# "The MDEQ Laboratory & Real-Time Monitoring Analytical Parameters as a part of Contaminant Warning Systems"

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# Analytical Testing at the State Laboratory

# SECURITY

Sample and
Specimen Receiving

Restricted Area
AUTHORIZED PERSONNEL ONLY
This area is restricted to persons with official state business and approved identification cards.
Access to the general public is prohibited.
Community Health Laboratory: (517)335-8063
DEQ Drinking Water Laboratory: (517)335-8184
DEQ Environmental Laboratory: (517)335-9800

SAMPLE/SPECIMEN DELIVERY
Access for sample/specimen delivery is restricted to authorized personnel and the regulated community with proper identification. Follow signs to the north lobby entrance by gate.

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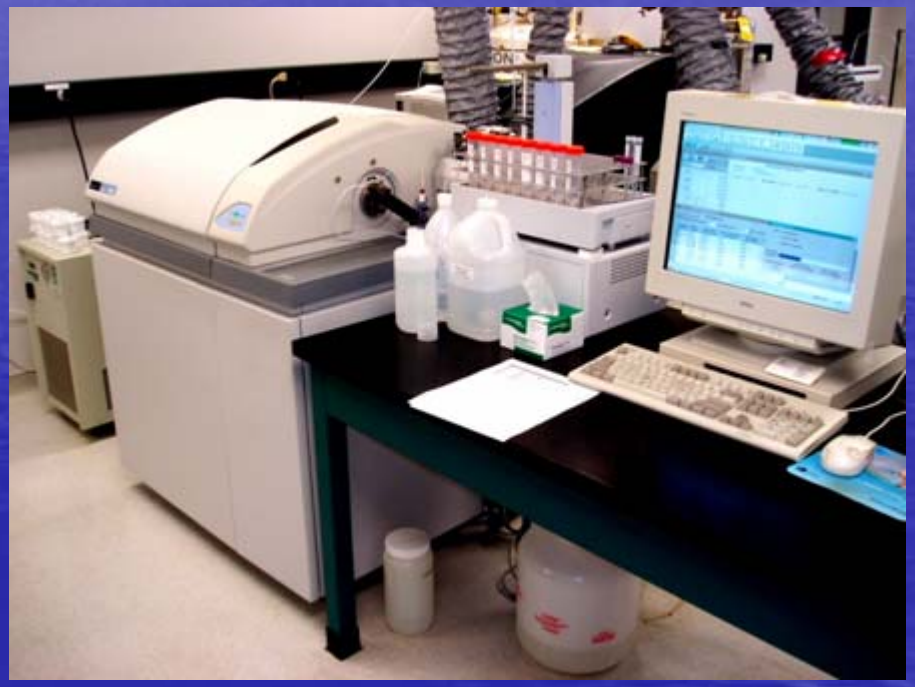
# ANALYTICAL TESTING AT THE MDEQ LABORATORY

FULL CAPABILITIES FOR REGULATED, UNREGULATED AND UNKNOWN COMPOUNDS IN POTABLE WATER, SURFACE WATER, SOIL, SEDIMENT AND AIR SAMPLES

# HPLC & Gas Chromatographs With Mass Spectrometers For Organic Compounds



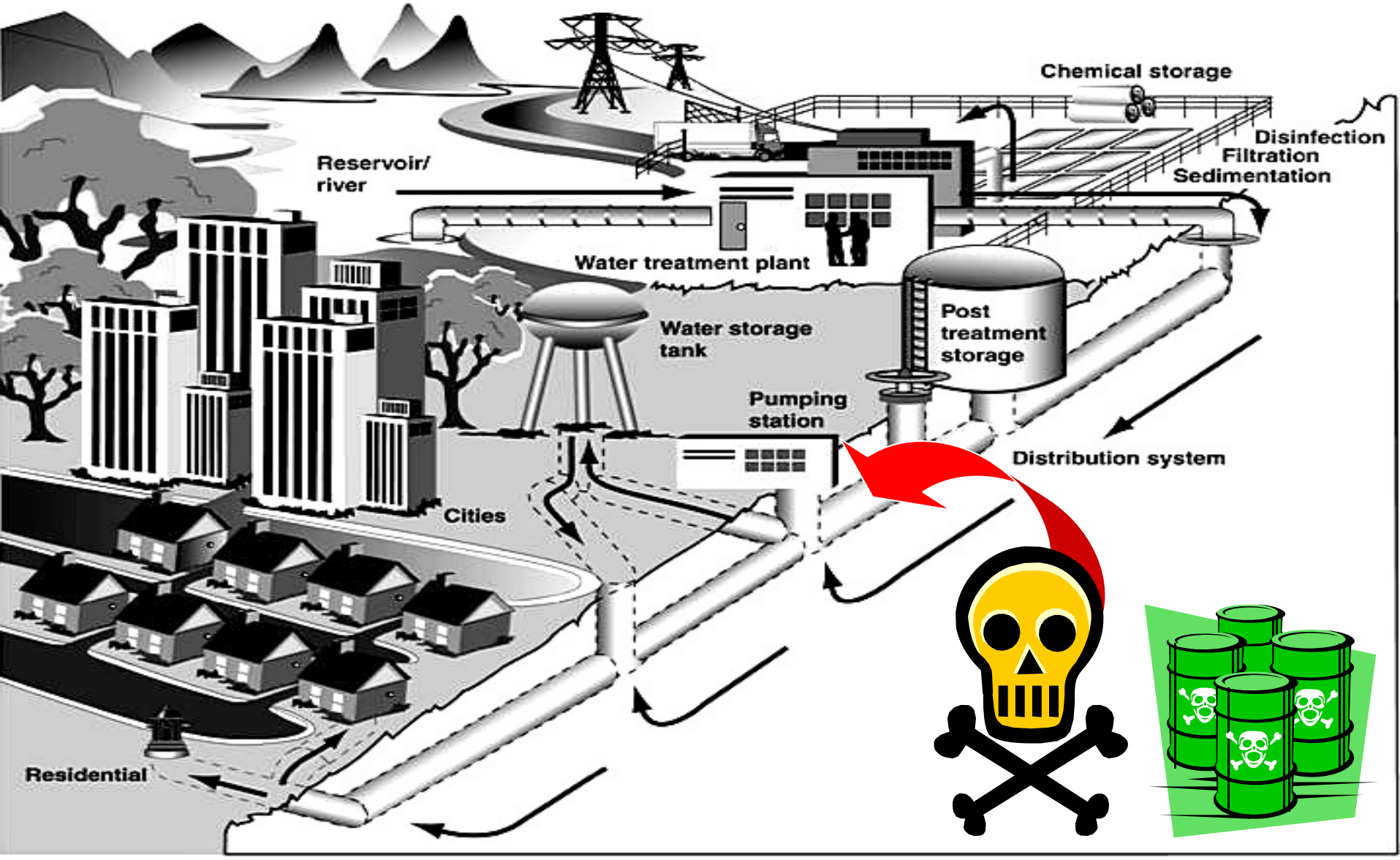
# Inductively Coupled Plasma With Mass Spectrometer For Metals

# LABORATORY TESTING VS REAL-TIME MONITORING

| | |
|---|---|
| • EPA METHODS WITH FULL QUALITY CONTROL | • FAST SCREENING WITH QUICK RESULTS |
| • CONTROLLED LAB ENVIRONMENT | • MOBILE OR ON-SITE TESTING |
| • IDENTIFIES SPECIFIC COMPOUNDS | • NON-SPECIFIC SCREENING |
| • LEGALLY DEFENSIBLE IN COURT | • NEEDS CONFIRMATION TESTING OF SAMPLES |

TESTING TIME IS CRITICAL FOR "RAPID RESPONSE" TO POTENTIAL TAMPERING OF DISTRIBUTION SYSTEM

# WHY PERFORM REAL-TIME MONITORING?



# HOWEVER……

- **HIGH RISK: water distribution.**

This component of the water supply is the most vulnerable. Pipelines wander for thousands of unprotected miles; aqueducts snake through largely unpopulated areas. A person with a crude knowledge of hydraulics and a bicycle tire pump and access to a kitchen faucet could introduce toxins into any local water distribution system, thus endangering thousands. There are few robust security methods in place to protect these distribution systems.

Source: Internet

# THE DISTRIBUTION SYSTEM IS VULNERABLE

Concerns over the safety of drinking water, and the security of drinking water distribution systems date back to approximately 300 B.C. during the construction of Aqua Appia, one of the aqueducts of the Roman Empire. The Romans were concerned that their water supply systems would be rendered useless by enemy action. To avert this threat, some of their aqueducts were buried up to 50 feet in the ground (Herschel,1973).

# WHAT IS REAL-TIME TESTING AND WHAT IS AVAILABLE?

**-BIOMONITORING**

**-INLINE MONITORING**

LOT'S OF PAPERS DISCUSSING THE NEED FOR REAL-TIME MONITORING, BUT FEW PAPERS WITH ACTUAL PRODUCTION TESTING INSTRUMENTS AND DATA ARE AVAILABLE

# BIOMONITORING

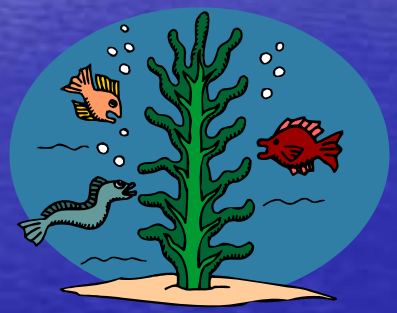
## "Drinking Water Early Warning Detection and Monitoring Technology Evaluation and Demonstration"

Susan S VonderHaar, Dana Macke, Rajib Sinha, E.Radha Krishnan – IT Corporation, 11499 Chester Road, Cincinnati, Ohio

Roy C. Haught – United States Environmental Protection Agency, National Risk Management Research Laboratory Cincinnati, Ohio

# Assessment of toxicity in water samples by monitoring the behavior of living organisms.

The U.S. EPA is evaluating the following technologies:



a) Algae toximeter

c) Daphnia toximeter

b) Clam monitor

d) Fish monitor

# HOW DO THEY WORK?

Instruments monitor the growth, respiration, clam mantle opening (gaping), swim characteristics, velocity, fluorescence response, ‘curviness’ of swimming patterns, gill pulse, body movements and a host of other parameters that would show organism discomfort from an exposure or change in water quality.

# REAL-TIME BIOMONITORING WORKS BEST WITH SOURCE WATER TESTING

- Live organisms fare better in source water then treated water.
- Must establish baseline, especially if different sources are used during the year
- Complex and high maintenance….must constantly feed and replenish organisms

# REAL-TIME IN-LINE MONITORING FOR DISTRIBUTION SYSTEMS

LITTLE INFORMATION WITH SUPPORTING TEST DATA

**"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM",**
**July 2005 Journal AWWA 97:7 Byer & Carlson**

**"WATER MONITORING EQUIPMENT FOR TOXIC CONTAMINANTS TECHNOLOGY ASSESSMENT",**
**October 2004, National Technology Alliance and the Chemical, Biological and Radiological Technology Alliance**

Slides that follow contain information from these reference papers

# COMPOUNDS OF IMMEDIATE CONCERN FOR MONITORING

- Industrial chemicals: cyanide & heavy metals
- Organic chemicals: chlordane, chlorinated pesticides, etc.
- Biological Toxins: botulinum & ricin
- Chemical warfare agents: VX & Sarin
- Radionuclides

# INSTRUMENT CRITERIA

- Sensitive enough to detect wide variety of potential chemicals that may be introduced into the system at the levels that are toxic to humans
- Readily available
- Inexpensive
- Easy to use and maintain
- Provides mobile and rapid testing

# What is available now for "REAL-TIME MONITORING?

- DO, temperature, ORP, salinity, nitrate, ammonia, various probes, portable GC/MS
- pH, conductivity, chlorine residual, turbidity, and TOC (total organic carbon)

# Biological Toxins: botulinum & ricin

BOTULINUM toxin inactivated in ~20 minutes with free available chlorine (3ppm)

RICIN can be removed by carbon absorption and RO

*****Possible detection of biofilm toxicity die off and sloughing with turbidity meter or particle counter.

# Industrial chemicals: cyanide & heavy metals

**CYANIDE**

- Ionizes to form cyanide or cyanic acid depending on water pH

**HEAVY METALS**

- Will increase conductivity

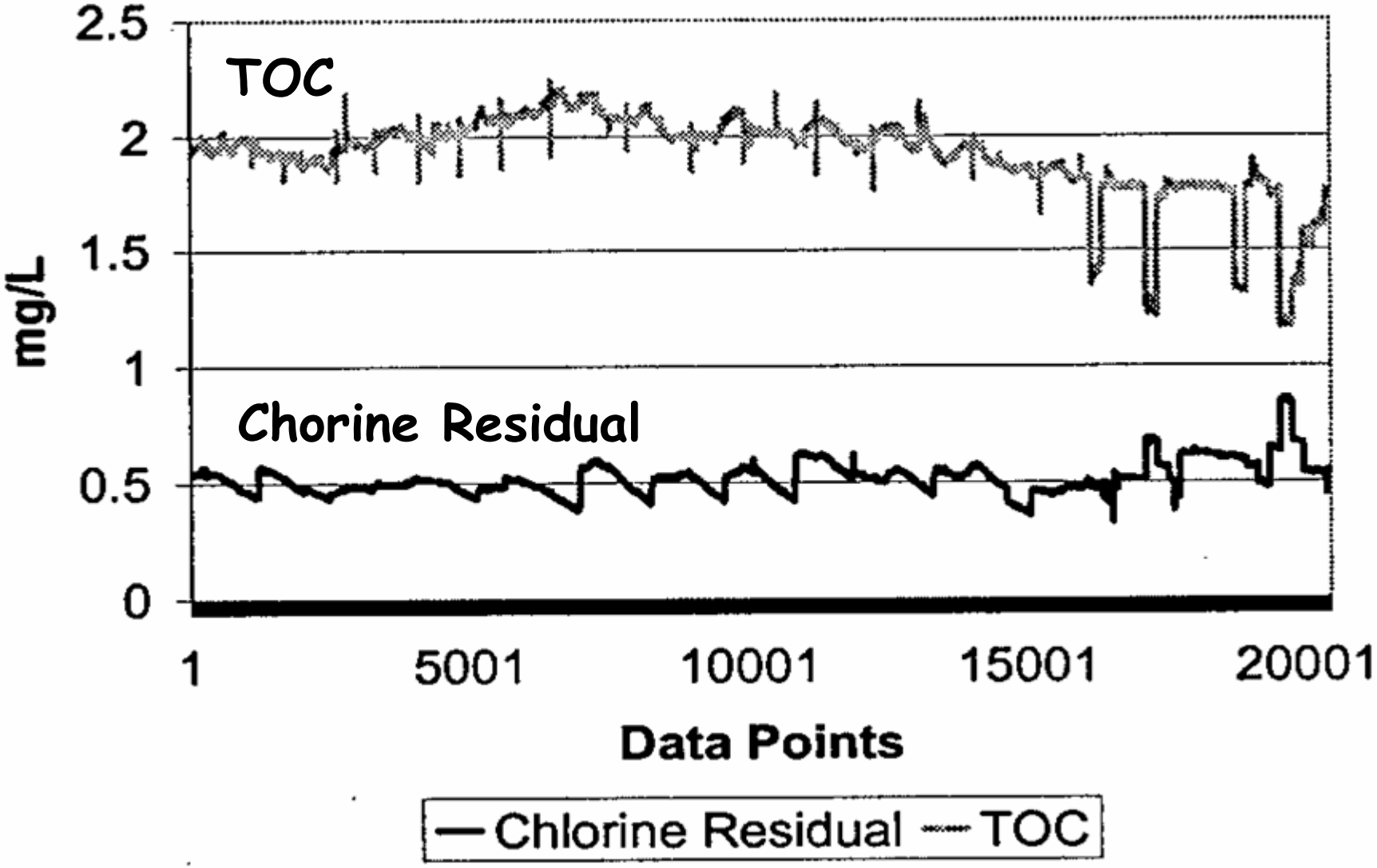
# ORGANIC CHEMICALS: CHLORDANE, CHLORINATED PESTICIDES, ETC.

- The organic carbon molecules will increase the TOC meter readings
- Free chlorine is a strong oxidizer of some organic compounds and reduced metals which will decrease the concentration of free/total chlorine

# BUT FIRST, NEED TO ESTABLISH RANGE OF NORMAL DATA "BASELINE"

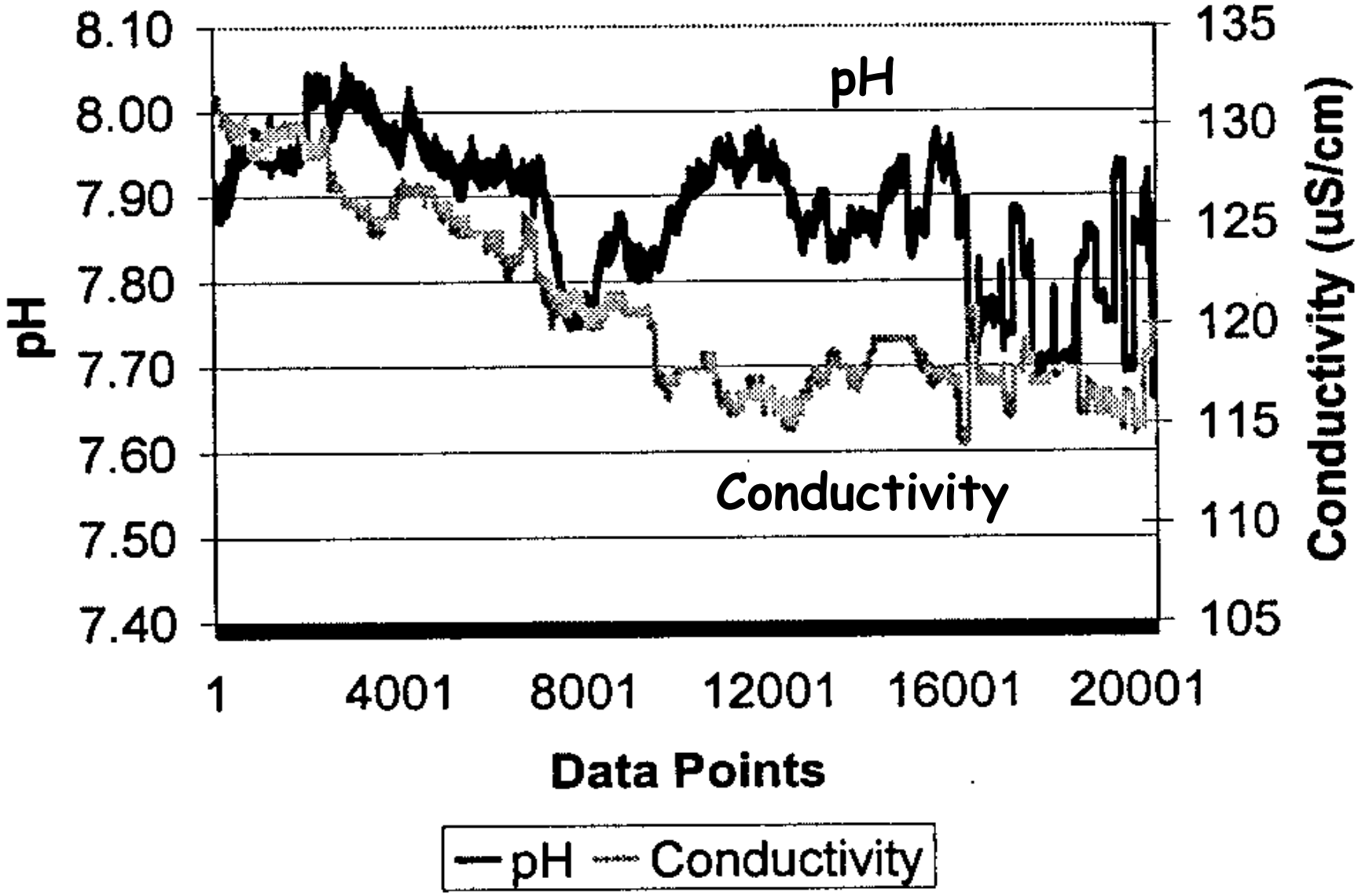
- In order to identify an abnormal test result, need to know what is a "NORMAL" test result.
- Variation in water quality shows up in baseline monitoring.
- Variation caused by seasonal changes, change in water source, system work at treatment plant or on distribution lines, etc.
- Best baseline studies > 1 year of data points

# BASELINE DATA



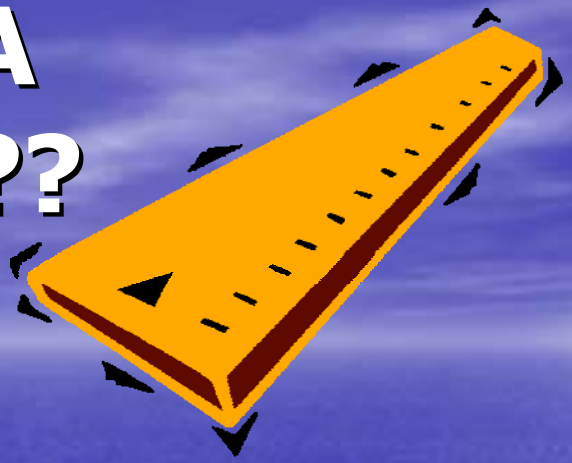

"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p28,

# pH / Conductivity BASELINE




"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p28,

# HAVE BASELINE DATA POINTS - NOW WHAT??



- Data relies on proper calibration, precision and accuracy of monitoring instruments to prevent bias
- Does the data exhibit a normal distribution?
- Can test for normality, kurtosis, skewness, etc.

- Now, must determine the range of acceptable measurements.

# Calculate Min, Max, Mean and 3 σ to identify "normal" ranges

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

$\sigma$ = lower case sigma
$\sum$ = capital sigma
$\bar{x}$ = x bar

**Table 1** On-line monitoring baseline water quality results.

| | Chl Res (mg/L) | Conduct (uS/cm) | pH | TOC (mg/L) | Turbidity (NTU) | Laser Turbidity (NTU) |
|---|---|---|---|---|---|---|
| Min | 0.33 | 113.91 | 7.66 | 1.17 | 0.08 | 0.06 |
| Avg | 0.52 | 120.96 | 7.88 | 1.92 | 0.11 | 0.10 |
| Max | 0.86 | 131.50 | 8.06 | 2.24 | 0.75 | 1.00 |
| 3σ | **0.20** | **14.08** | **0.25** | **0.56** | **0.07** | **0.12** |

"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p25,

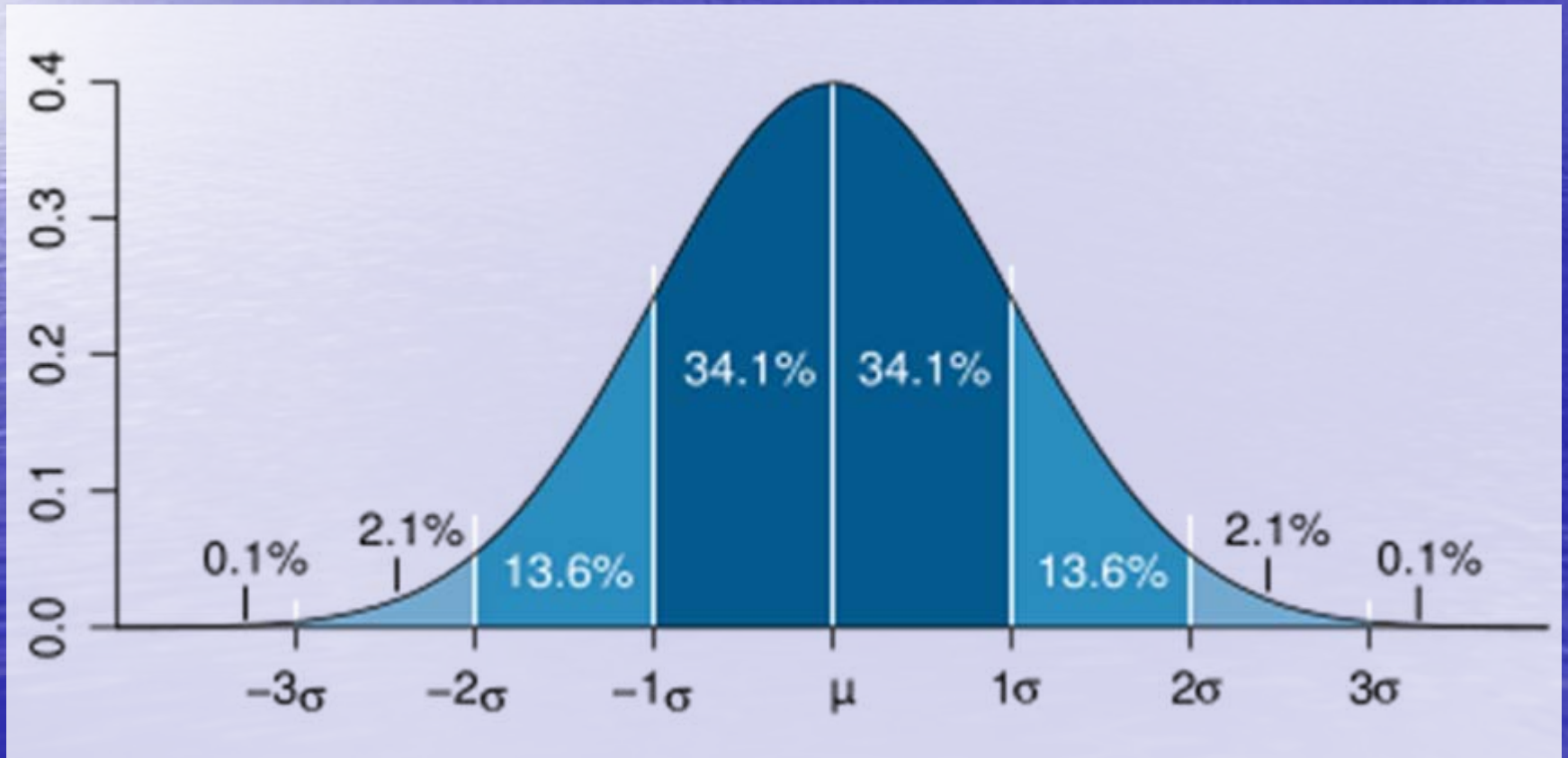
For **normal distribution:**

1 standard deviation = 68.27 %

2 standard deviations = 95.45 %

3 standard deviations = 99.73 %

4 standard deviations = 99.994 %.



# ACCEPTABLE RANGES DEFINED

**Table 1** On-line monitoring baseline water quality results.

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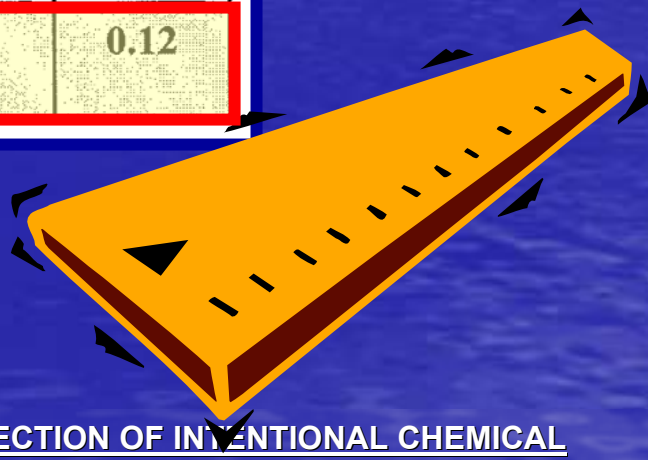
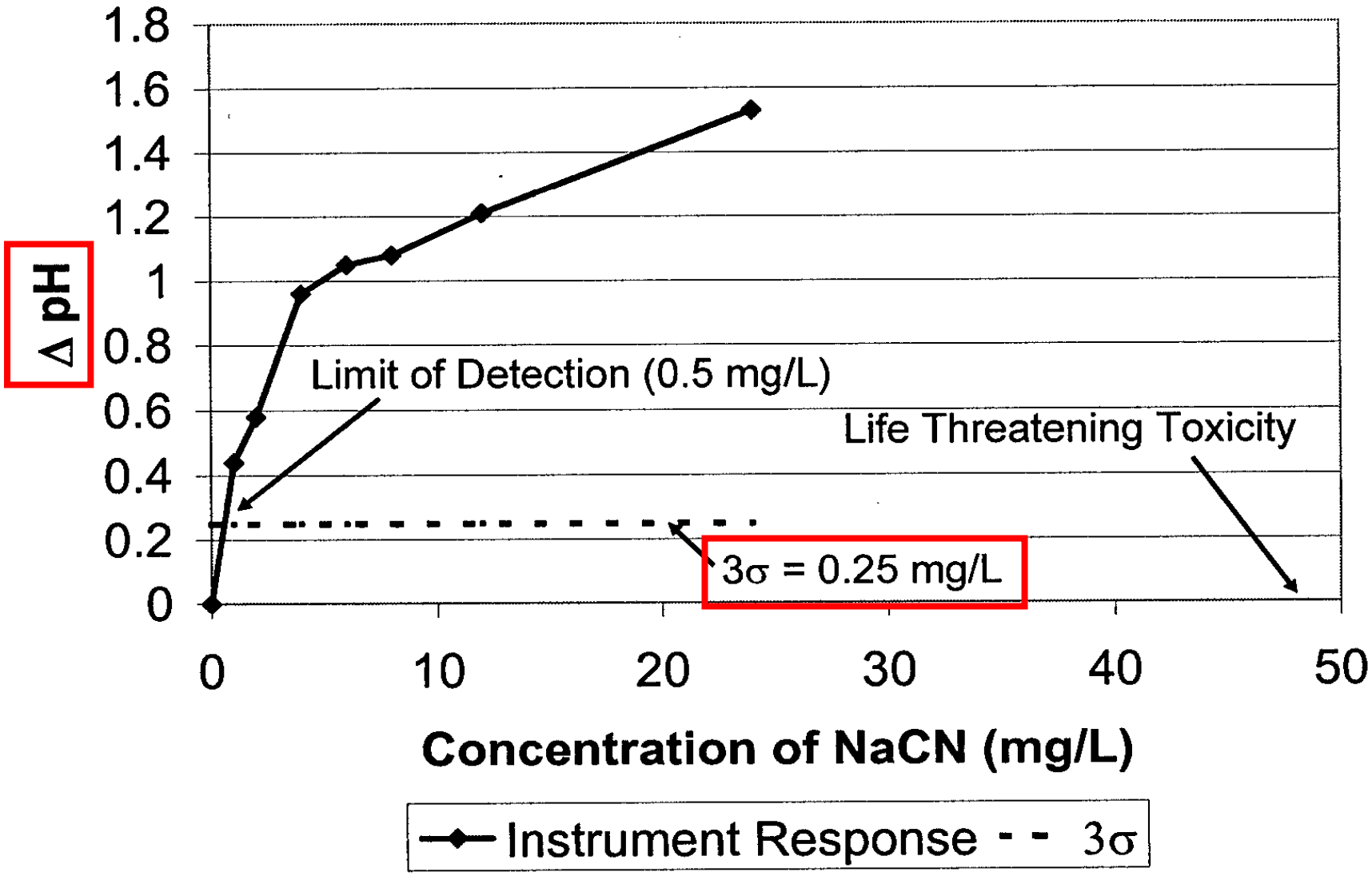
| $\Delta =$ 3σ | 0.20 | 14.08 | 0.25 | 0.56 | 0.07 | 0.12 |



## 3σ = 99.73% INCLUSION OF DATA POINTS

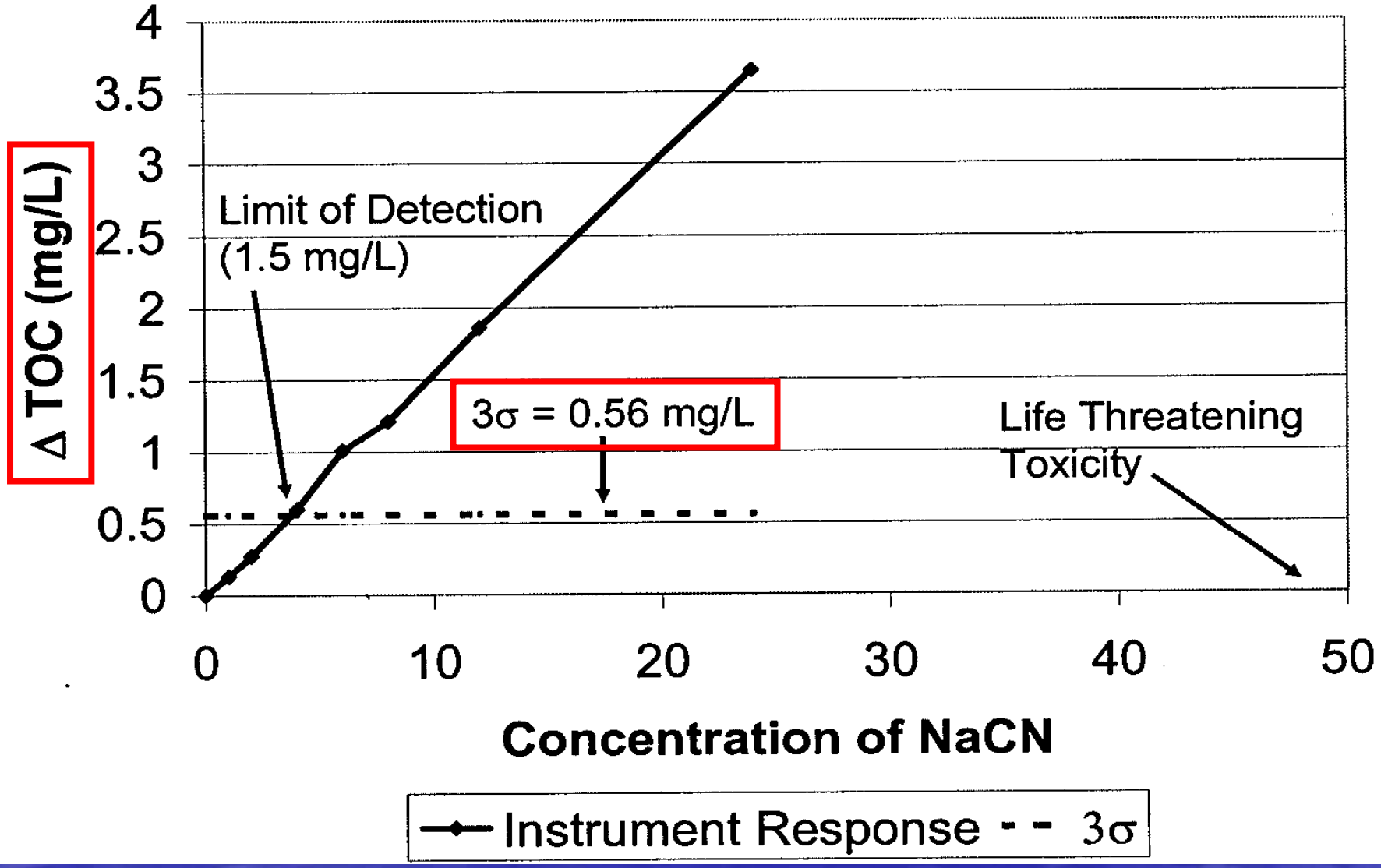
"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p25,

# EXAMPLE: CYANIDE Δ pH



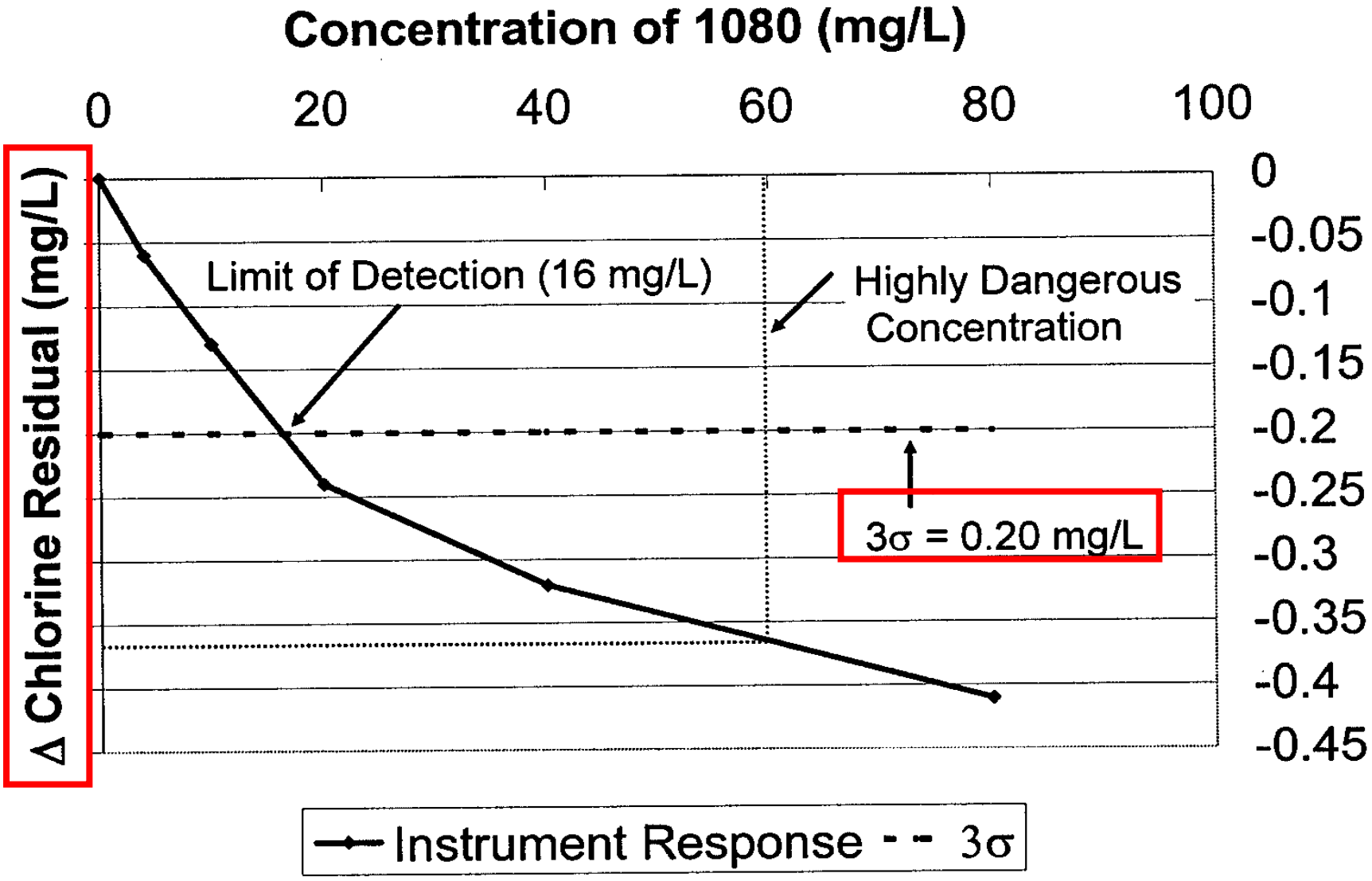

"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM ", p30

# CYANIDE: Δ TOC



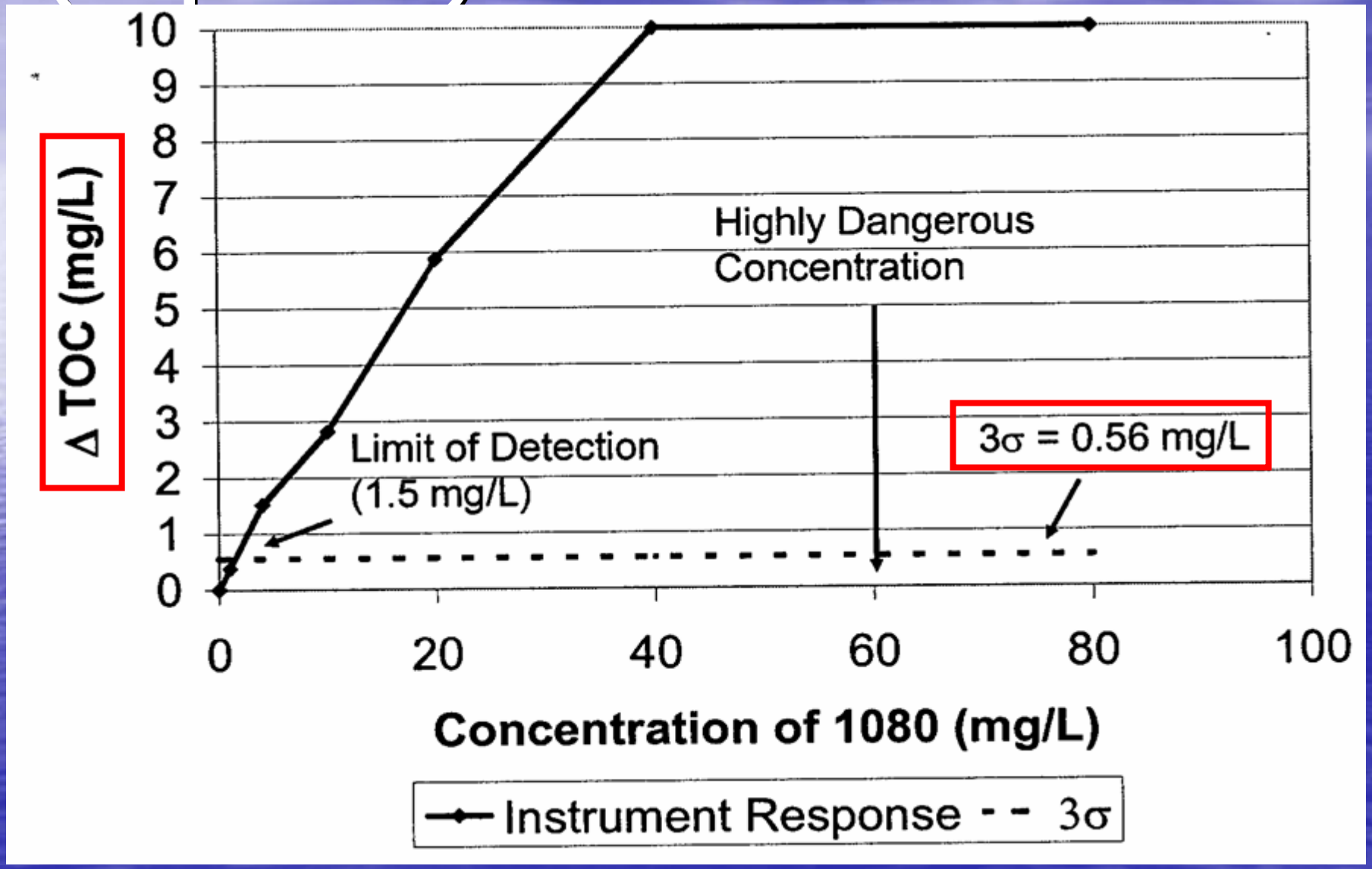

"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p30,

# Sodium Fluoroacetate rodentocide (Cmpd 1080) Δ Chlorine residual




"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p29,

# Sodium Fluoroacetate rodentocide (Cmpd 1080) Δ TOC




"REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM", p29,

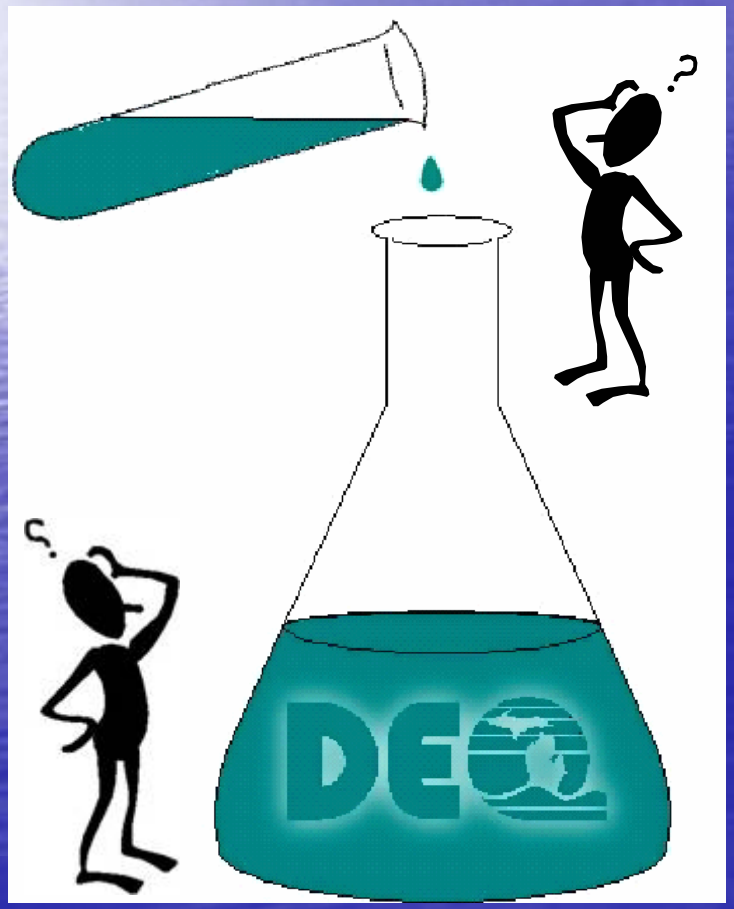
# MONITORING TEST RESULTS MUST BE CAREFULLY EVALUATED

- REMEMBER…..This is a <u>non-specific</u> "Real-time" test, prone to false positive and false negative results
- Must understand what action to take with the results presented
- Must establish a baseline

# EMERGING TECHNOLOGY

- MULTI-PARAMETER PROBES
  - Dascore Six-Cense
  - Hach PipeSonde
- Electrochemical sensors: electronic nose, electronic tongues (Alpha M.O.S.)
- Nanotechnology
- Lab-on-a-chip
- New technology and need is driving force

# "The MDEQ Laboratory & Real-Time Monitoring Analytical Parameters as a part of Contaminant Warning Systems"



QUESTIONS??