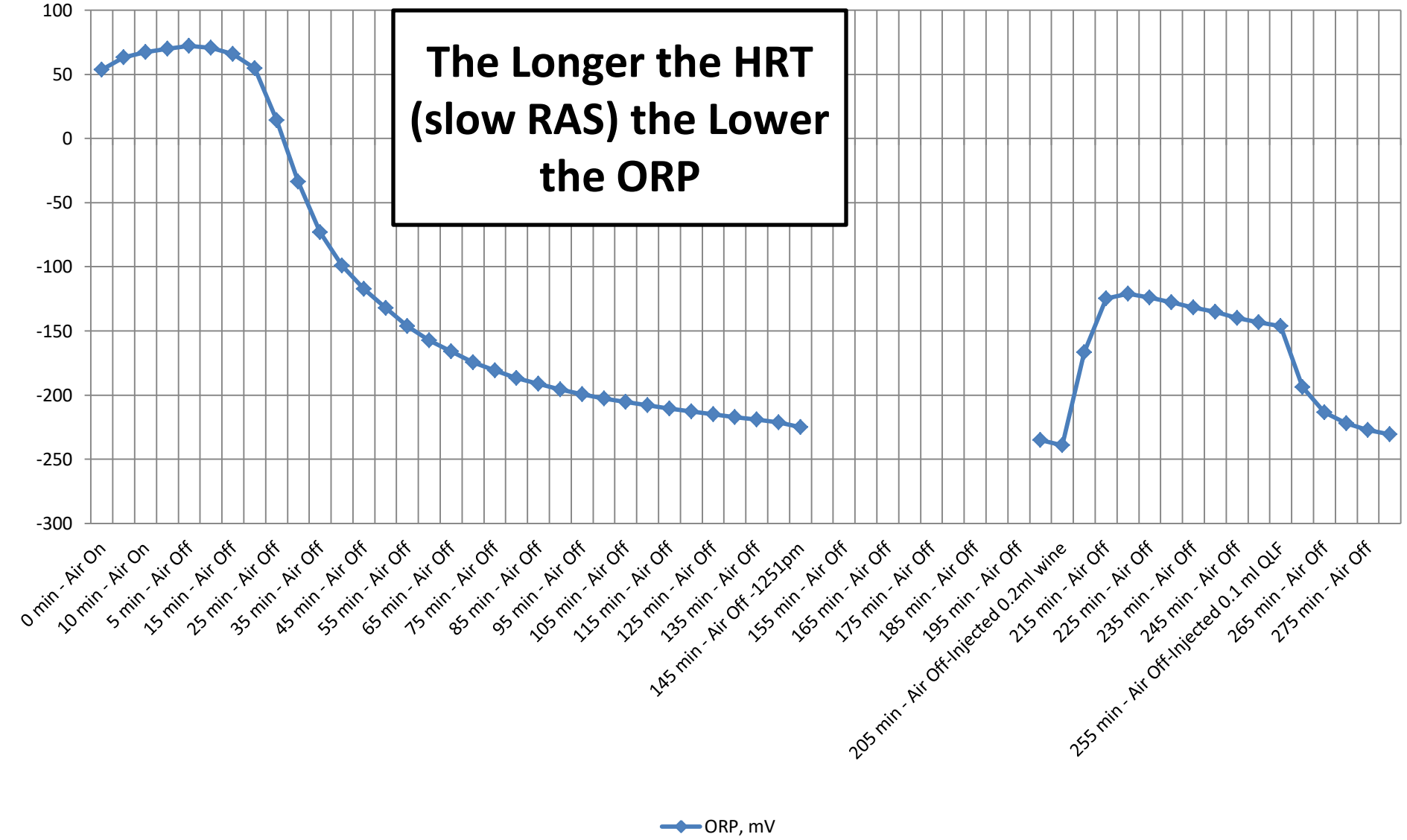
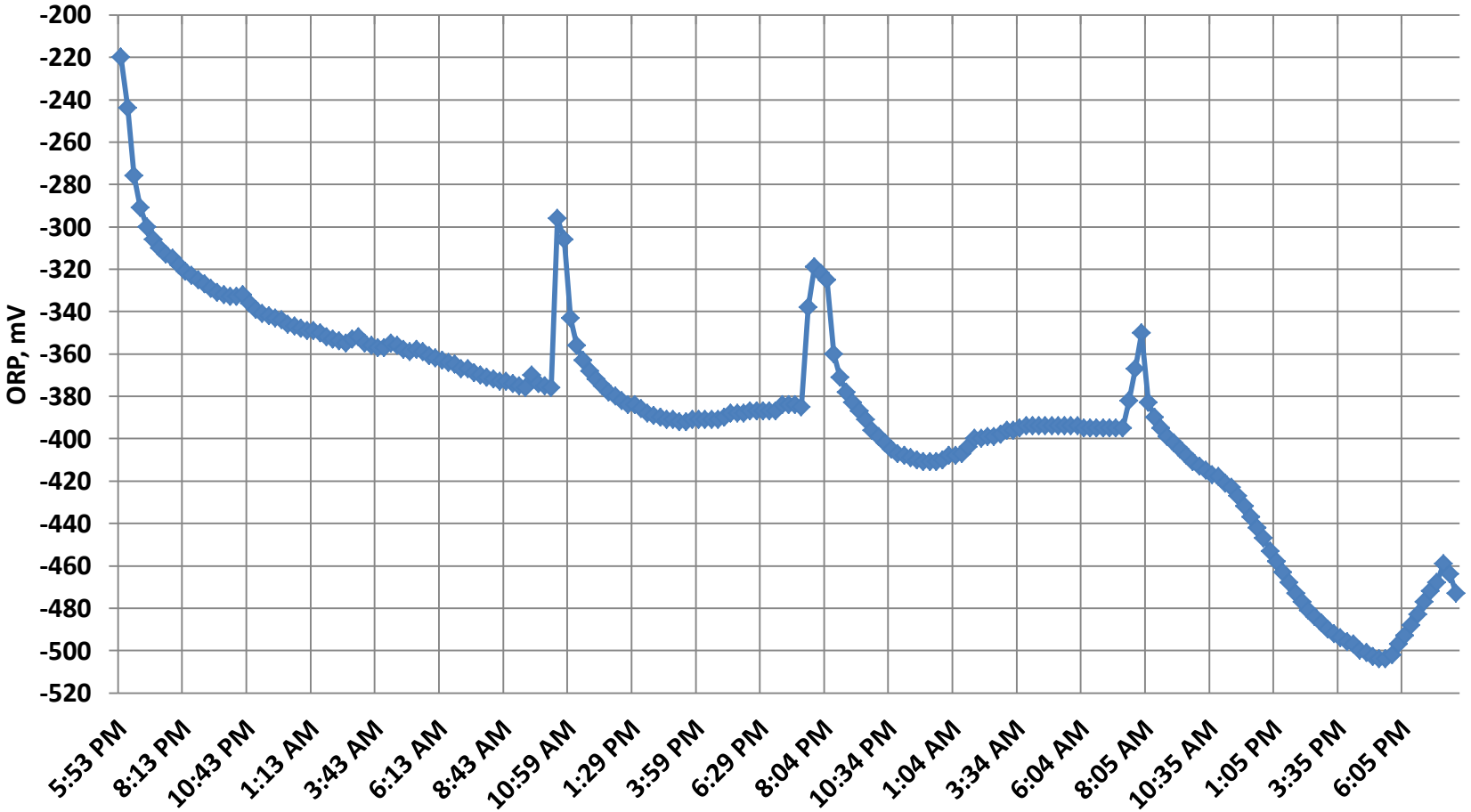
AN Zones ORP & PO_4 - P



HRT – ORP in AN, AX zones & Clarifier Blanket



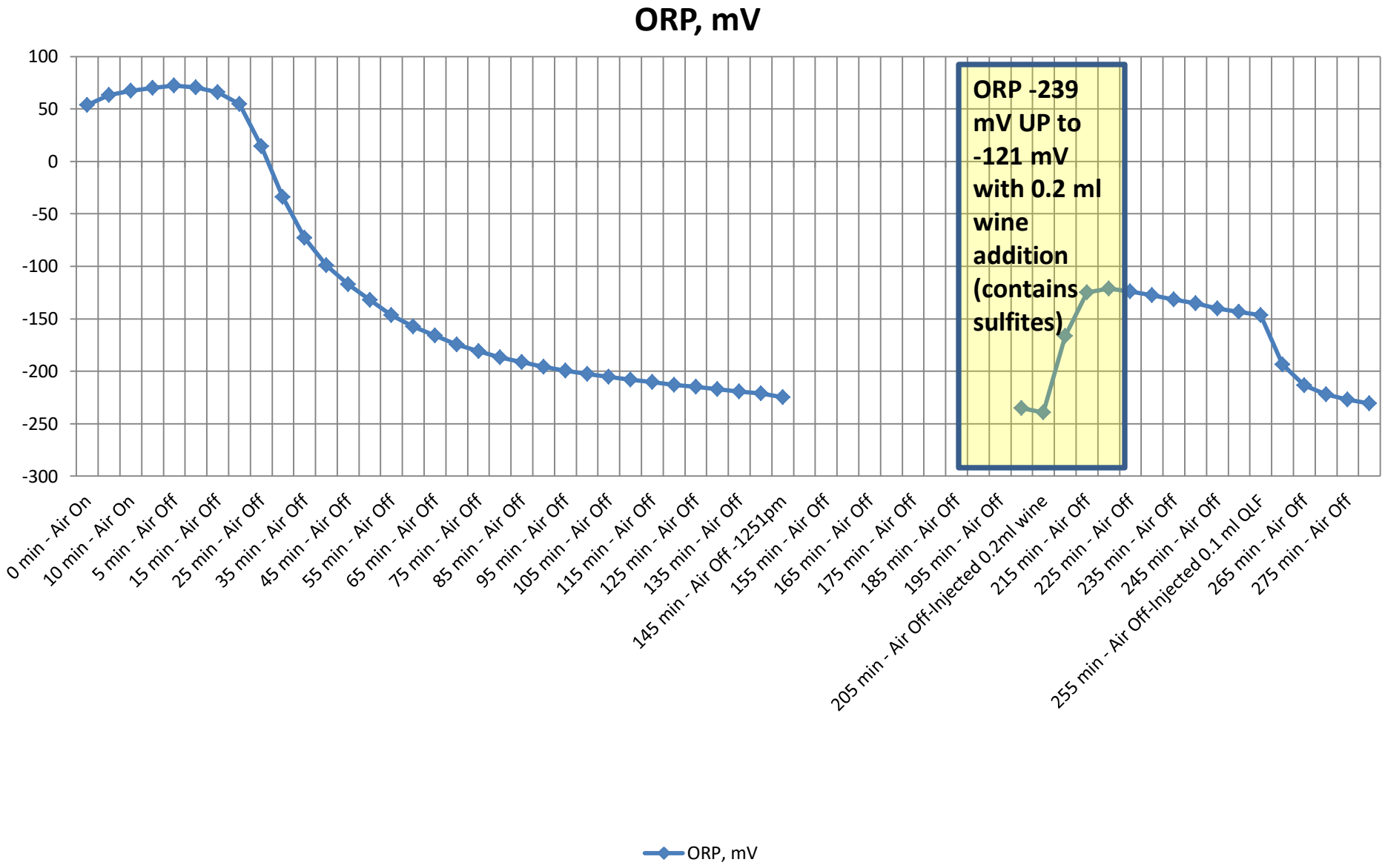
On/Off Mixer AN Zone



What Will Adversely Affect an AN Zone?

- O_2
- NO_3-N
- sulfite (SO_3^{2-})
- NO_2-N
- High ORP (0_2 or NO3-N from Odor Control Chem) influents (RAS, side stream, Inf)

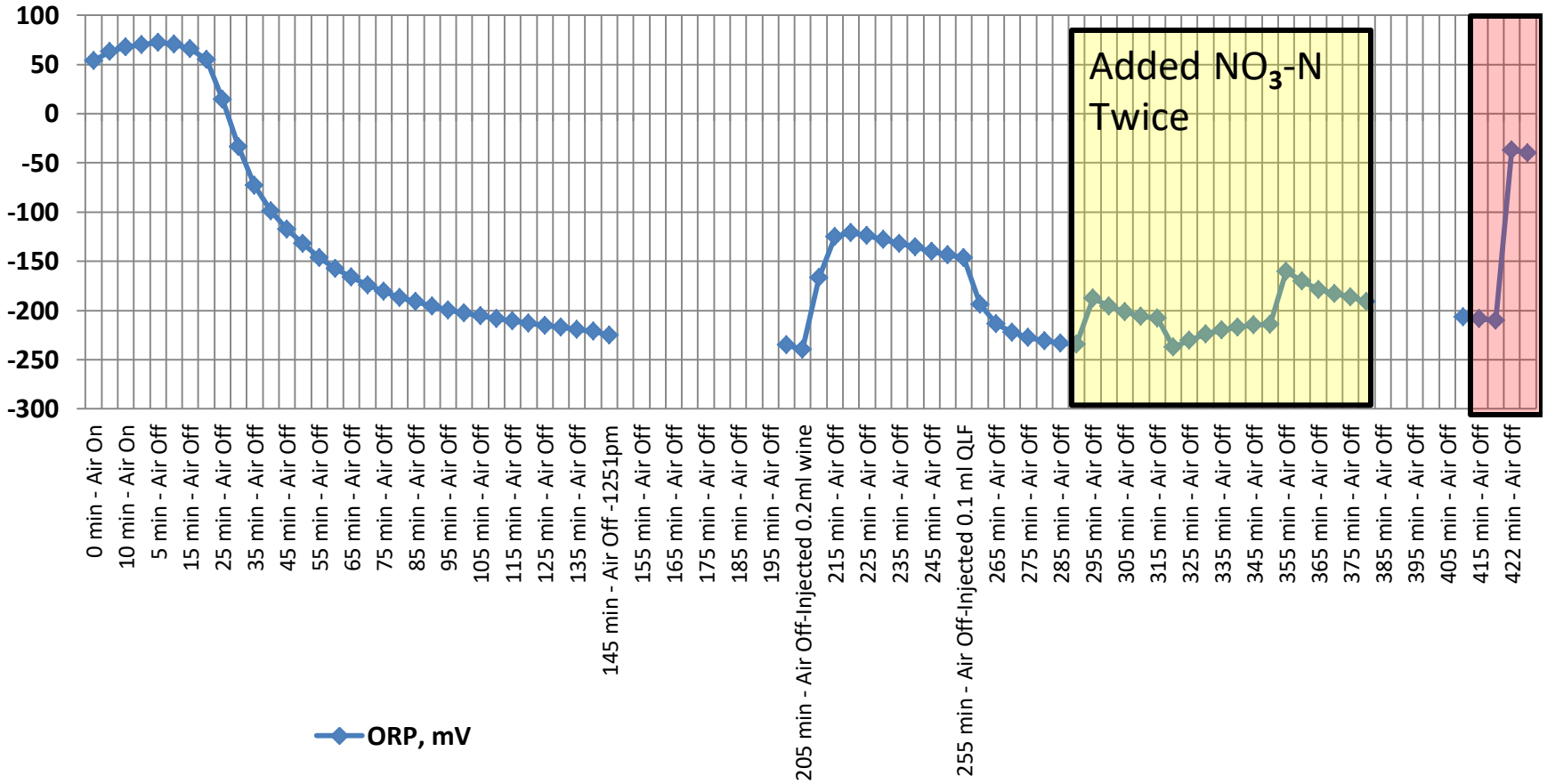
Bench-Trial Added Wine



Wouldn’t you know!!

- Used wine to show how adding a fermented sugar source to how it drives down ORP and it goes up???? What’s with that???
- Sulfites SO_2 used as a anti-fermenting agent in wine as a preservative
- Added oxygen to sludge drove up ORP

Added NO_3-N(yellow) or O_2(pink)



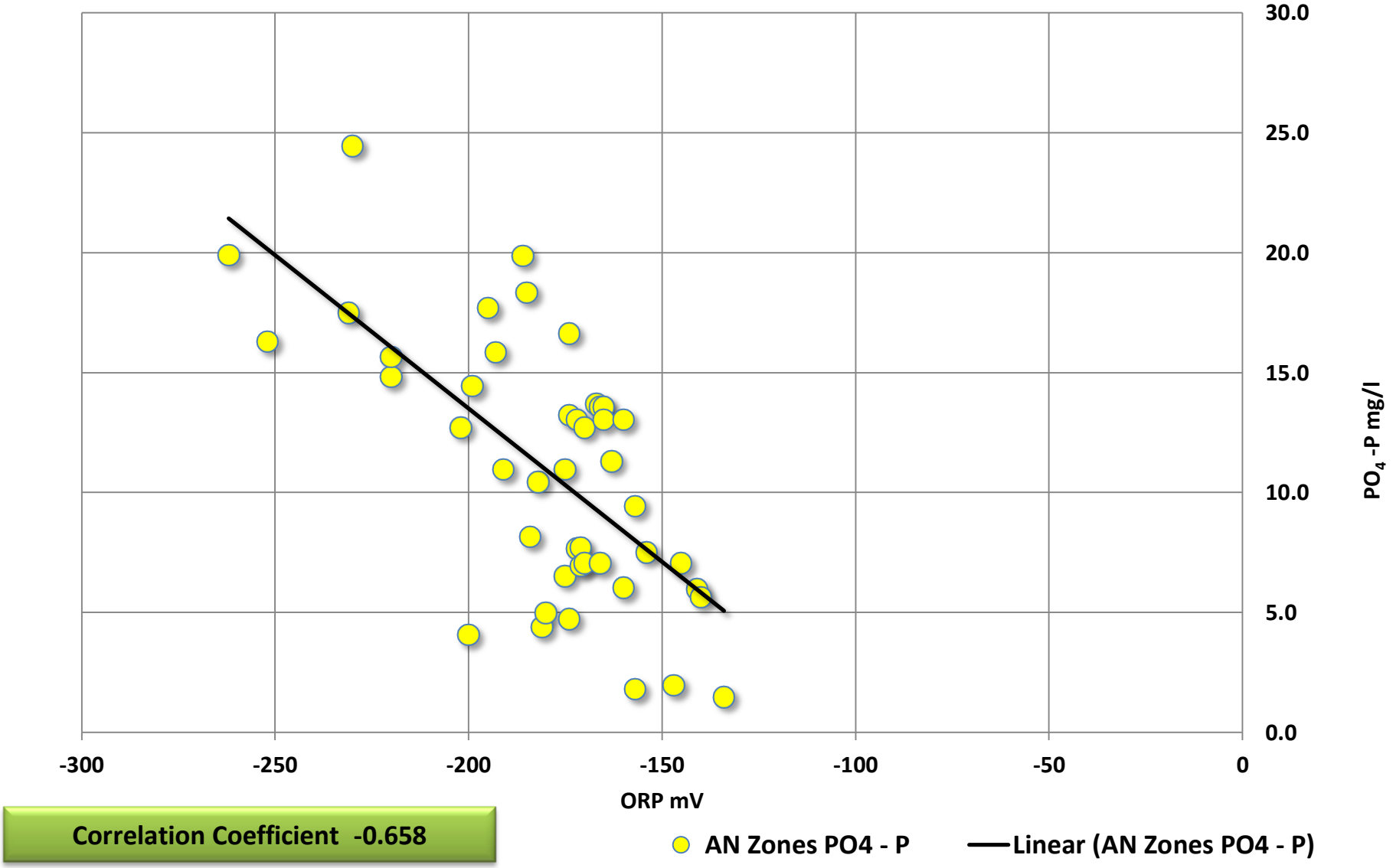
Aerobic Zones

- “During nitrification, the oxidation of ionized ammonia (NH_4) to nitrate is performed by nitrifying bacteria when the ORP of the wastewater is +100 to +350mV” MOP-37
- “Lower ORP could indicate an inactive sludge in the aerobic zone even though D.O. levels could be around 2 ppm” (Have to go Higher) MOP-37
- Linden -379 mV in AN and -170 in aerobic zone with 2 ppm D.O. (NO ammonia removal)

What Happen in a Final Clarifier?

- Use data from bench trial
- Graph showing P release vs. ORP
- P release is gradual – even with NO_3-N
- The lower the ORP the more NO_3-N converted
- Floating/rising sludge

AN Zones ORP & PO_4 - P



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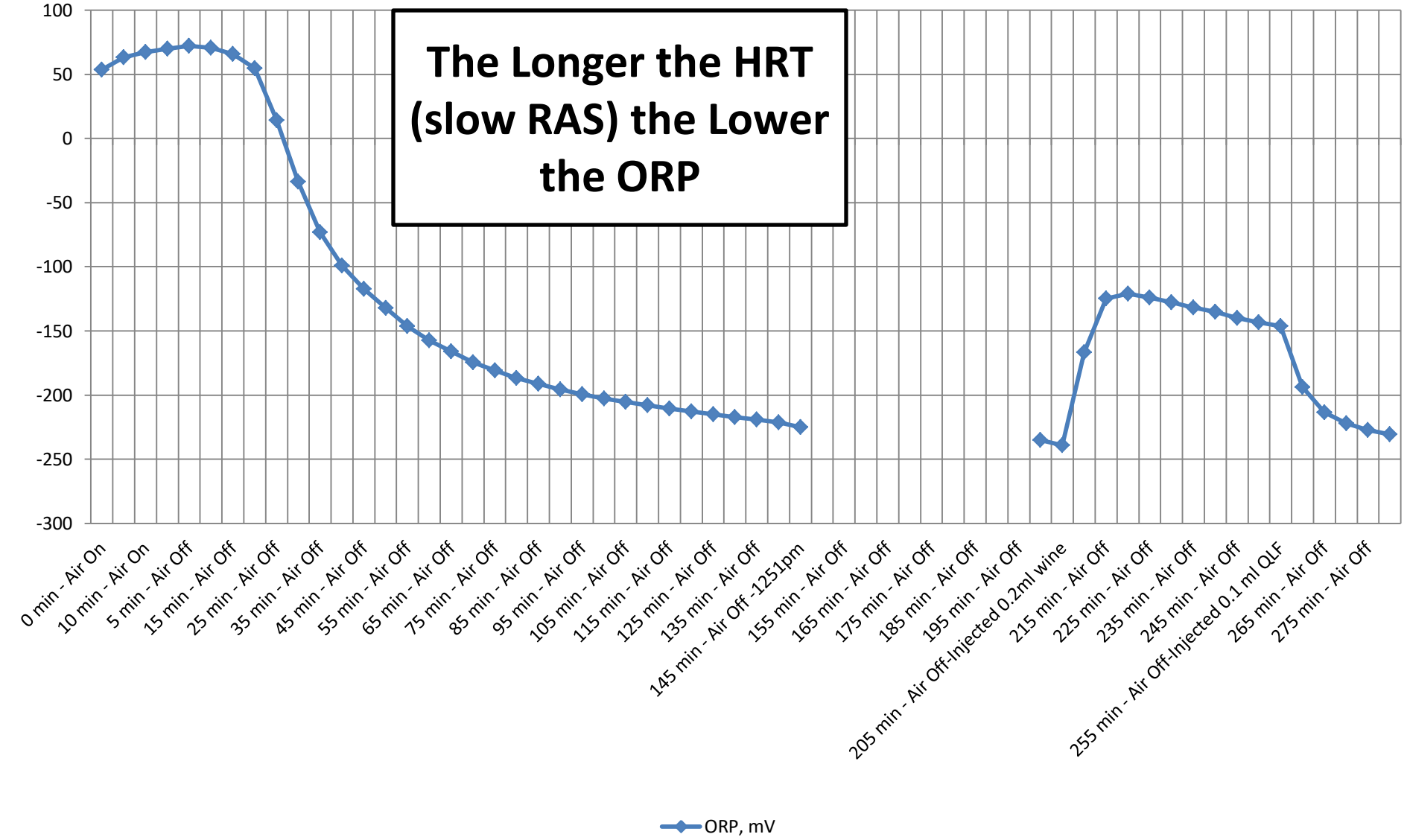

VFAs Production & ORP

- Most WWTP with BNR need more VFAs (BOD)
- Process of VFAs production
- ORP low does not mean enough VFAs
- Eleva-Strum steady -200 mV sewage is coming about at that – force mains
- To product more need to trap solids and ferment.
- You're looking at lbs./hr. VFAs and you need fermenting solids to increase VFA production

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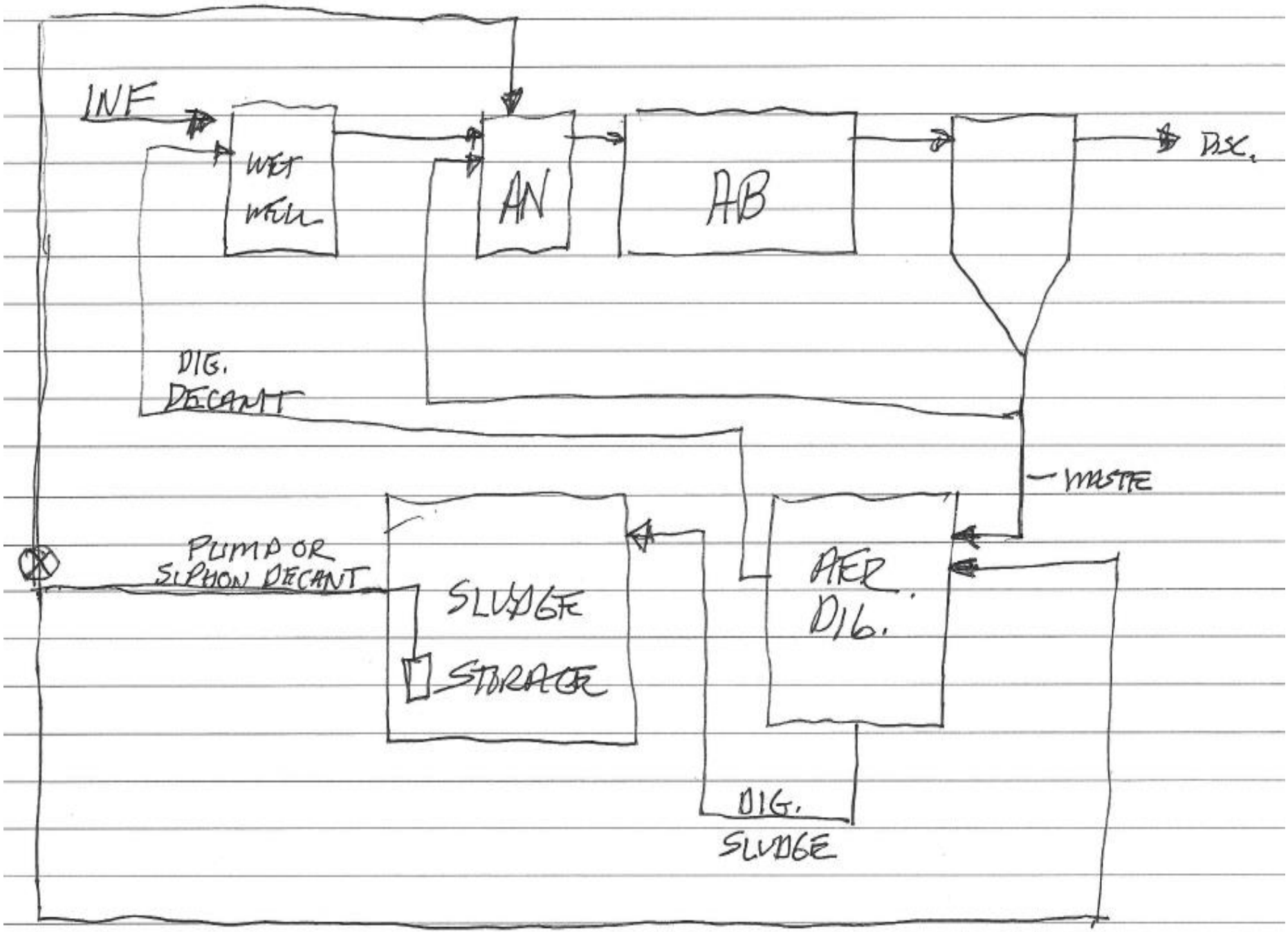
7. Case Studies/Bench Work

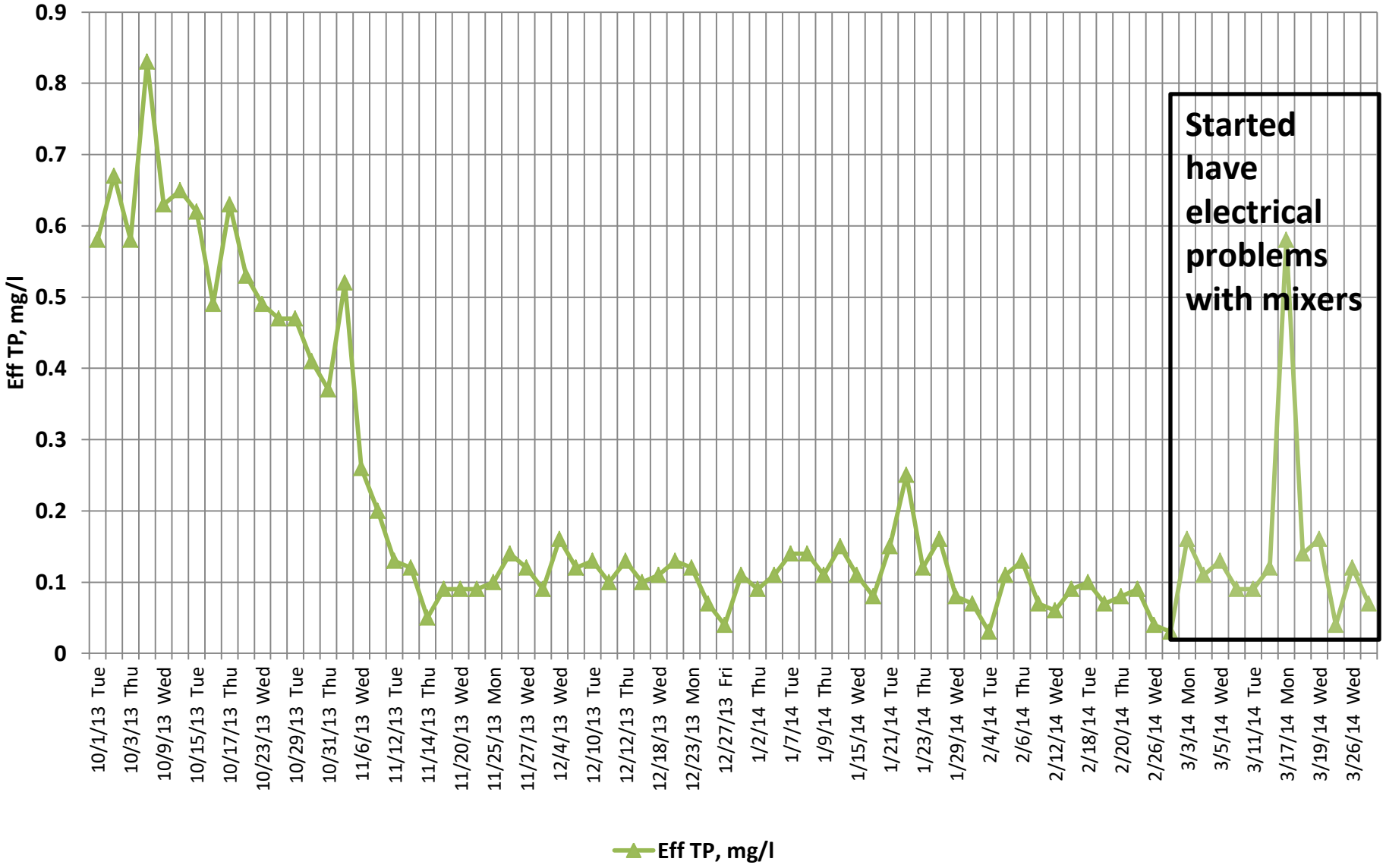
- Linden
- Lake County Mill Creek
- Dodgeville
- Eleva-Strum

Linden

- Problem-aerobic decant
  - Hard to get decant
  - High in NO_3-N & PO_4-P


INF
WET WELL
AN
AB
DISC.
DIG. DECANT
WASTE
PUMP OR SIPHON DECANT
SLUDGE STORAGE
AER. DIG.
DIG. SLUDGE

Dodgeville- On/Off Mixer Trial




Thank You
Greg Paul
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