Nitrification 101
(Nitrification Action Plans)

Texas Commission on Environmental Quality

Water Supply Division

October 2015

Outline

- History and extent of chloramination in Texas
- What is nitrification?
- History of nitrification in Texas
  - Case studies
  - 2005 Special Study
- Nitrification Action Plans (NAPs)

Take-home Message

- Nitrification can cause residual loss in chloraminated distribution systems.
  - And form nitrite (NO_2^-) & nitrate (NO_3^-)
- Texas water systems need chloramines to maintain residuals and meet disinfection byproduct (DBP) regulations.
- Nitrification can be detected and controlled using a NAP.

History / Extent of Chloramination in Texas

Texas has history of chloramine usage

- Historically, public water systems (PWSs) used chloramines to keep a stable residual.
  - Example--Austin started chloraminating in 1950s
- Later, systems started using chloramines for disinfection byproduct (DBP) control.
  - Total Trihalomethane Rule 1989
    - Most systems > 100,000 population converted
  - Stages 1 & 2 DBP Rules
    - 2002 for large
    - 2004 for small
    - Starting in 2013, LRAAs added stringency
      - » Locational Running Annual Averages

About 1,200 of Texas' 7,000 PWSs distribute chloramines

- Surface water ~1,200
  - About 90% of 350 PWSs with surface water treatment plants (SWTPs) chloraminate
  - ~850 PWSs purchase and redistribute chloraminated SW
- Ground water ~12
  - High-carbon groundwater in northeast Texas
  - High bromide water in coastal Texas

Chloramination clarification

- Chloramination *facts*:
  - **Chloramines smell fine** unless they are dosed or maintained wrong.
    - *Fiction*: Some web sites say that chloramines smell bad. Monochloramine—the disinfectant species—smells like chlorine. Di- and tri-chloramine stink.
  - Experience proves that **chloramines do not cause health issues**.
    - *Fiction*: Some web sites blame various symptoms on chloramines, but 25% of Americans are okay drinking chloraminated water

What is nitrification?

The chemicals of interest

- Normal chloramine reactions,
  - in the monochloramine zone:

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

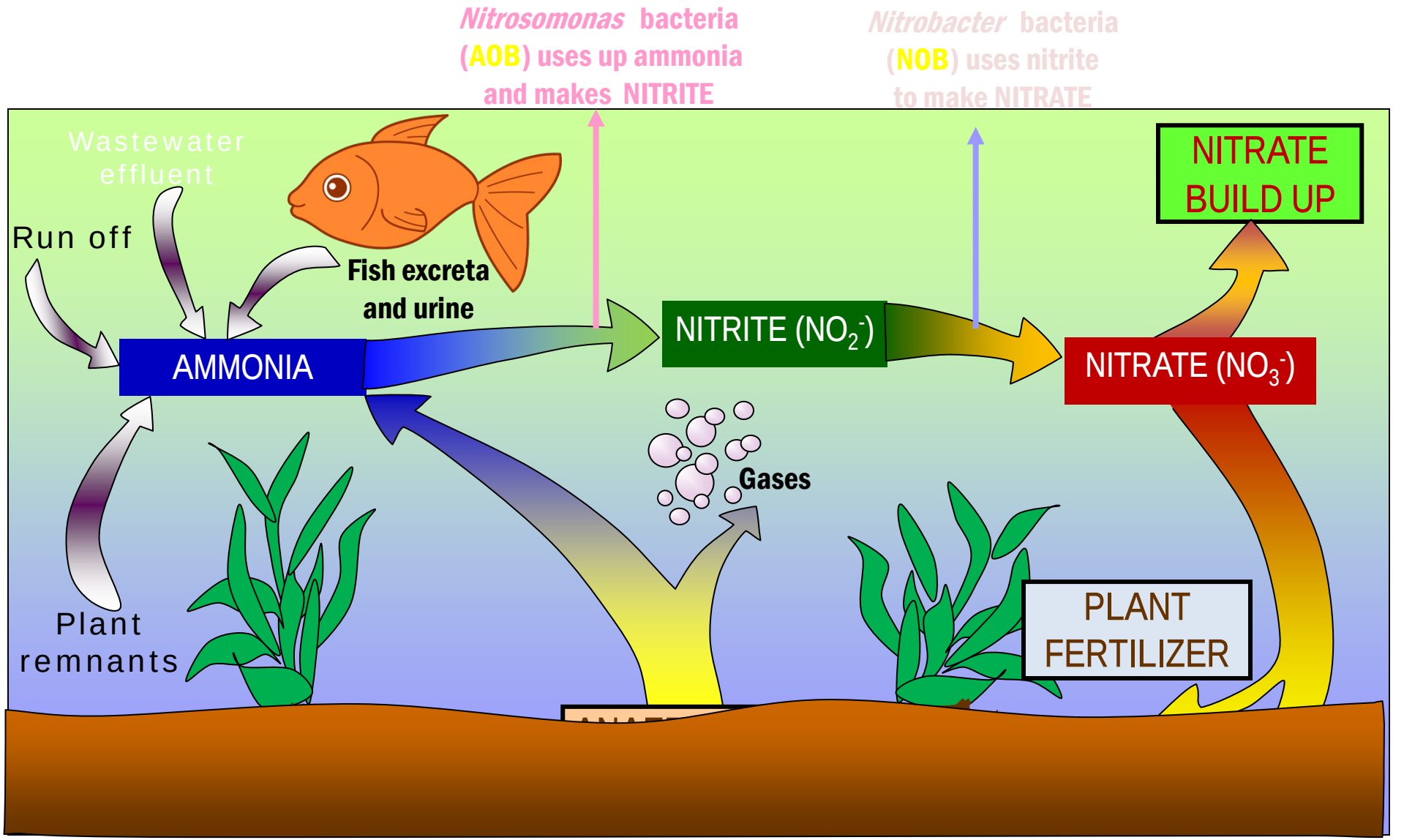
$$2\ NH_2Cl \leftrightarrow NHCl_2 + NH_3$$

- Nitrification

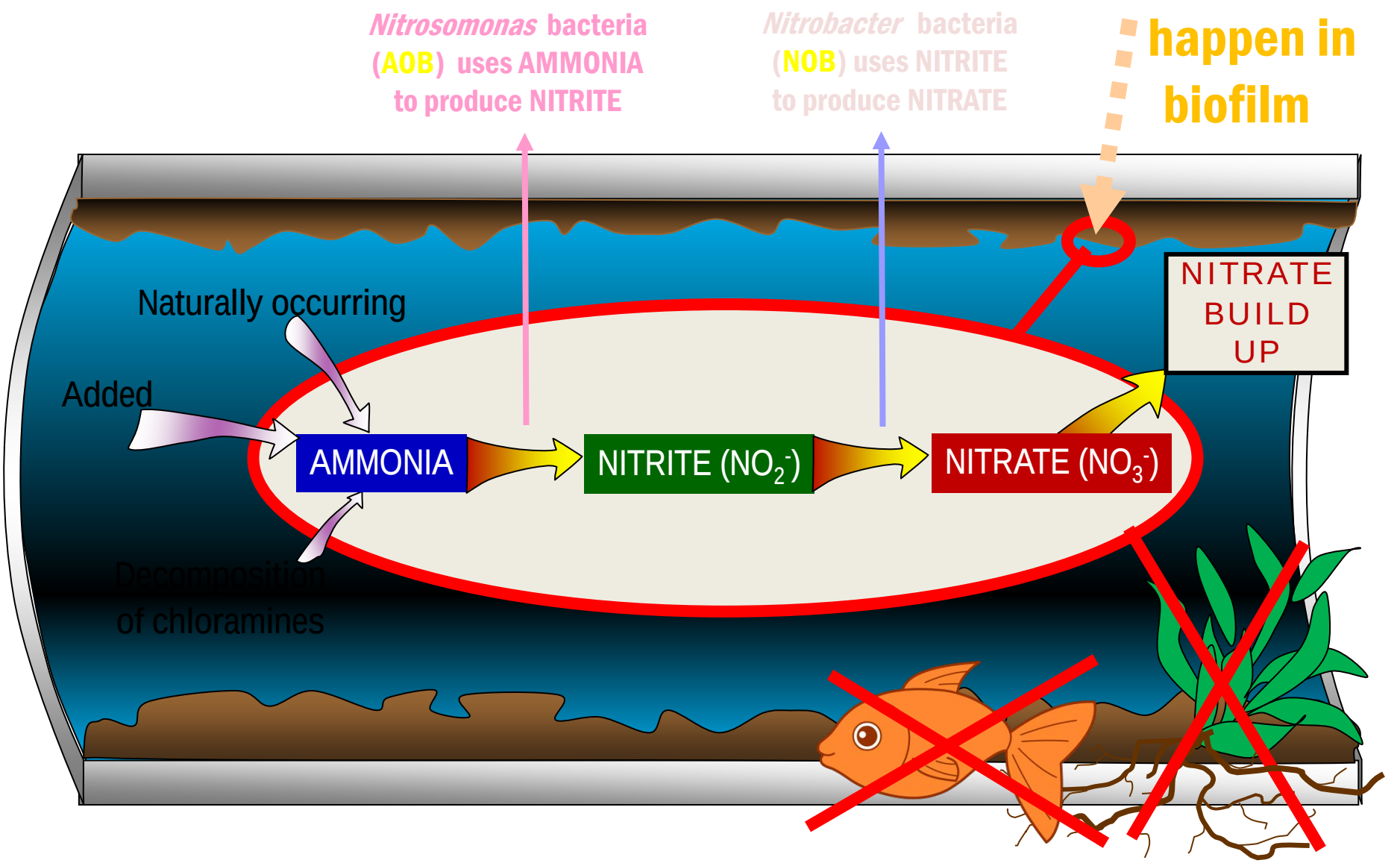
$$NH_3 + O_2 \rightarrow AOB \rightarrow NO_2^- + 3H^+ + 2e^-$$

$$NO_2^- + H_2O \rightarrow NOB \rightarrow NO_3^- + 2H^+ + 2e^-$$

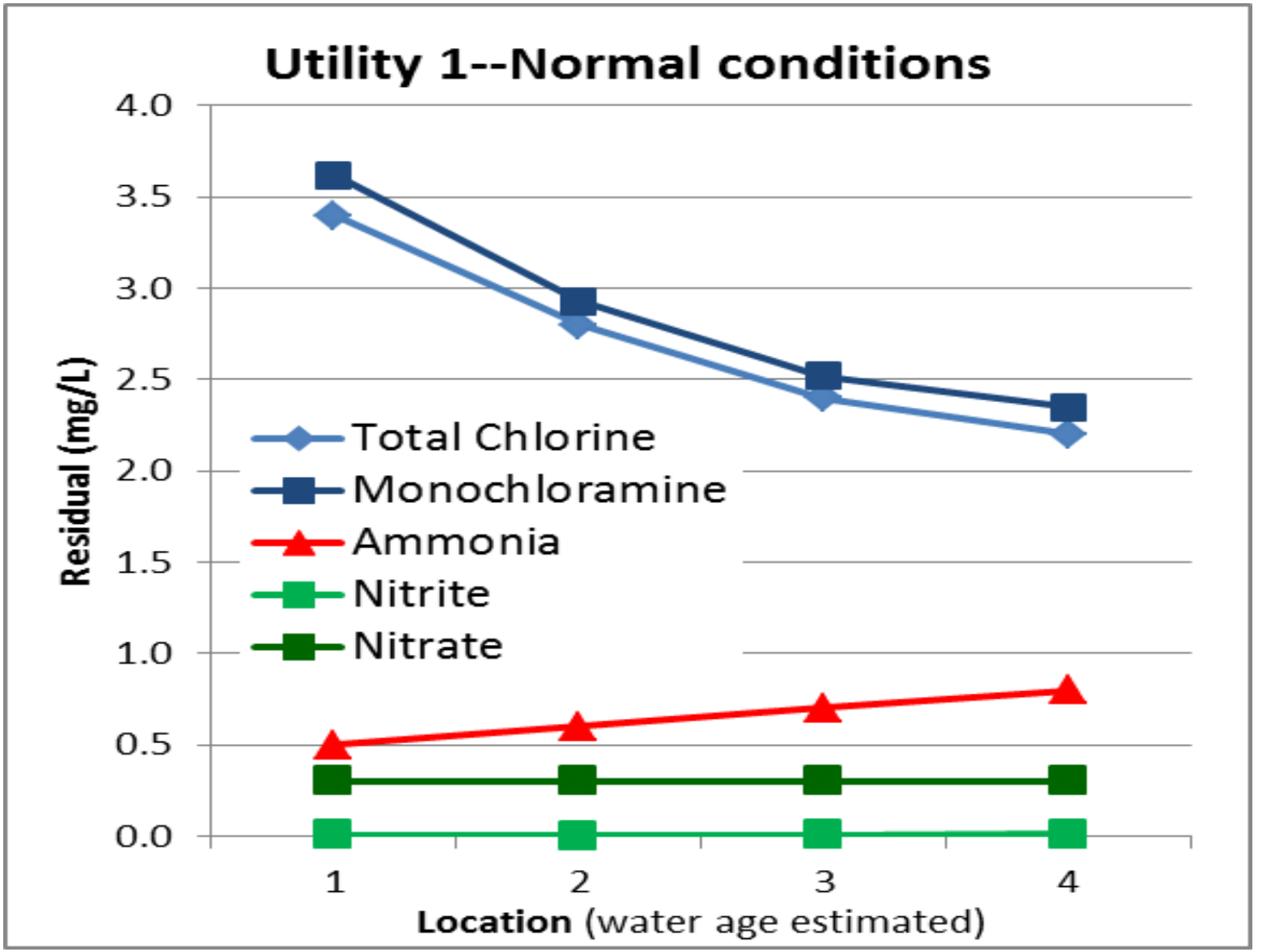
Nitrification in the environment



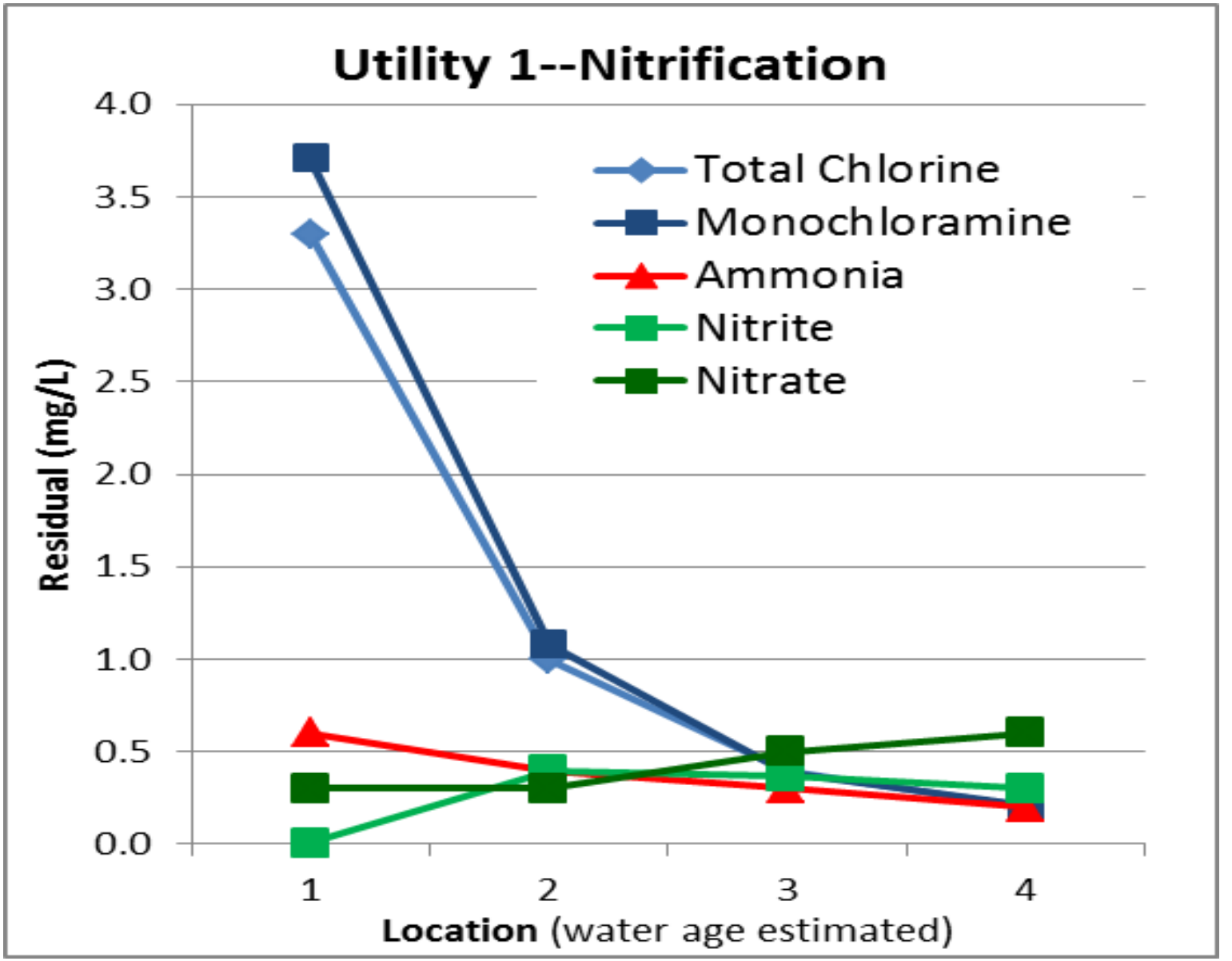
Nitrification in a pipe



Example: Without nitrification



Example: Nitrification



Nitrification in Texas

2003 Case study

- City with SWTP
  - Fish kill complaint
- Water quality:
    - Water temp 27 °C (Texas in May)
  - Nitrite: **1.56 mg/L**
  - Monochloramine **1.5 mg/L**
  - Ammonia **0.5 mg/L**
- Other sites Ammonia ~ **1.75 mg/L**
- *We learned:*
  - *Nitrification can occur WITH good residual*
  - Don't ignore complaints about dead fish

2005 Summer—
Special Study

- Sampled **1,029** 'high-risk' systems
  - Surface water, chloraminating, and their downstream consecutive purchasers
  - Sampled in distribution—at DBP sites
    - Nitrate,
    - Nitrite, and
    - Ammonia

2005 Summer—Special Study
continued

- Results—of **1,029** systems
  - **149** systems showed some evidence of nitrification
  - **11** systems exceeded 1 mg/L NO_2^-
    - Highest NO_2: **2.08 mg/L** (case study)
    - No NO_3- over the MCL (10 mg/L) was found
  - **9** of those systems were identified as having issues
    - Case-by-case assistance was provided

2005 Summer—Special Study
continued

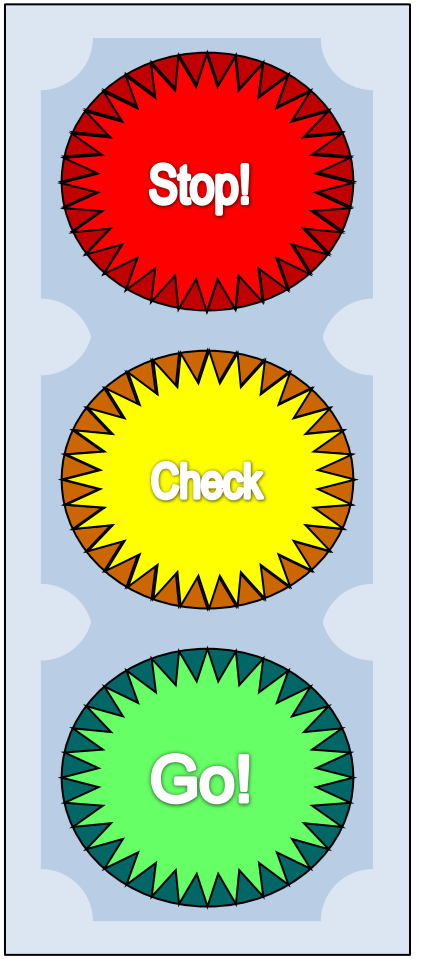
- We learned:
  - Nitrification can happen under a range of conditions,
  - Approximately 10% of systems may experiencing nitrification, but apparently only 1% have extreme problems.

2007 Case study

- City with SWTP
- Widespread residual loss
  - No existing flushing program
  - Positive bacteriological results
  - Boil water notice required
  - Extended free chlorine burn
- Resulted in innovative flushing and nitrification detection and response plan
  - Nitrification Action Plan

Nitrification Action Plan

Everyone Needs a NAP



21 slides

A Nitrification Action Plan is like a Monitoring Plan

- It includes
  1. A sample site map,
  2. Sample schedules,
  3. Analytical methods,
  4. Site-specific goal/baselines and trigger levels, and
  5. Actions.
  6. *It should be documented and shared.*

1. NAP sites

- Distribution nitrification monitoring sites:
  - Should represent low, medium, and high water age.
  - Can be the same as coliform sites
    - But they don't have to be.
  - Critical control points
    - "A point where control can be applied and is essential to prevent or eliminate nitrification"
      - EG: Before booster chloramination

2. Routine NAP schedules

- NAP monitoring must be done weekly,
  - May be done more frequently.
- Small systems, <750 people or 250 cnx.
  - Monitor monochloramine and ammonia with every weekly total chlorine sample.
- Large systems, select CCPs at low, average and high water age for weekly sampling.

3. Analytical methods

- Total chlorine: Use EPA approved method (see 30 TAC 290.119)
- Monochloramine and ammonia:
  - EPA does not have approved methods.
  - Use methods that achieve the required accuracy
- Document on the Lab Approval Form
  - Attach to Monitoring Plan

4. Goals/baselines and trigger levels

- Nitrification is controlled by defining what "normal" is and looking for trends that are "abnormal."
  - Therefore, initial data must be analyzed to define normal levels,
  - And additional data must be analyzed or hypothetical levels must be projected for levels that are a concern: trigger levels.

Chemicals that you need trigger levels for

- Total Chlorine & Monochloramine:
  - At least the regulatory minimum for Total PLUS a Safety Factor.
- Ammonia:
  - A little bit means you are in the right 'zone.'
  - When it goes away – something is eating it.
- Nitrite & nitrate:
  - If distribution is more than baseline… Trigger!
- Also for pH, heterotrophic plate count if used.

Baseline (Green light – Go!)

Parameters in normal operating range – all systems ‘go’

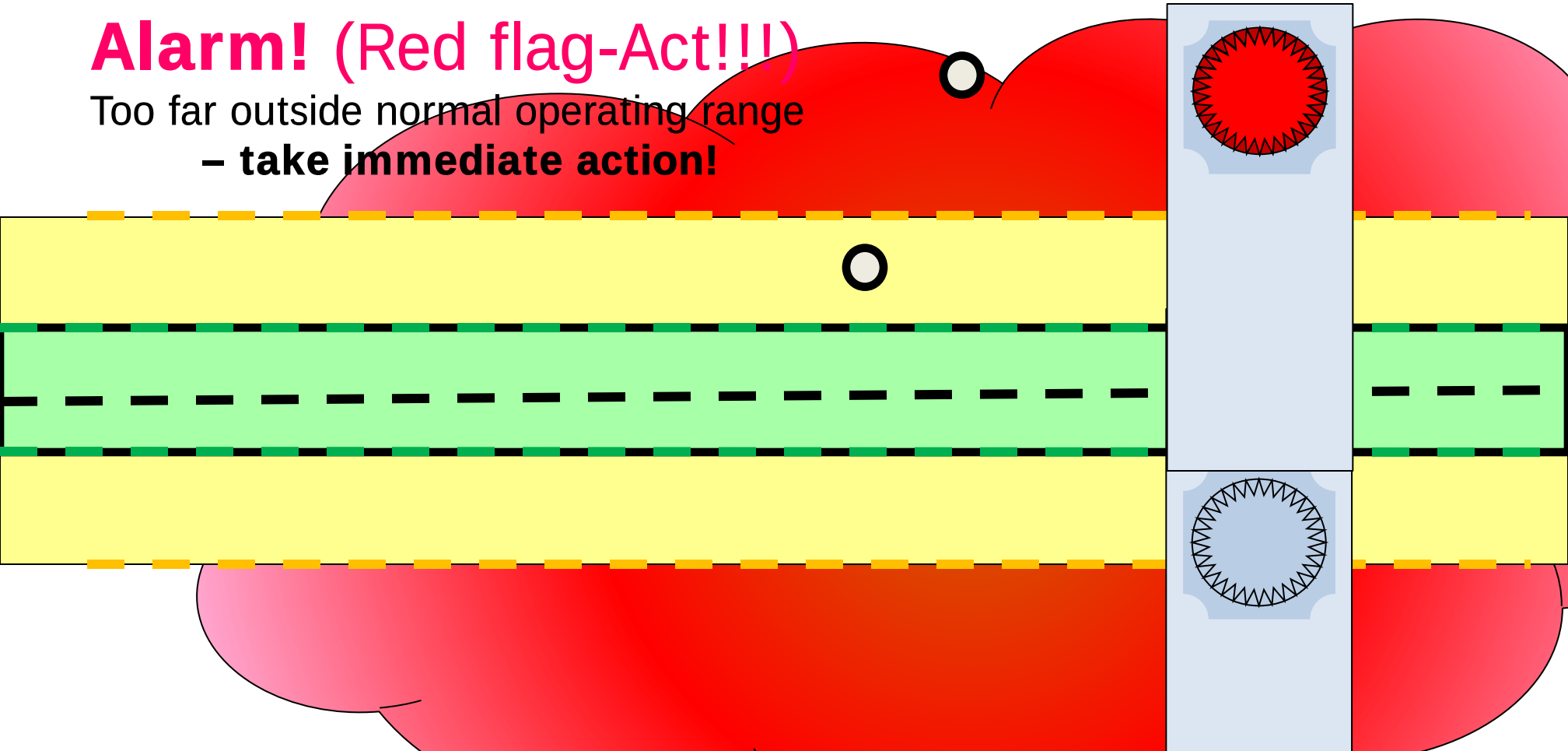
Alert (Yellow flag-Act.)

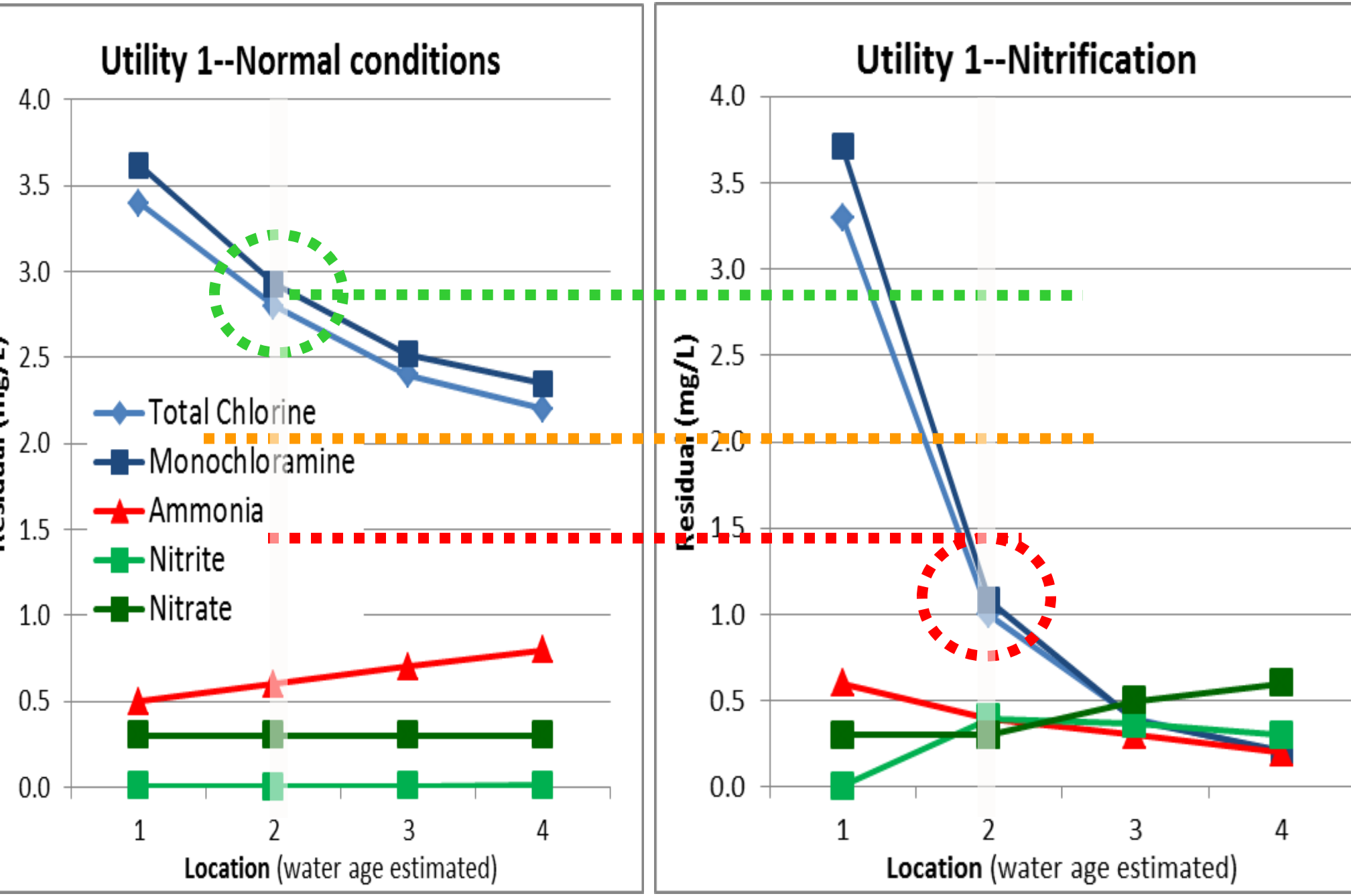
Outside normal operating range – take precaution

Alarm! (Red flag-Act!!!)

Too far outside normal operating range

– take immediate action!




Utility 1--Normal conditions
Utility 1--Nitrification
Residual (mg/L)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Total Chlorine
Monochloramine
Ammonia
Nitrite
Nitrate
1
2
3
4
Location (water age estimated)

5. Action!

- **Preventive action:**
  - Routine operating conditions
    - Do this even when your levels are ok
- **Corrective: Trigger 1**
  - Intermediate--Do this when levels are not quite ok
- **Corrective: Trigger 2**
  - Do this when nitrification is bad

Most preventive and corrective actions overlap

- Preventive and corrective actions:
  - Verify results.
  - Flush.
  - Dose chlorine and ammonia correctly.
  - Minimize water age.
- Operational corrective action:
  - Temporary conversion to free chlorine.

- Possible long-term corrective actions
  - Increase pH
    - Chloramine decays more slowly at higher pH
    - Con: Caustic feed
  - Feed chlorite
    - Low chlorite concentration can prevent nitrification
  - Permanent conversion to free chlorine
    - **With** aeration for trihalomethane (chloroform) removal.

- Those potential long-term corrective actions that require engineering should be considered only if the operational controls are <u>unsuccessful</u>.
  - Additional studies must be performed to evaluate their long-term, site-specific success at your PWS.
    - (One size does NOT fit all.)

NAP Actions: More sampling

- Monitoring: Additional monitoring should be done to
  - Verify results
    - After an ‘abnormal’ result is found, go back to that site and collect another sample to make sure the sample was accurate.
  - Determine where nitrification is happening
    - If the level is verified, collect samples nearby to see how far the abnormality extends.

NAP Actions:
More flushing

- Routine flushing is required at every dead-end main.
- Additional flushing may be needed to bring fresh water with a high chloramine residual into an area that has nitrification.

NAP Actions:
Dose chemicals correctly

- For systems that operate water plants or booster stations, base the chemical dose on results of monitoring – not theoretical levels.

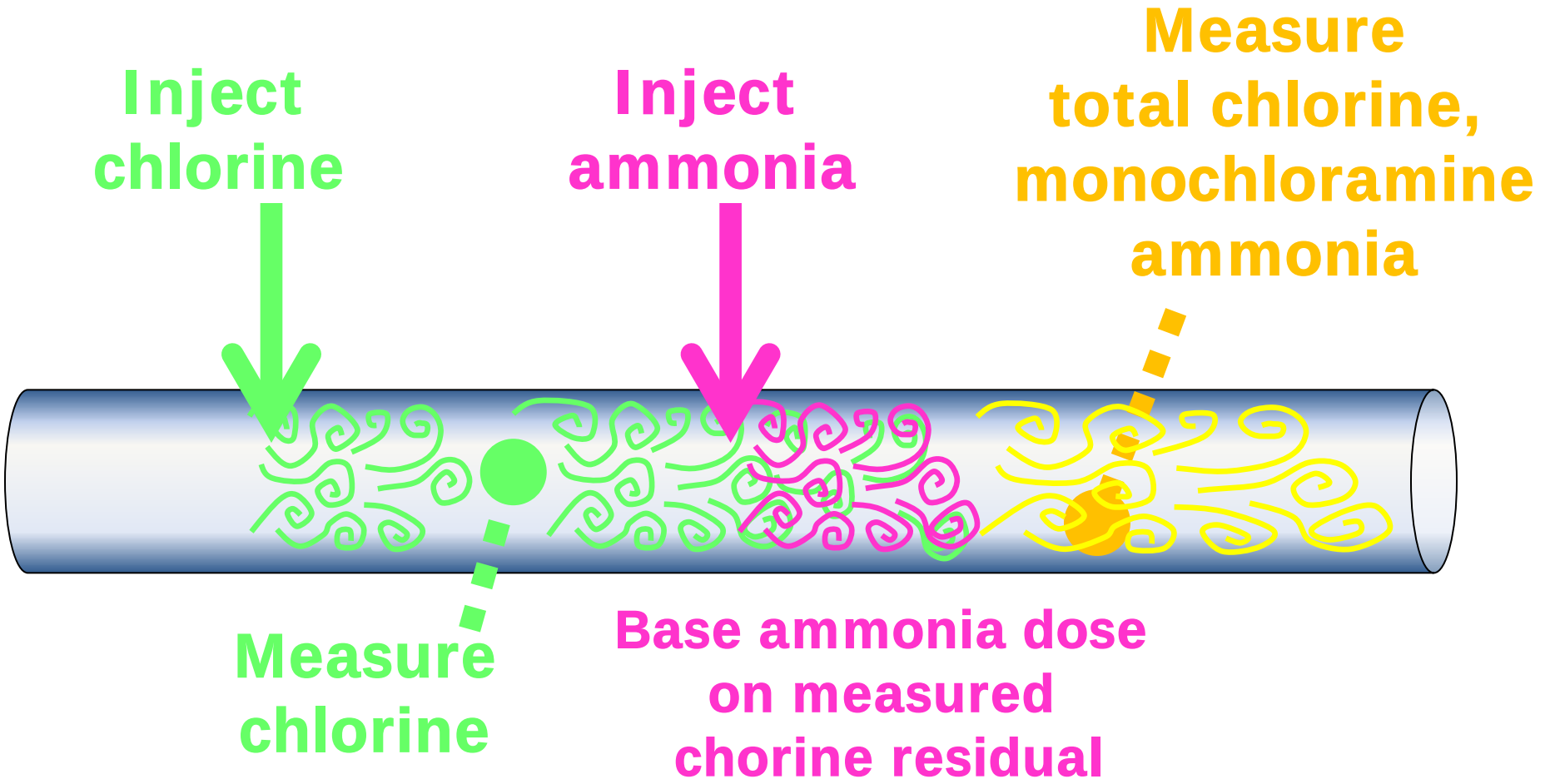
NAP Actions: Increase total chlorine / decrease ammonia

- Ammonia
  - Minimize ammonia entering the distribution system – target of just detectable
- Total chlorine residual
  - Sources suggest over 2.0 is best
  - The lower the residual, the greater the risk

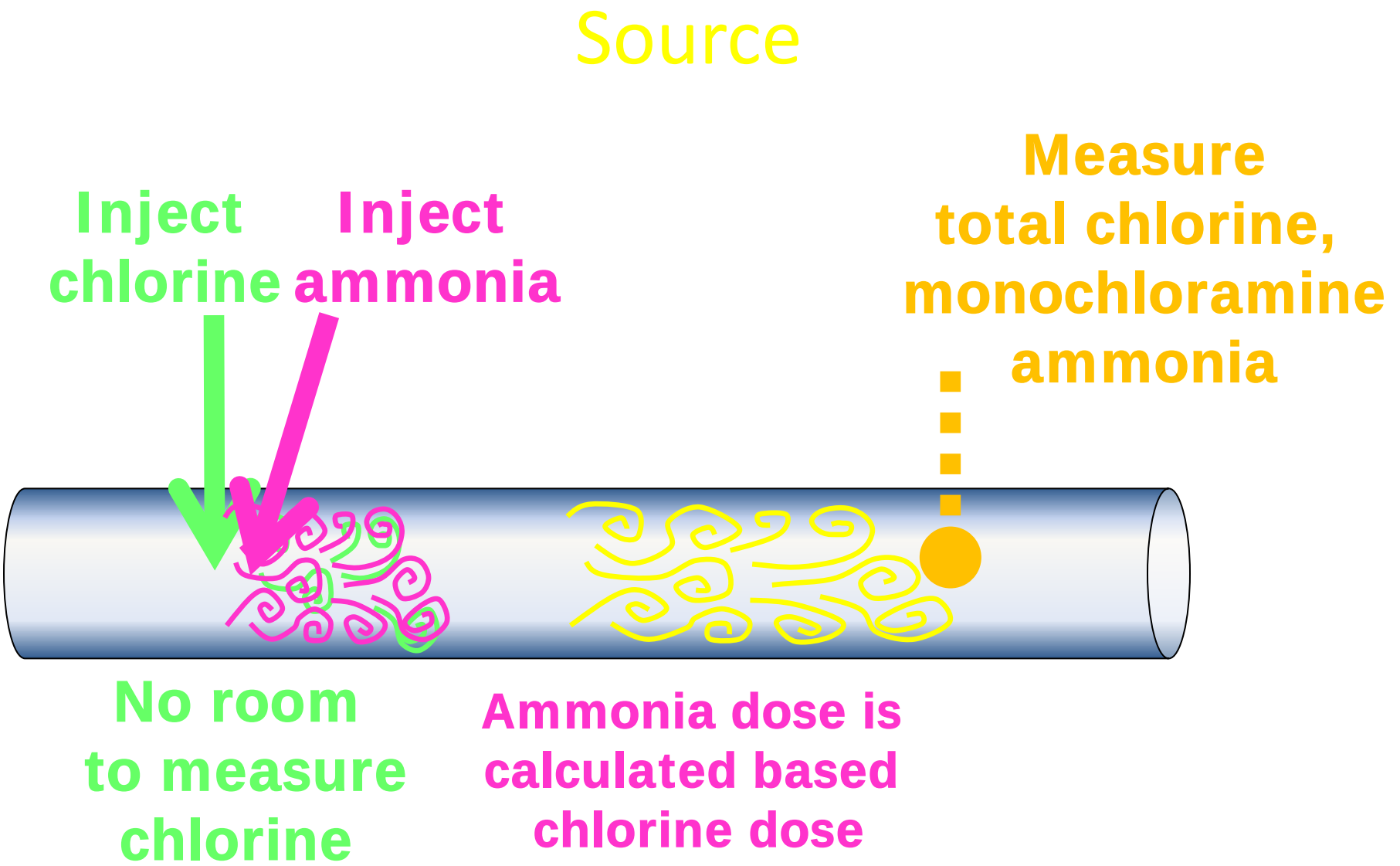
Order of addition, mixing

- Order of addition:
  - Source:
    - Chlorine first for dosing raw water
      - NOTE: SWTP can get exception to add ammonia first– with additional viral log inactivation.
  - Booster:
    - Add **ammonia** first to water with **chloramines.**
    - Add **chlorine** first to water with **free chlorine.**

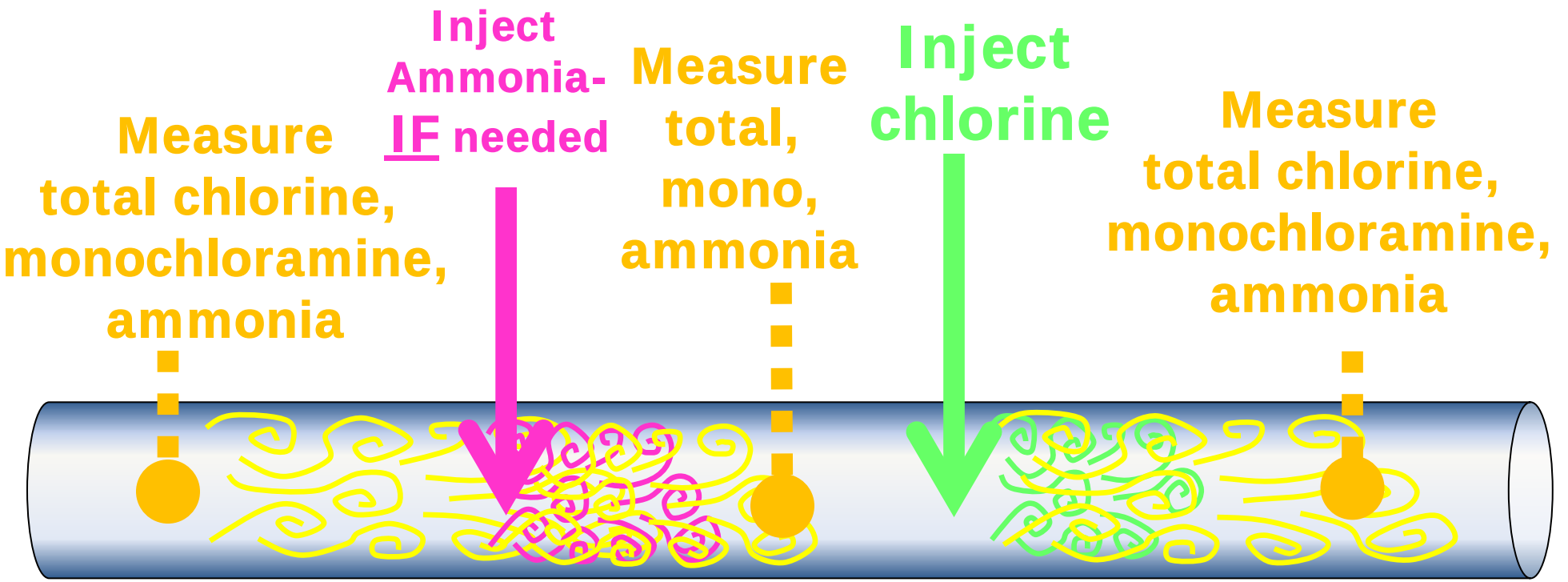
Ideal chloramination design: Source



Reality of chloramination design:



Ideal chloramination design: Booster



Base ammonia dose on desired monochloramine residual

Base chlorine dose on measured ammonia residual

NAP Actions: Minimize water age

- Routinely, exercise valves to ensure no unintended dead spots.
- Consider the impact of hydraulic dead-ends, where water goes back and forth,
  - Although the pipe may be continuous, water age may increase in these places.
- Prioritize flushing at higher water age locations.

NAP Actions:
Free chlorine

- A temporary conversion to free chlorine will 'starve' the nitrifying bacteria that 'eat' ammonia.
  - Notify TCEQ before doing a temporary free chlorine conversion: DBP@tceq.texas.gov
    - We will delay disinfection byproduct monitoring for 4 weeks.
- Have a plan to flush the chlorine in then flush it out.

6. Share the NAP with all operators

- Document the plan (see next slide)
- Share it with the folks who work in distribution

Nitrification Action Plan Example

Chloramine-Effectiveness Sample Suite

Site	Chemical	Goal	Yellow Flag		Red Flag	
			Trigger	Actions	Trigger	Actions
Entry Point	Total / Mono	4.0	3.5	1) Verify results 2) Check and adjust dose	3.0	1) Verify results 2) Adjust dose
	Ammonia	0.1	0.2		0.3	
Average Water Age	Total / Mono	2.0	1.5	1) Verify results 2) Measure nitrite and nitrate 3) Adjust dose 4) Identify affected area (check upstream and downstream) 5) Flush area 6) Flush dead ends →*Till levels return to normal*	1.0	1) Verify results 2) Measure nitrite and nitrate 3) Adjust dose 4) Identify affected area (check upstream and downstream) 5) Flush area 6) Flush dead ends 7) Convert to Free Chlorine →*Till levels return to normal*
	Ammonia	0.5	+/- 20%		+/- 50%	
Far Reaches	Total / Mono	1.0	0.7		0.5	
	Ammonia	0.9	+/- 20%		+/- 50%	

Nitrite/Nitrate

Site	Chemical	Baseline	Yellow Flag		Red Flag	
			Trigger	Actions	Trigger	Actions
All Sites	Nitrite	1.23	> 1.5	1) Verify results 2) Identify source changes IF confirmed-modify BL 3) Identify area, 4) Flush area →*Till levels return to normal*	> 2	1) Verify results 2) Identify affected area 3) Flush 4) Perform free chlorine burn →*Till levels return to normal*
	Nitrate	0.12	+/- 20%		+/- 50%	

Take-home Message

Take-home Message

- Chloramines are an important tool.
  - They can help maintain residuals, and
  - Avoid unwanted disinfection byproducts.
- Nitrification is a potential risk of chloramination.
- Nitrification can be detected and controlled using a
  Nitrification Action Plan