Screening Water and Wastewater for Safety, Security, and Toxicity

Maryland Center for Environmental Training 301-934-7500 <u>info@mcet.org</u> www.mcet.org

Screening Water and Wastewater for Safety, Security, and Toxicity

WWW 5710

7 contact hours

9 CC10 hours

Description

The activated sludge process has limitations when handling toxic influents of unknown origin and strength. Once the bug population is destroyed or inactivated due to toxicity or high BOD loading, regrowth is a painful time consuming process. Time is of the essence when this occurs, so an immediate screening of the process can provide real-time information for decision-making. Simple screening tools will be discussed, such as: chemical oxygen demand tests, quick biological scans, rapid biological toxicity screening, and oxidation reduction potential (ORP). Participants will also discuss how quick screens of key areas of their water system for safety and security vulnerabilities can be beneficial; examine how case-histories and low-cost ideas and applications can be used to monitor strategic areas of their water system, and how these tools can be used as an early-warning mechanism to prevent disinfection residual violations, or assess the system for intrusions. Monitoring system components, applications and integration from hardware to data acquisitions and transmission will also be covered.

Learning Objectives

- 1) Identify the limitations of the activated sludge process when handling toxic influents.
- 2) Discuss ways to strategically monitor water and wastewaters for intrusions.
- **3)** Explain why simple measuring tools like ORP, COD, and Oxygen uptakes are beneficial when making quick decisions when the bug population is inactivated due to toxicity.
- **4)** Discuss how a measurement like ORP may provide an early-warning tool for distribution systems.

Outline

- I) INTRODUCTION (30 Minutes)
 - a) Early warning monitoring
 - b) Low in cost
 - c) Easy to install & maintain
 - d) Generate continuous surveillance data
 - e) Promote general health of the water/wastewater system (Negative transient pressure)
- II) SAFETY/SECURITY ISSUES (60 Minutes)
 - a) Most venerable part of the water system
 - b) Miles of unattended pipeline

- c) Potential easy access
- d) Meters, Hydrants, Back-flow preventers
- e) Potential for selective contamination

III) POTENTIAL CONTAMINATIONS & UPSETS (60 Minutes)

- a) Biological
- b) Chemical
- c) Mixed Liquor toxicity/inhabition

IV) COMMON SENSE APPROACH

- a) Limit access
- b) Limit venerability
- c) Low-cost hardware
- d) Simple to maintain
- e) Accountability

V) KEY MONITORING PARAMETERS (60 Minutes)

- a) That indicate change in water quality
- b) But not necessarily be a hazard
- c) Measuring these key parameters at key locations in wastewaters waters & distribution systems

VI) KEY MEASUREMENTS (60 Minutes)

- a) Oxidation Reduction Potential (ORP/Redox)
- b) Conductivity/TDS
- c) Chemical Oxygen Demand
- d) Oxygen Uptakes Rates, (DOUR/SOUR)
- e) Basic Water Quality Measurements

VII) WORKING WITH THE KEY PARAMETERS (120 Minutes)

- a) Define
- b) Application in Managing the Process Verification protocol
- c) Measurement apparatus
- d) Typical installations

VIII) MONITORING SYSTEMS (60 Minutes)

- a) Instrumentation
- b) Verification
- c) Installations
- d) Case History

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SCREENING WATER & WASTEWATERS FOR SAFETY, SECURITY, & TOXICITY

EARLY WARNING MONITORING FOR PUBLIC HEALTH AND SECURITY

Contact Info

Mike Harrington

Cell: 410-739-2331

E-mail: cmhco@verizon.net

Office: 410-928-3591

Potential Wastewater Threats

Accidental discharges Toxic specific purpose discharges Non-point sources discharges

"Mid-Night Dumper"

Quick Observations & Assessments

Common Observations pH Temperature Microbiological scans Alkalinity Color

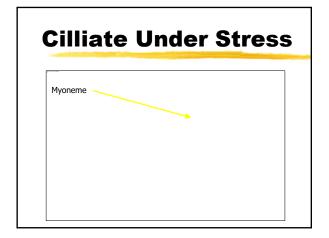


Identifying Organisms Under Duress, Potential Toxic Condition?

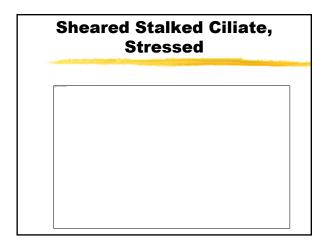
What does this mean for

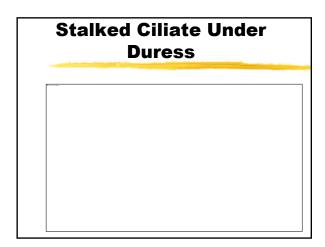
process control?











Other Screening Assessments

Abbreviated Chemical Oxygen Demand test

Oxygen uptake screens (SOUR)

Oxidation Reduction Potential (ORP)

Chemical Oxygen Demand, short-form

Chemical Oxygen Demand

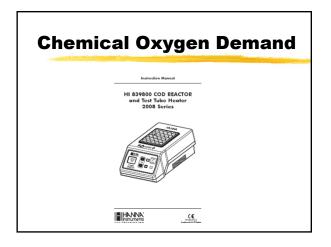
Abbreviated test for about 30 - 45 minutes, not typical 2 hrs. Choose Mercury, Mercury-free, Dichromate, or Manganese methods Test-in-tube method preferred Minimal sample size, smaller waste disposal issue

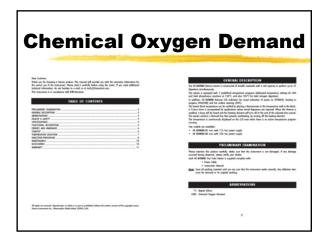
COD Determinations

Quickly determine high biological load, or slug

Estimate treatability

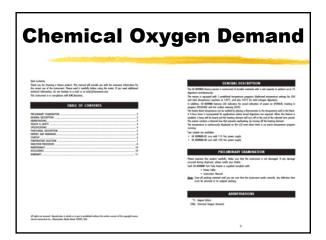
Quick 30 to 45 minutes screen test Approximate BOD loads, (ball-park COD is approx 2.5X BOD)







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Toxicity Screening Via DOUR/SOUR/OUR

The oxygen uptake test is useful in detecting toxicity. When toxins are present, the oxygen rate decreases. If extraordinary BOD loading, then oxygen uptake accelerate.

If one knows the range of uptake rates that are normal.

It is easy to see when toxins depress the uptake test and the results can be used to screen wastewater for toxicity



•EPA recommended Test for toxicity

•Performed on a variety of biodegradable polymers

•No toxicity for the coated cups

POLYTOXTM contains specialized microbial cultures that can determine the relative toxicity of water and waste water streams in about 30 minutes, with no expensive instrumentation required. The respiration rate is the oxygen consumed by aerobic and facultative bacterial cultures and is expressed as mg of O_2 consumed per liter per minute.

Features and Benefit - Polytox

•Cost effective product

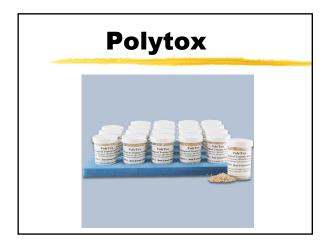
•Run with standard Dissolved Oxygen meter •Easy-to-use

•Reliable, consistent results in less than 30 minutes

•Free of nitrifying microorganisms

•Non-pathogenic

•Available in package of 20 vials



POLYTOX Equipment

- Standard (300 ml) BOD bottle(s).
- Dissolved oxygen probe and meter.
- magnetic stirrer or self-stirring dissolved oxygen probe suspending **POLYTOX**®
- Aeration device (e.g., aquarium pump, tubing and air stone).
- One and two liter containers to be used for aeration of the distilled or deionized water

POLYTOX Equipment

Wastewater or chemical (test) samples. pH adjusting solution(s) (e.g., dilute sodium hydroxide or sulfuric acid). Thermometer. Funnel. Stopwatch.

POLYTOX, Protocol

- Duration/contact time: 19 and 21 minutes
- Containers: 1 liter size for the aeration of the control(s), 2 liter size for the aeration of the test(s)
- Air Supply: clean, oil-free air
- Water: Deionized and/or distilled water

POLYTOX Protocol

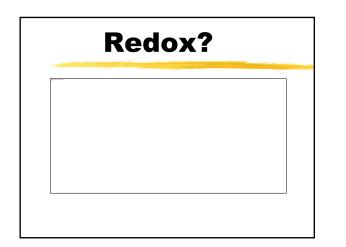
Reactor Vessel: BOD bottle(s) Test Solution: The freshly prepared wastewater or chemical solution (e.g., aerated solution with pH and temperature adjusted) Control: Baseline respiration rate for the

POLYTOX® populations only

Temperature: 20 + 2°C.

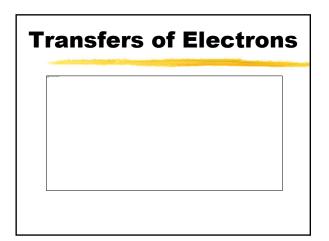








Why	Red	ox?	



What is REDOX(ORP)

Oxidation Reduction Potential is.....

A measurement of a waters capacity to oxidize and reduce



Common Oxidizers We Use

Chlorine Hydrogen Peroxide Potassium Permanganate Ozone Oxygen Air Chlorine Dioxide Iodine/Bromine

Common Reducers We Use

Sulfur Based, (Sulfur Dioxide, Sodium Thiosulfate, Sodium Bisulfite) Anoxic Anaerobic Metals, (FE, MN, CN, AS)

The Word "Potential"

Webster says the definition of the word "potential" is the possibility of doing something, or perform some work!

Things to Remember ORP

Oxidizers give up electrons

Reducers, accept electrons

Thates interaction between Oxidizers and Reducers produces a voltage signal

The word "Potential" means the possibility to perform work

Redox v/s Oxidation

Chlorination/Dissolved Oxygen

Down to Earth Examples

Redox Measurement

Redox Electrode

Seven Deadly Sins of Probe and Meter Measurements

Probe /meter selection Proper filling solutions Probe storage errors Limiting ions and demand in dilution waters Infrequent calibrations Forgetting temperature compensation Reused standards/buffers

Generates Millivolts

KEY ORP POINTS

All measurements are taken on-site

All measurements in Millivolts (mV)

ORP probes not typically temperature compensated.

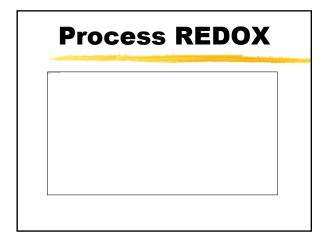
May take longer time window to get stabilized readings

Expect more probe maintenance than w/ typical pH probes.

Field Redox Measures

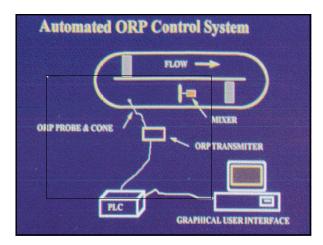
Field Redox Measures

Field Redox Measures



Process Applications

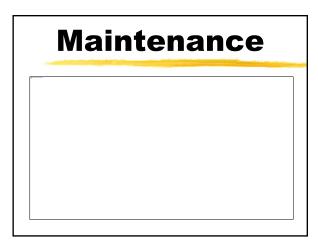
Collection system monitoring Nitrification/Denitrification Phosphorus removal Toxicity screening Chlorination/Dechlorination Sludge digestion

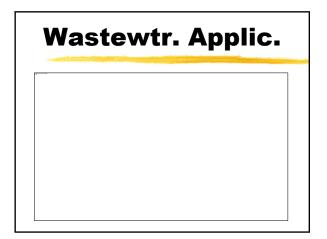






Verification/Reference



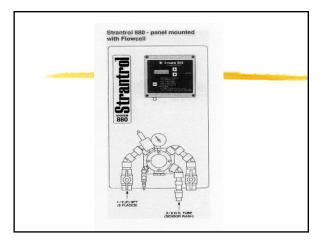


Wastewtr Applic.

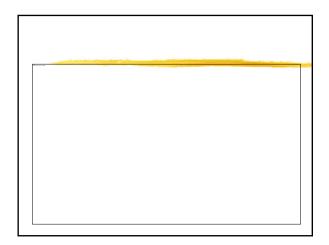
Chlorination

Process Disinfection REDOX

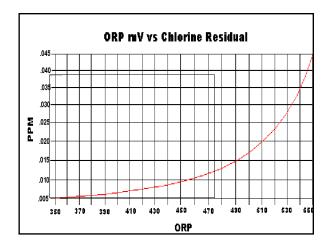
Dechlorination



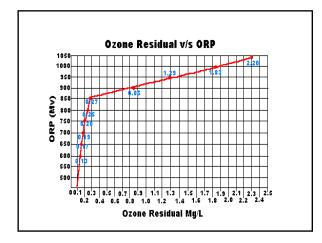
Case History, Lancaster, PA	istory, Lancaster, PA	



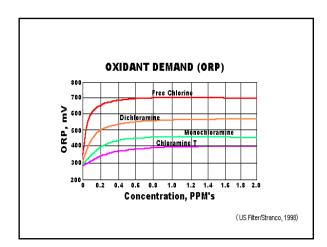
















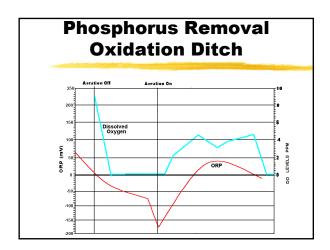
Phosphorus Removal

Aerobic and Anaerobic process Anerobic zone releases phosphorus (bacteria)

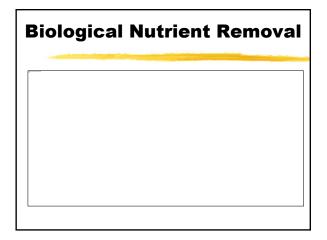
Aerobic zone absorbs (bacteria)

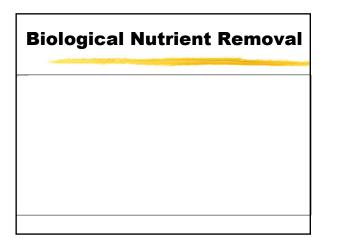
Target REDOX:

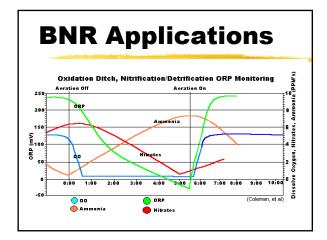
Anaerobic Zone: -200 to -300 mV Aerobic Zone: > +100 mV



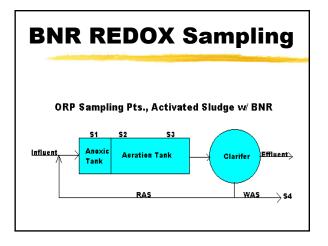


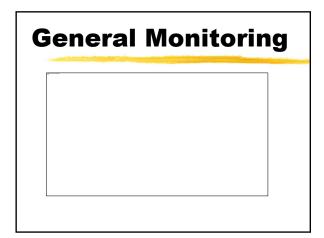


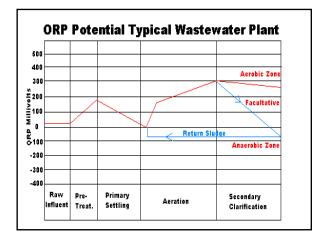




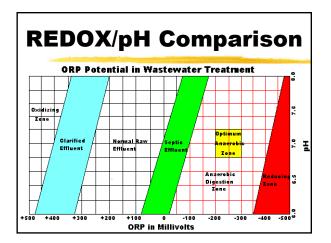










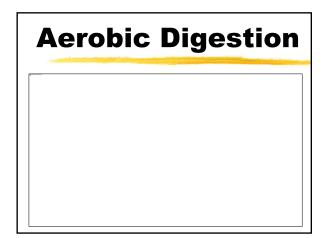




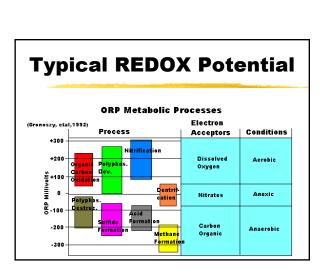
Toxicity Screening

Odor Control

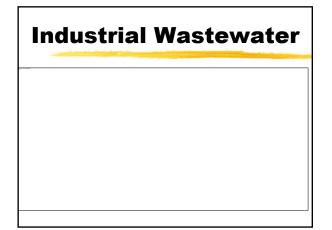
Anaerobic Sludge Digestion



Organic Carbon Reduction



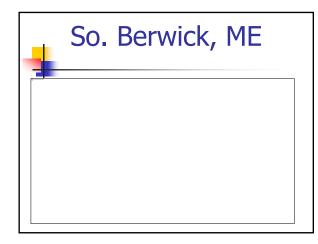


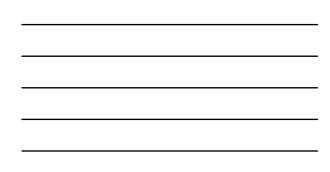


Industrial Wastewater

Case Histories







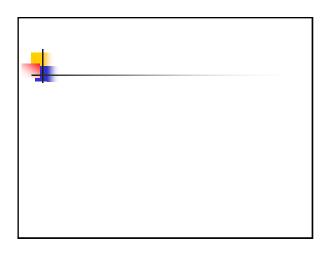




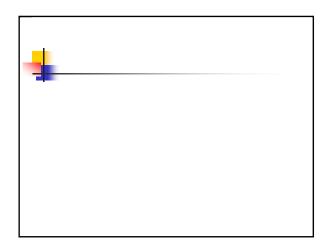


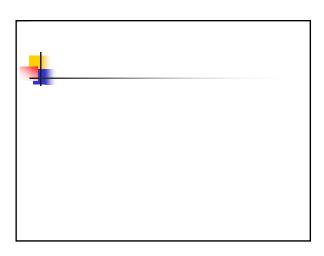
		10.09.15 AM
SBR1	SBR2 SBR2 SBR2 SBR2 SBR2 SBR3 SBR2 SBR3 SBR2 SBR3 SBR2 SBR3 SBR2 SBR3 SBR2 SBR3	Phase Time Remaining SBR1: 114 SBR2: 09 Decant Time Accumulated SBR1: 0 SBR2: 0



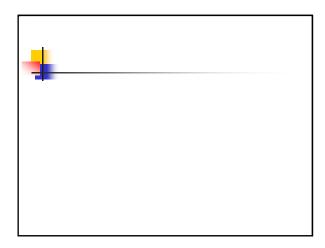






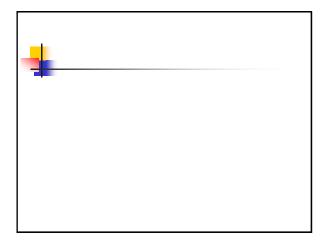




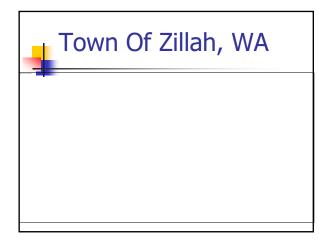


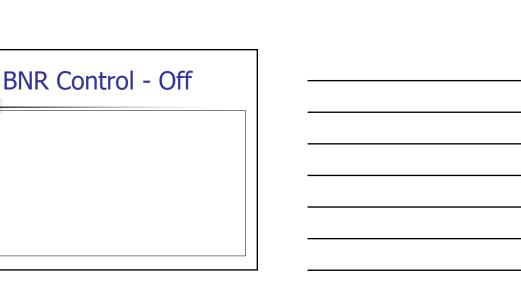


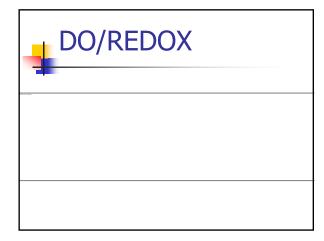




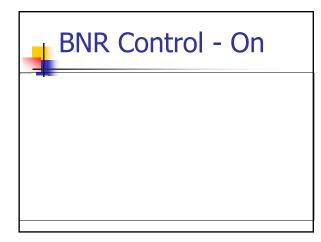
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Indication & Control



WASTEWATER SCREENING CONCLUSION

Quick simple screening of wastewaters a must to avoid toxic shocks

Visuals, pH, temp, Alkalinity a must Quick COD's. (45 minutes)

OUR, SOUR screens, powerful tools

ORP monitoring, very useful simple probe based measurement

WATER DISTRIBUTION SCREENING & MONITORING

Simple low-cost screening for basic water quality issues Quick screening for toxics Don't forget Cyber Security in the Treatment facility and Distribution (Operator Monitor) Terrorist Threat?

WATER DIST. OBJECTIVES

- Early warning monitoring
- Low in cost
- Easy to install & maintain
- Generate continuous surveillance data
- Promote general health of the distribution system by assessing:
 - Water Retention time, (stagnation)
 - Slime formation and build-up

DISTRIBUTION SAFETY/SECURITY ISSUES

- Most venerable part of the water system
- Miles of unattended pipeline
- Potential easy access
 - Meters
 - Hydrants
 - Back-flow preventers
- Potential for selective contamination
- Even the small system may be venerable to terrorist threat

Digital Intrusions via Remote Access

- Unauthorized intrusions that potentially gain direct access to process controls
- Hacker's looking to upset and cause an alarm response
- Unauthorized direct access to SCADA
- Even potential terrorist threats
- The need for active operator monitoring, notification & prevention software

SCADA Intrusion, Real Example

<u>Police</u> say an attempt to contaminate a <u>Florida</u> city's water supply with sodium hydroxide has failed despite a <u>hacker</u> gaining remote access to the local water treatment plant's computer system.

Pinellas County Sheriff Bob Gualtieri said during a news conference on Monday that a plant worker at the city of Oldsmar's water treatment facility first noticed unusual activity with its computer system at 8 a.m. on Friday, when a hacker briefly access the system.

At about 1:30 p.m., a hacker accessed the system again, taking control of the mouse and directING it to the software that controls water treatment. The hacker then briefly increased the amount of sodium hydroxide from 100 parts per million to 11,100 parts per million.



SCADA Intrusion Example

Sodium hydroxide, also known as lye, is the main ingredient in liquid drain cleaners. It also is used to control water acidity and remove metals from drinking water at treatment plants.

After the hacker exited the system, a worker at the plant was able to intervene and reverse the change.

"Because the operator noticed the increase and lowered it right away, at no time was there a significant adverse effect on the water being treated," Gualtieri said. "Importantly, the public was never in danger."

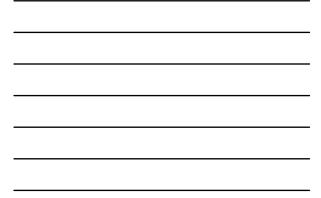
Gualtieri noted that even if the worker had not intervened right away, it would've taken between 24 and 36 hours to hit the water supply system and that there are other safeguards in place where the water would have been checked before it was released.

POTENTIAL CONTAMINATIONS Biological

Chemical

Г

BIOLOGICAL CONTAMINATION						
High Priority	Medium Priority	Low Priority				
E-coli Fecal Coliform	Staph	Brucella				
Legionella Salmonella	Listeria	Hepatitis				
Anthrax	Cholera	Cocksackie Virus				
Blue/Green Algae Toxin	Plague					



Emerging Biological Pathogens

Legionella, (legionnaires disease) Covid-19 (corona virus)

Cocksackie virus (A & B3), Undisinfected secondary wastewater, fecal matter, fecal contaminated potable waters

Salmonella - comes from ingesting food or water contaminated with warmblooded animal feces.

Emerging Biological Pathogens

Brucella – food related, but can be spread through both potables and untreated wastewater from food processor

Blue-green algae toxin - (red tide)- surface water related, prefers elevated temperatures to re-emerg.

Naegleria fowleria – (fresh water flesh eating amoeba)

Toxic Cyanobacteria - health problem arising as a consequence of eutrophication.



Simple No-Cost Blue-Green Algae Test Protocol

The jar test

If your lake or pond water appears very green, the jar test can help determine if the color is from blue-green algae, or just an overabundance of more beneficial types of planktonic algae.

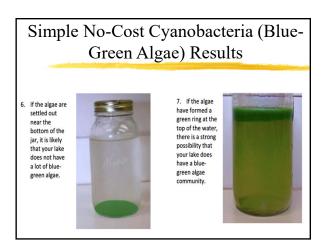
Materials

- Clear jar (pint to quart size) with a screw top lid, such as a canning jar or pickle jar with label removed
- Rubber or latex gloves



Procedure

- With the gloves on, collect a sample just below the surface of the water (avoid collecting just the top layer of scum).
- 2. Fill the jar about three-quarters full. Do not fill the jar completely; algae give off gases that may cause
- pressure buildup in the jar that could break it. 3. Wipe any scum off the outside of the jar and screw the lid on.
- 4. Put the jar in the refrigerator and leave it undisturbed overnight.
- Carefully remove the jar from the refrigerator and see where the algae has accumulated. Do not shake or agitate the jar at all or the algae will mix into the water again and negate your test results.



CHEMICAL CONTAMINATION

VX (50ug/l) Sarin (50ug/l) Cyanide (25mg/l) Arsenate (100- 130 mg/l)	Acids (unk) Alkali's (unk) Arsenite (100-130 mg/l) Sodium Fluoroacetate (unk)
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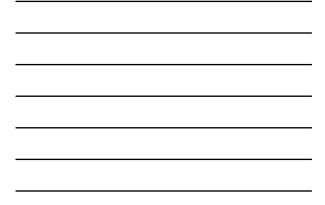
Common Sense 1st

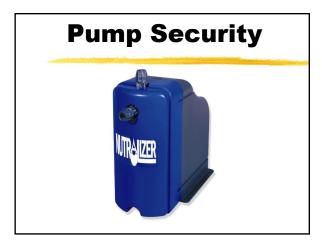
Limit access Limit venerability Low-cost hardware Simple to maintain Accountability











SAFETY/SECURITY CONCEPTS

Install monitoring devices

Collect and process data over time

Generate historical data over time

Look for deviations from established norms

Follow-up with confirming sample collection and lab based testing

Early Case History, Washington D.C.

Fort Reno Tank was selected as the first location for remote monitoring system implementation

Four water quality parameters were selected for monitoring in this Case Study - Temperature, Chlorine, Turbidity, pH

The study was later on expanded to two other locations Bryant Street and Blue Plains

The existing WASA's SCADA system was adapted for data collection

Overview of the Case Study

In 1996, following a number of Coliform violations EPA Region-3 directed DC Water and Sewer Authority (WASA) to implement several corrective actions

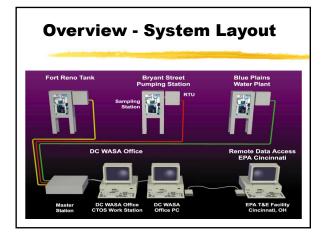
One of the corrective actions proposed was remote monitoring of water quality. In 1997, EPA initiated a study to install a remote monitoring network

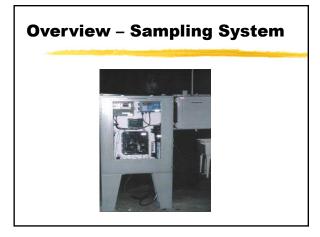
System Selection and Implementation

Off-the-shelf online monitoring instrumentation for Temperature, Chlorine, Turbidity and pH with 4-20 mA external outputs were used

- A custom water sampling system was built for each site
- A Preliminary Assessment for selecting and implementing the appropriate Data Acquisition System was performed. Key factors are outlined as follows:

Initial and ongoing \$ - EPA/WASA





System Selection and Implementation

Ease of use and programmability -Proprietary Hardware Networkable - Yes System Scalable - Yes Data/System Redundancy - Yes System Security - One Way Data Transfer Remote Access Capability - Not Available System Response Time - More than adequate Historical Trend Data Storage/Transfer Capability - Limited Storage Availability of Local Support - WASA

System Selection and Implementation

Software Features – Graphics, Trending and Reports

Remote Access - Added a Windows-based PC workstation to dial into using pc Anywhere/ Reachout Software (added security, prevents remote access to the WASA SCADA system)

Trending - Export Program in Access97 Reporting - Queries to chart in Excel97 Power Availability - Yes

Discussion

3. How to select and implement/integrate the various SCADA system components for data collection?

a. Implement new or integrate with existing SCADA system b. Communication media – Cable/wire, cellular, satellite, RF, etc.

c. Data collection and handling

Discussion

- 4. Intended use and interpretation of real-time data?
- a. What do the numbers mean?
- b. Do we need data filters? How do we verify and report the data?
- 5. Monitoring system maintenance and management?
- a. Proper training/retention of people
- b. Instrument calibration and recordkeeping
- c. Commitment from management \$ xxx,xxx's

Discussion

What parameters should be monitored, selection criteria for monitoring instrumentation? a.Conventional (Physio-chemical) pH, ORP, DO, Turbidity, etc. b.Biological – Daphnia, fish, clam, other Both

TWO KEY MONITORING PARAMETERS

That indicate change in water quality

But not necessarily a hazard Measure these two key parameters at key locations in the distribution system

LOCATION SELECTION PROTOCOL

Easy installation & access

Easy maintenance Critical protection point in the distribution system Easy data collection & transmission

INSTALLATION INCLUDES

2 Parameter monitoring installed at key locations in the distribution

2 Parameter information is data-logged Transmission to central location Standard SCADA software and hardware with graphic display and alarms Integration with exist SCADA systems.

ONE or TWO KEY PARAMETERS

Oxidation Reduction Potential (ORP/Redox)

Conductivity/TDS

OXIDATION REDUCTION POTENTIAL

ORP/REDOX

OXIDATION REDUCTION POTENTIAL

Define

Applications Verification protocol Measurement apparatus Typical installations

WHAT IS OXIDATION REDUCTION POTENTIAL

Oxidation Reduction Potential is.....

A measurement of a waters capacity to oxidize and reduce

DOWN	DOWN TO EARTH EXAMPLES			
1				

ORP TECHNOLOGY

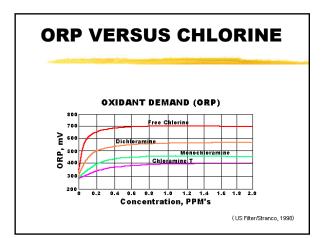
Meter and probe technology

Typically not temperature compensated Combination ORP measurement cell and reference cell, (Much like pH electrodes)

KEY ORP POINTS

All measurements are taken on-site All measurements in Millivolts (mV) ORP probes not typically temperature compensated. May take longer time window to get

stabilized readings Expect more probe maintenance than w/ typical pH probes.





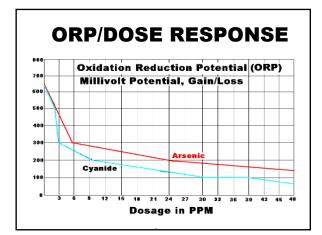
pH/ORP RELATIONSHIP

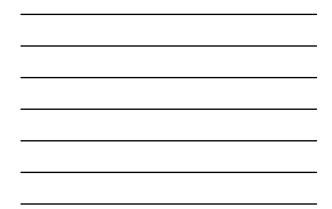
ORP VERSUS CONTROLLED CONTAMINATE DOSE STUDIES

Investigation into how two common toxics might respond in distribution system Bench-top lab controlled dosing Chlorinated treated potable water samples Controlled additions of: Sodium Cyanide Sodium Arsenite

DISTRIBUTION WATERS BACKGROUND DATA

pH: 8.55 Measured Total Residual Chlorine: 0.89ppm Corresponding initial ORP measured: +655Mv Temperature: 19.8 Degrees C





CONDUCTIVITY/TDS

Total Dissolved Solids Anything that passes through a 0.45 micron filter

Includes:

Carbonates, Bicarbonates, (ALK,

Hardness)

Chlorides, Sulfates, Borate's, Phosphates Most potable waters should be < 500 PPM

CONDUCTIVITY/TDS

Measured with meter & probe Multi-parameter meter Conductivity - (Specific Conductance) Micromhos Microsemiens Total Dissolved Solids PPM PPT

DISTRIBUTION WATER CONDUCTIVITY

Tends to increase whenever chemical compound is added

Common treatment chemicals

Alum

Ferric Chloride

Chlorine Caustics

As well as toxic substances

CONDUCTIVITY V/S CONTROLLED CONTAMINATE DOSE STUDIES

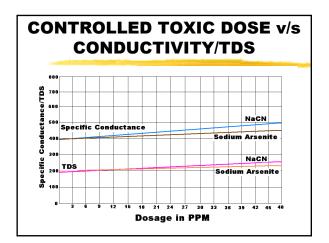
Investigation into how two common toxics might respond in distribution systems Bench-top lab controlled dosing Chlorinated treated potable water samples Controlled additions of: Sodium Cyanide Sodium Arsenite

DISTRIBUTION WATER BACKGROUND DATA

pH: 8.55

Measured Total Residual Chlorine: 0.89ppm Initial Conductance/TDS: 399ms/ 197ppm

Temperature: 13.6 Degrees C





IINSTRUMENTATION SELECTION

ORP & Conductivity instrumentation selection protocol

ORP & Conductivity Probe selection protocol

Data-logging instrumentation protocol SCADA instrumentation selection and interface.

SELECTING MONITORING POINTS in the DISTRIBUTION

Obtain updated valid distribution valve and piping maps and schematics.

Select critical points in the distribution for monitoring

Large high populations activity sites

Stadiums

Large industrial users Colleges/Universities

Colleges/ Universitie

Where large volume of general population congregate

SELECTING MONITORING POINTS in the DISTRIBUTION

Critical junctures with large pipe diameter distribution lines.

Probes & meter installation sites with ease of installation.

Power source availability

- Data transmission pathway
- Protection from vandals

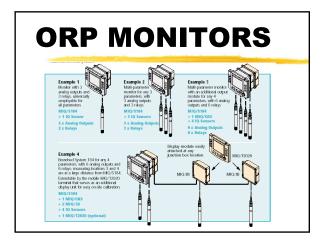






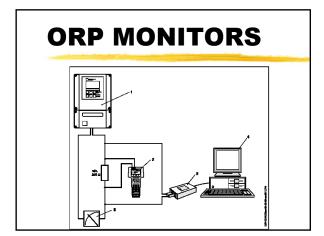


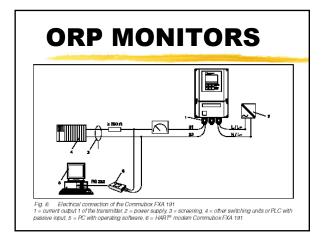




ORP MONITORS

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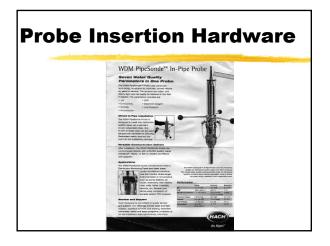


ORP/CONDUCTIVITY PROBE SELECTION

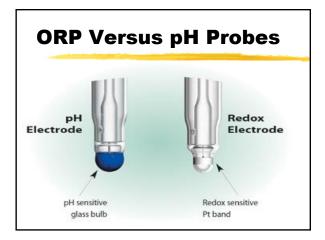
Standard probe tip or flat surface Glass probe Probe body type(ORP & Conductivity) Plastic Stainless Steel Pressure Ratings Plastics - typically to 80PSI Double-juncture Reference element

ORP & CONDUCTIVITY PROBE SELECTION

Probe installation Compression insert/value isolation Saddle Threaded insert





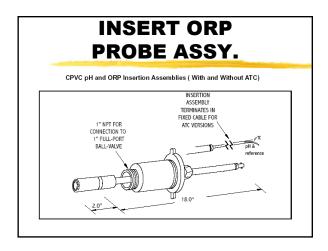
















FLAT SURFACE ORP PROBE

VERIFYING ORP CALIBRATIONS

Four Calibration Methods

Light's Solutions, (453mV @ 20° C)

PrePackaged Calibration Standards, (pt size) 200mV

400mV

600mV

Zobel's Solution (228mV @ 20° C)

pH Buffer 4 & 7 saturated w/ Quinhydrone Saturated Buffer 7 should read approx.+ 90mV Saturated Buffer 4 should read approx. +270mV

SATURATED BUFFER CALIBRATIONS

Prepare electrode by cleaning Liquid soap & soft bristled toothbrush Saturate 50-100mL of each buffer w/ about 0.2g of Quinhydrone Connect probe to meter and immerse in each solution. Wait for table reading Always rinse probe between each submersion with DI or tap-water

CALIBRATION INTERPRETATIONS

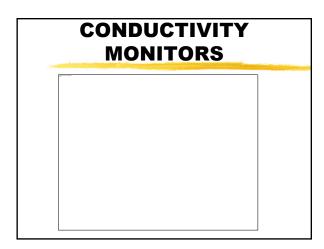
Test verifies function of platinum & reference cells

If probe responds w/ adequate difference between the 4 & 7 saturated buffers

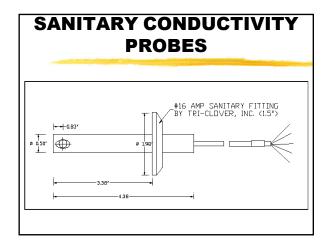
But..is out of calibration range

Indicates a plugged reference cell or contaminated filling solution.

Discard all solutions when done, no >2 hrs.











CONDUCTIVITY CALIBRATIONS

Pourable multiple component salts standards

Supplied in uS & TDS concentration

Use at least one standard for each range of the meter

Pour enough to standard into separate vessel to cover bottom of probe

CONDUCTIVITY CALIBRATION PROTOCOL

Pour only enough solution in a beaker to cover measurement element

Calibrate as close as possible to actual sample temperature.

Wait for meter/probe to stabilize Adjust meter calibration as needed Dispose of calibration solutions when done



Conclusions

Simple probe based monitoring of distribution systems can be viable for small systems Low-cost ORP/Conductance measurements

may give early warning to potential issues.

Easy maintenance and operations are key to success here.

Follow-up with verification tools will be key to make this early-warning system work