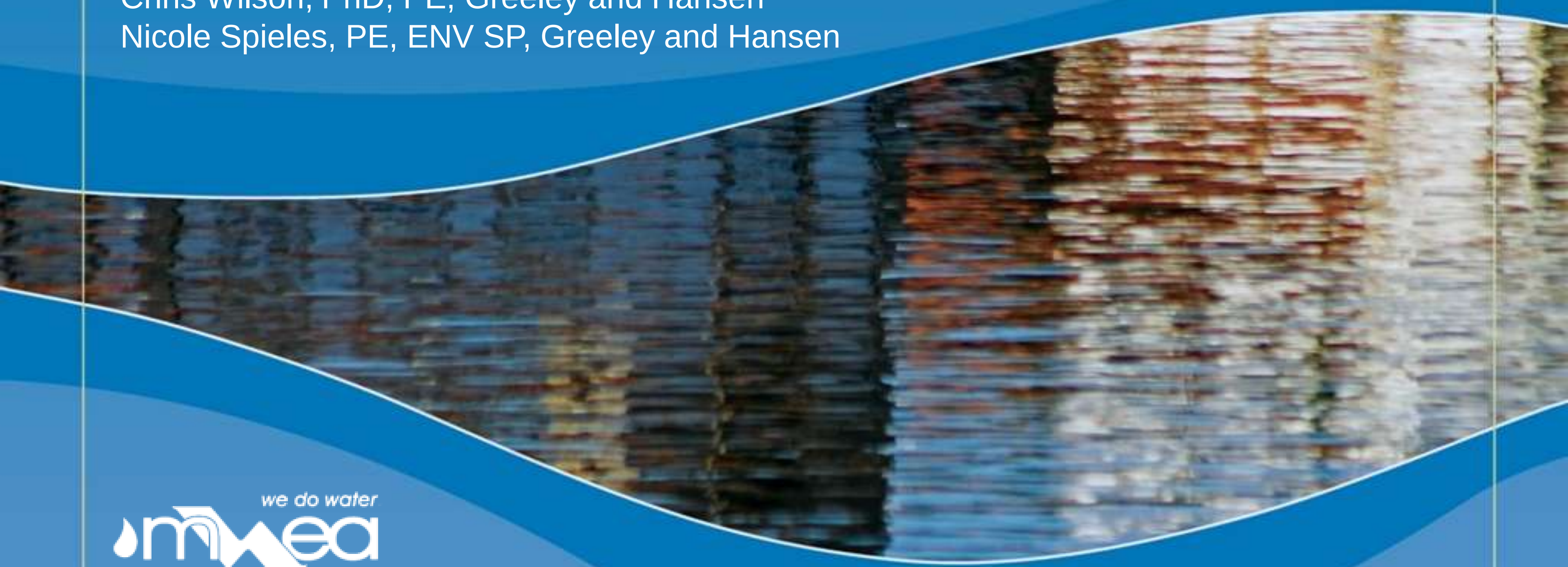
GREELEY AND HANSEN

PREDICTION OF SULFIDE EMISSION IN SEWERS

Chris Wilson, PhD, PE, Greeley and Hansen
Nicole Spieles, PE, ENV SP, Greeley and Hansen



we do water
mwea

Acknowledgement

- Dimitrios Katehis, PhD, PE, Greeley and Hansen
- Yuan Fang, PhD, PE, Greeley and Hansen
- Ed Cronin, PE, Greeley and Hansen

This Presentation Describes The Sewer Sulfide Modeling As A Practical Asset Management Tool

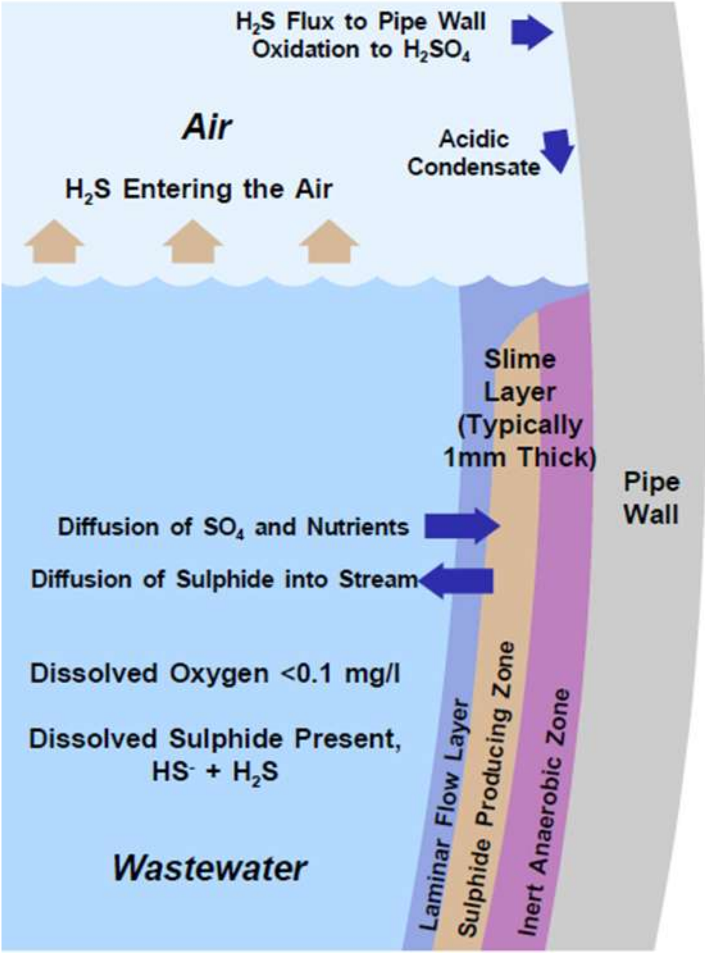
- Sulfide Generation and Corrosion in Sewers
  - Biological and Physical Processes Causing Sewer Corrosion
  - Impact of Sewer and Wastewater Characteristics on Corrosion Potential
- Sulfide Modeling and Description of a Simplified Tool
  - Basic Approaches to Sulfide Modeling
  - Sensitivities and Limitations of Mechanistic Sulfide Modeling
  - Impact of Sewer Hydraulics on Corrosion
  - Simplification of Tool for Practical Asset Management Guidance
- Sulfide Modeling Tool Application: Case Study
  - Case Study Area
  - What Does Modeling Tell Us About Causes of Sulfide Generation & Emission?
  - What Do Generation and Emission Patterns Tell Us About Sewer Operation?
  - What Does Sewer Operation Tell Us About Sulfide and Odor Mitigation?

This Presentation Describes The Sewer Sulfide Modeling As A Practical Asset Management Tool

- Sulfide Generation and Corrosion in Sewers
  - Biological and Physical Processes Causing Sewer Corrosion
  - Impact of Sewer and Wastewater Characteristics on Corrosion Potential
- Sulfide Modeling and Description of a Simplified Tool
  - Basic Approaches to Sulfide Modeling
  - Sensitivities and Limitations of Mechanistic Sulfide Modeling
  - Impact of Sewer Hydraulics on Corrosion
  - Simplification of Tool for Practical Asset Management Guidance
- Sulfide Modeling Tool Application: Case Study
  - Case Study Area
  - What does Modeling Tell us About Causes of Sulfide Generation & Emission?
  - What do Generation and Emission Patterns Tell us About Sewer Operation?
  - What does Sewer Operation Tell us About Sulfide and Odor Mitigation?

Fundamental Sulfide Corrosion Mechanisms In Sewers Are Well Understood

- Sulfate and Organics are Present in All Wastewaters
- Slime Layer (Biofilm) Coats Sewer Pipe Below the Water Line
- Sulfate Reduction Under Anaerobic Conditions in the Biofilm
- Oxygen in Wastewater Inhibits This Process
- In a Partially Filled Pipe, Dissolved and Atmospheric Sulfide Will Try to Reach Equilibrium
- Atmospheric Sulfide Oxidized by Aerobic Biofilm on Pipe Crown, Forming Sulfuric Acid
- Sulfuric Acid Corrodes Sewer Material



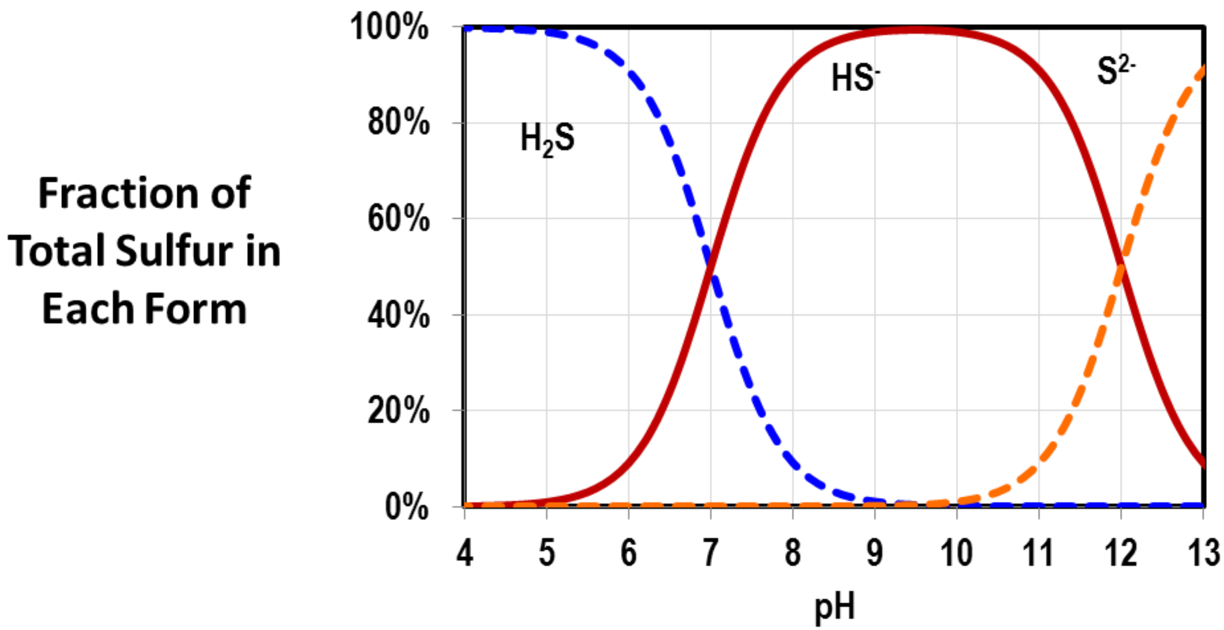
Fundamentals of Sulfide Production Tells Us Much About Controlling Corrosion

- Higher the Dissolved Sulfide Concentration, Higher the Potential Atmospheric Concentration

Partial Pressure of H_2S in Sewer Gas **=** **Henry's Law Constant, K_H** **×** **Aqueous Sulfide Concentration**

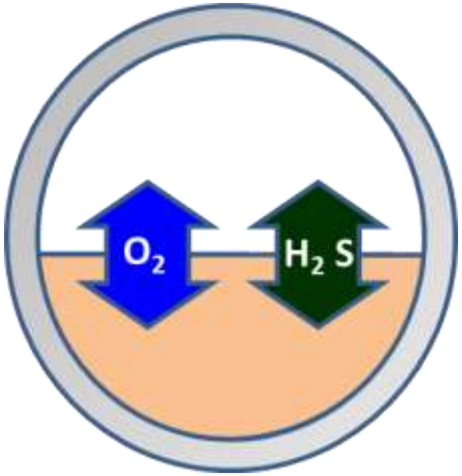
Fundamentals of Sulfide Production Tells Us Much About Controlling Corrosion

- Higher the Dissolved Sulfide Concentration, Higher the Potential Atmospheric Concentration
- Sulfide Undergoes Acid-Base Chemistry
  - Only the Acid Fraction (H_2S) Volatilizes
  - pKa is a Function of Temperature



Fundamentals of Sulfide Production Tells Us Much About Controlling Corrosion

- Higher the Dissolved Sulfide Concentration, Higher the Potential Atmospheric Concentration
- Sulfide Undergoes Acid-Base Chemistry
- Hydraulics Matter Greatly
  - Agitation of Water Promotes Liquid-Gas Equilibrium
  - Oxygenation of Water Reduces Dissolved Sulfide Concentration
  - Transfer of Dissolved Sulfide to Atmosphere Increases Corrosion Potential



An Effective Predictive Sulfide Corrosion Tool Is One That Captures The Following:

- Sewage Age
  - Longer Sewage Detention Time Causes Oxygen Depletion, Fermentation and H_2S Formation
- Temperature
  - Increased Temperature Favors Bacterial Growth and Reduces DO
- Sewage pH
  - Fermentation Causes Lower pH Increasing the % of Sulfide in the Form of H_2S
- Turbulence
  - Increased Turbulence Promotes H_2S Emission from Wastewater to Sewage Atmosphere

This Presentation Describes The Sewer Sulfide Modeling As A Practical Asset Management Tool

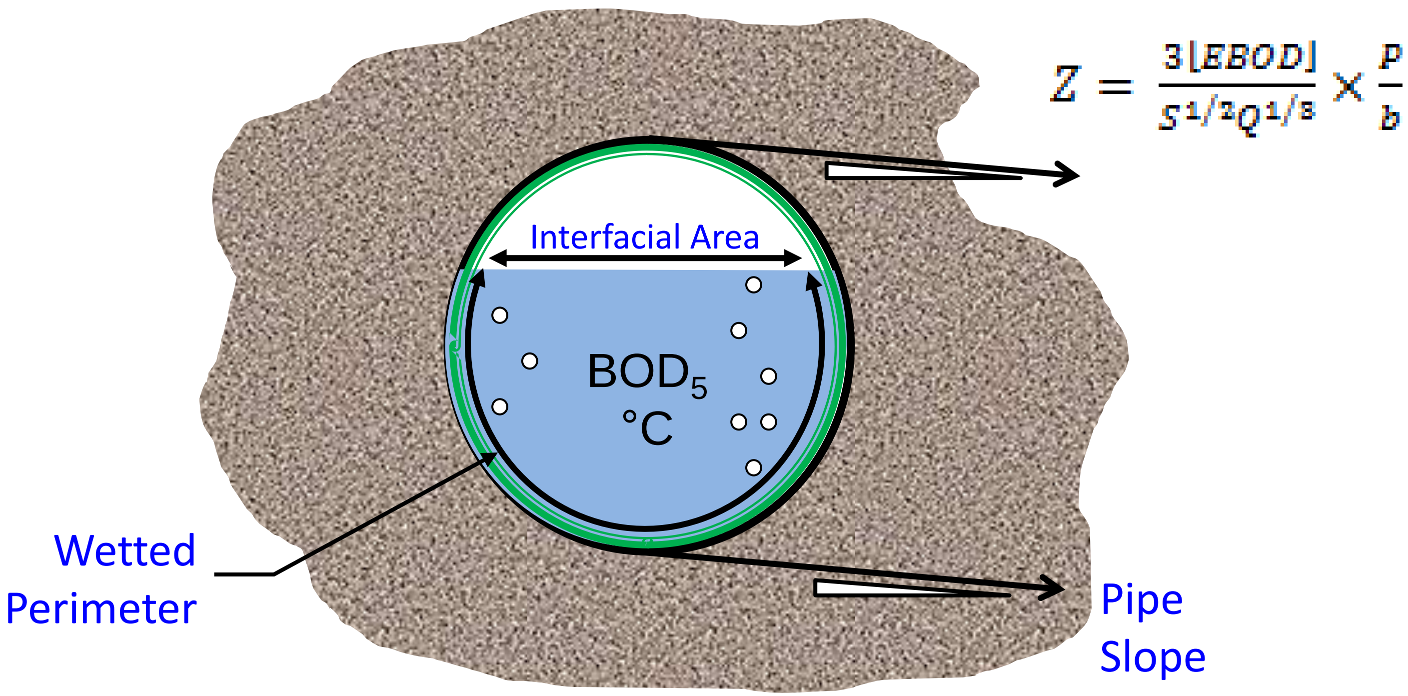
- Sulfide Generation and Corrosion in Sewers
  - Biological and Physical Processes Causing Sewer Corrosion
  - Impact of Sewer and Wastewater Characteristics on Corrosion Potential
- Sulfide Modeling and Description of a Simplified Tool
  - Basic Approaches to Sulfide Modeling
  - Sensitivities and Limitations of Mechanistic Sulfide Modeling
  - Impact of Sewer Hydraulics on Corrosion
  - Simplification of Tool for Practical Asset Management Guidance
- Sulfide Modeling Tool Application: Case Study
  - Case Study Area
  - What does Modeling Tell us About Causes of Sulfide Generation & Emission?
  - What do Generation and Emission Patterns Tell us About Sewer Operation?
  - What does Sewer Operation Tell us About Sulfide and Odor Mitigation?

Prediction of Sulfide Generation And Corrosion In Sewer Networks

- Three Basic Approaches to Predictive Assessment:
  - Empirical Equations
    - Yes-or-No Answers
  - Qualitative Indicators
    - Z-Formula
    - Pomeroy Method for Pressure Sewers
    - Pomeroy and Parkhurst Method for Gravity Sewers
  - Mechanistic Modeling
    - WATS – Wastewater Aerobic/Anaerobic Transformations in Sewers
    - Adaptation of the WATS Model

Qualitative Indicators Provide Guidance, But Miss Some Of The Important Predictive Variables

- Qualitative Indicators, e.g. "Z-Formula"
  - BOD, Flowrate
  - Pipe Slope, Wetted Perimeter, Surface Width



$$Z = \frac{3[EBOD]}{S^{1/2}Q^{1/3}} \times \frac{P}{b}$$

Qualitative Indicators Provide Guidance, But Miss Some Of The Important Predictive Variables

$$Z = \frac{3[EBOD]}{s^{1/2}Q^{1/3}} \times \frac{P}{b}$$

TABLE 6.3. Examples of Sulfide Problems in Gravity Sewers as Estimated by the Z-formula.

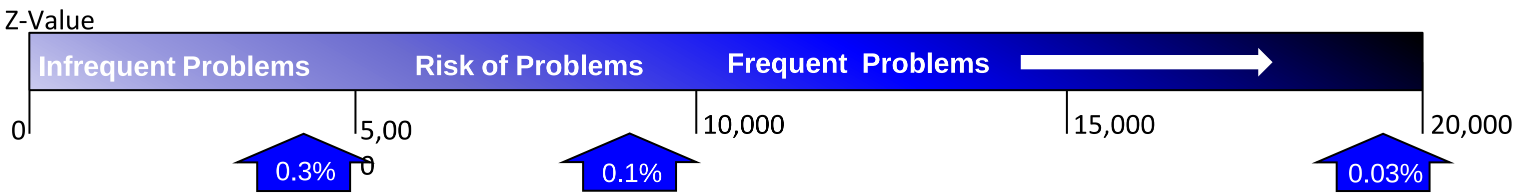
Slope, *s* (%)	Velocity, *u* (m s⁻¹)	Flow, *Q* (L s⁻¹)	Load, *PE*	*Z*-value
0.03	0.32	45	19,000	19,370
0.1	0.58	82	35,000	8740
0.3	1.00	141	61,000	4220

Example

250 mg/L BOD

20°C

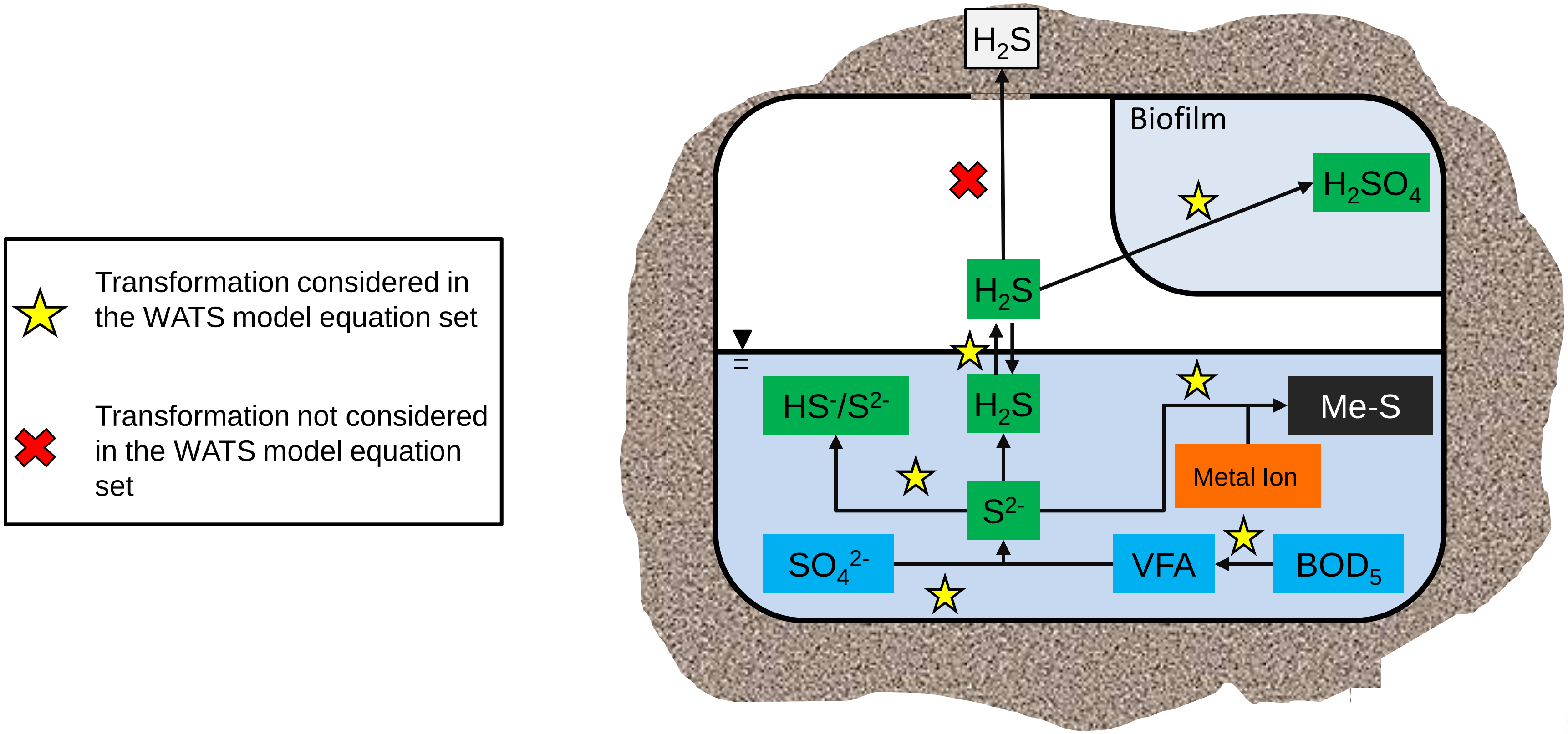
0.6 m diameter



- Limitations:
  - Recommended for Pipes with Diameter < 0.6 meters (≈ 24”)
  - Minimal Hydraulic Considerations; No Venting or Turbulence
  - No Direct Link to Corrosion
  - Only Serves as Screening Tool to Show Potential for Problems
  - Reality Check: Anaerobic Retention Time Vs. Turbulence?

Mechanistic Modeling Is Akin To Biological Process Modeling, Reflecting As Many Important Transformations As Practical

- Mechanistic Modeling
  - WATS – Wastewater Aerobic/Anaerobic Transformation in Sewers
  - Akin to IWA's ASM No. 1 for Activated Sludge



Mechanistic Modeling Requires Significant Computational Power And Expertise Of A Software Operator/Programmer

Processes	$X_{S(-II)}$	$S_{S(-II)}$	S_O	pH_2S	Process rate
Sulfide production		1			Equation 1
Sulfide precipitation*	1	-1			
Water phase sulfide oxidation, chemical		-1	-1.2		Equation 2
Water phase sulfide oxidation, biological		-1	-0.5		Equation 3
Biofilm sulfide oxidation		-1	-0.5		Equation 4
Reaeration			1		Equation 5
Sulfide emission		-1		1	Equation 6
Adsorption on moist sewer walls				-1	Equation 7

* Sulfide precipitation is assumed instantaneous

WATS in Peterson Matrix Notation

Process rate equations are described as follows (Nielsen et al., 2005):

Equation 1: $k_{S(-II),\,p}(S_F + S_A + X_{S1})^{0.5}(K_O/(S_O + K_O))(A/V)1.03^{(T-20)}$

Equation 2: $k_{S(-II),\,o,c}S_{S(-II)}S_O^{0.1}1.07^{(T-20)}$

Equation 3: $k_{S(-II),\,o,b}S_{S(-II)}S_O^{0.1}1.07^{(T-20)}$

Equation 4: $k_{S(-II),\,o,f}S_{S(-II)}^{0.5}S_O^{0.5}(A/V)1.03^{(T-20)}$

Equation 5: $K_La_{S_O}24(S_{OS} - S_O)$

Equation 6: $K_La_{S(-II)}24(\gamma S_{S(-II)} - S_{S(-II),eq})$

Equation 7: $k_{s(-II)gas,o,w}((pH_2S)/(K_{pH2S} + pH_2S))(A_c/V_g)1.03^{(T-20)}$

Source: Nielsen *et al*. (2003)

But, Captures Variables That Strongly Influence Sulfide Emission And Corrosion

Processes	$X_{S(-II)}$	$S_{S(-II)}$	S_O	pH_2S	Process rate
Sulfide production		1			Equation 1
Sulfide precipitation*	1	-1			
Water phase sulfide oxidation, chemical		-1	-1.2		Equation 2
Water phase sulfide oxidation, biological		-1	-0.5		Equation 3
Biofilm sulfide oxidation		-1	-0.5		Equation 4
Reaeration			1		Equation 5
Sulfide emission		-1		1	Equation 6
Adsorption on moist sewer walls				-1	Equation 7

* Sulfide precipitation is assumed instantaneous

WATS in Peterson Matrix Notation

Process rate equations are described as follows (Nielsen et al., 2005):

Equation 1: $k_{S(-II),\,p}(S_F + S_A + X_{S1})^{0.5}(K_O/(S_O + K_O))(A/V)1.03^{(T-20)}$

Equation 2: $k_{S(-II),\,o,c}S_{S(-II)}S_O^{0.1}1.07^{(T-20)}$

Equation 3: $k_{S(-II),\,o,b}S_{S(-II)}S_O^{0.1}1.07^{(T-20)}$

Equation 4: $k_{S(-II),\,o,f}S_{S(-II)}^{0.5}S_O^{0.5}(A/V)1.03^{(T-20)}$

Equation 5: $K_La_{So}24(S_{OS} - S_O)$

Equation 6: $K_La_{S(-II)}24(\gamma S_{S(-II)} - S_{S(-II),eq})$

Equation 7: $k_{s(-II)gas,o,w}((pH_2S)/(K_{pH2S} + pH_2S))(A_c/V_g)1.03^{(T-20)}$

Mass Transfer Relationships for Oxygen and Hydrogen Sulfide

Source: Nielsen *et al*. (2003)

Mechanistic Modeling Tells Us That Hydraulics Matter Intensely When Predicting Corrosion Potential

- Assumed That Sulfate and Organics Exist in Sufficient Quantities to be a Potential Problem
- Mass Transfer is Critical:

$$K_L a_{H_2S} = (1.736 - 0.196\,\mathrm{pH})\,K_L a_{O_2} \quad (4.5\ \mathrm{pH}\ 8.0,\ \text{at } 20°\mathrm{C}) \tag{1}$$

$$K_L a_{O_2} = 0.86(1 + 0.2F^2)(su)^{3/8} d_m^{-1} \alpha \tag{2}$$

where

u	= mean flow velocity ($\mathrm{m\ s^{-1}}$)
s	= slope of sewers ($\mathrm{m\ m^{-1}}$)
d_m	= mean hydraulic depth, i.e., the water cross-sectional area divided by the width of the water surface (m)
F	= Froude number = $u(gd_m)^{-0.5}$
g	= gravitational acceleration ($\mathrm{m\ s^{-2}}$)
α_r	= temperature coefficient for reaeration = 1.024
T	= temperature (°C).

Source: Nielsen *et al*. (2005)

Positives and Negatives Of Mechanistic Sewer Sulfide Modeling

- Applicability of Mechanistic Modeling
  - No Limitations on Size of System
  - Can be Calibrated to Specific System
    - Ongoing headspace sulfide monitoring
  - Broad Tool Across Collection System
  - May be Deployed to Predict Corrosion Rates in MM/Year; Basis for Action
- Limitations
  - Requires More Data Inputs than Other Approaches
    - Hydraulic modeling: Froude number, hydraulic mean depth, pipe geometry
    - Chemical parameters: BOD_5 , pH, temperature
  - Requires Computational or Programming Expertise to Solve Multiple Simultaneous Differentials
  - Application is a Blend of Experience and Science
    - Venting is not included in model, nor is gas transport
    - Understanding of system needed to pair sulfide emission with local hydraulics

There Are Reasonable Ways To Simplify This Approach And Retain The Benefits Of Mechanistic Vs. Qualitative Prediction

- Some Processes are Important for Predicting Aqueous Sulfide Concentration
  - Important to Calculate Headspace Concentrations
  - The Good News is We Can Measure This Directly and it is Reasonably Predictable for a Point in a Sewer!!!

Processes	Role in Proposed Simplified Model
1. Sulfide production	Omit – Impacts dissolved sulfide concentration
2. Sulfide precipitation*	Omit – Serves as sink for dissolved sulfide
3. Water phase sulfide oxidation, chemical	Omit – Serves as sink for dissolved sulfide
4. Water phase sulfide oxidation, biological	Omit – Serves as sink for dissolved sulfide
5. Biofilm sulfide oxidation	Omit – Serves as sink for dissolved sulfide
6. Reaeration	Omit – Serves as brake on sulfide production
7. Sulfide emission	**RETAINED**
8. Adsorption on moist sewer walls	**RETAINED**

There Are Reasonable Ways To Simplify This Approach And Retain The Benefits Of Mechanistic Vs. Qualitative Prediction

- Predictive Tool is Very Simple at Steady State:

Sulfide Emission: $K_L a_{S(-II)} 24(\gamma S_{S(-II)} - S_{S(-II),eq})$

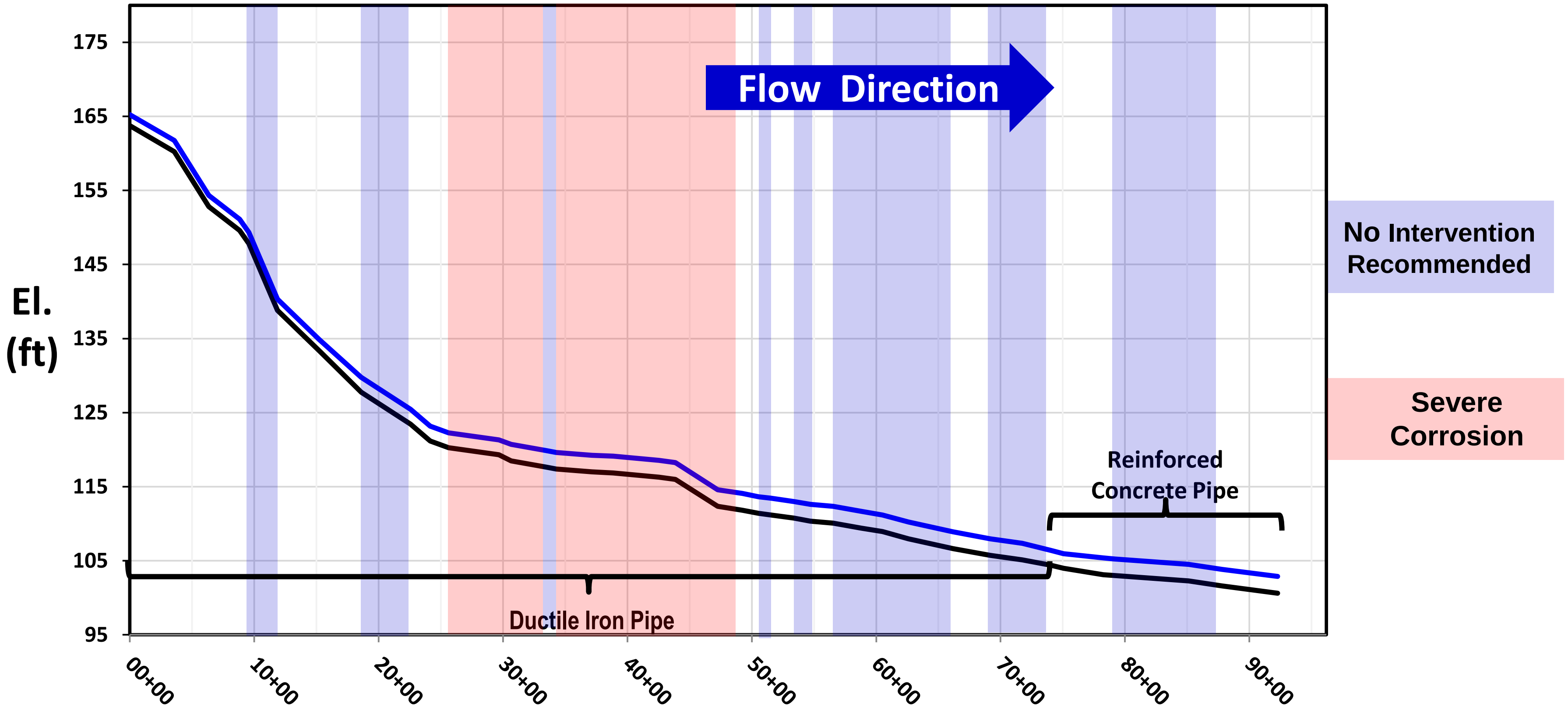
Adsorption: $\frac{\Delta p_{H2S}}{dt} = 0 = -1 \times k_{s(-II)gas,o,w}((pH_2S)/(K_{pH2S} + pH_2S))(A_c/V_g)1.03^{(T-20)}$

- Set these Equations Equal to One Another and Solve for pH_2S
  - We Know by Literature, Assumption, or Measurement Every Other Parameter in These Equations
  - Now it is a Suitable Job for a Spreadsheet ☑

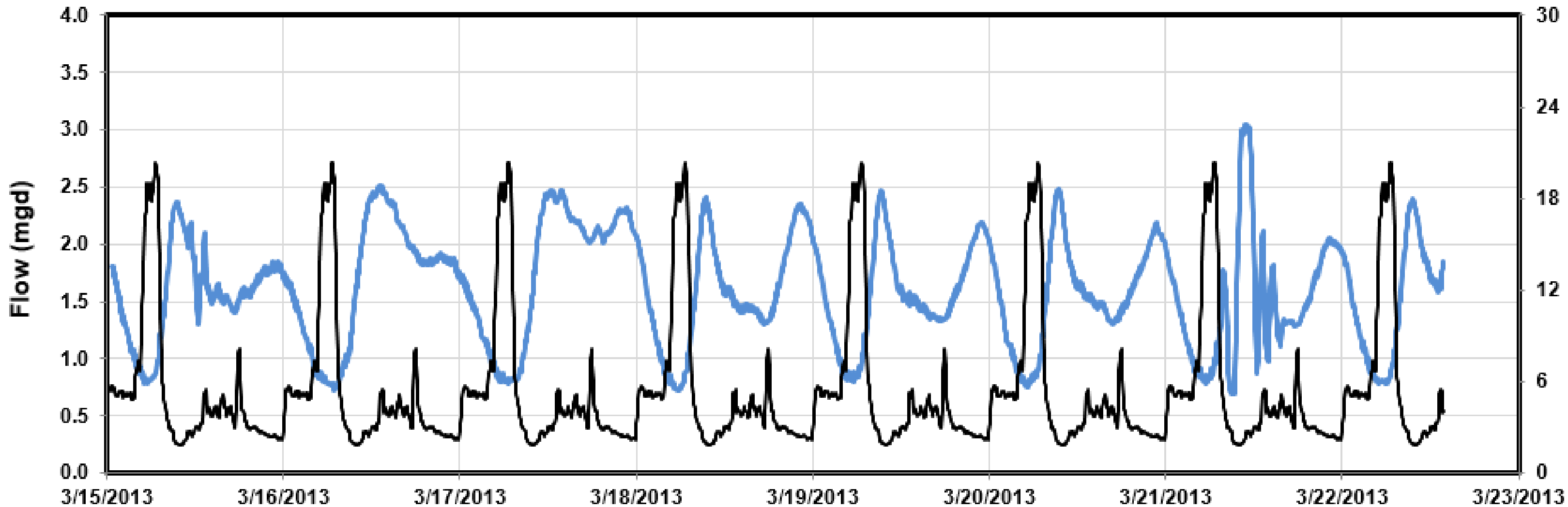
This Presentation Describes The Sewer Sulfide Modeling As A Practical Asset Management Tool

- Sulfide Generation and Corrosion in Sewers
  - Biological and Physical Processes Causing Sewer Corrosion
  - Impact of Sewer and Wastewater Characteristics on Corrosion Potential
- Sulfide Modeling and Description of a Simplified Tool
  - Basic Approaches to Sulfide Modeling
  - Sensitivities and Limitations of Mechanistic Sulfide Modeling
  - Impact of Sewer Hydraulics on Corrosion
  - Simplification of Tool for Practical Asset Management Guidance
- Sulfide Modeling Tool Application: Case Study
  - Case Study Area
  - What Does Modeling Tell Us About Causes of Sulfide Generation & Emission?
  - What Do Generation and Emission Patterns Tell Us About Sewer Operation?
  - What Does Sewer Operation Tell Us About Sulfide and Odor Mitigation?

Case Study: 27” Ductile Iron And Reinforced Concrete Pipe With Known Corrosion Damage



Hydraulics Of This Pipe Section Drive Specific Areas Of Concrete Corrosion



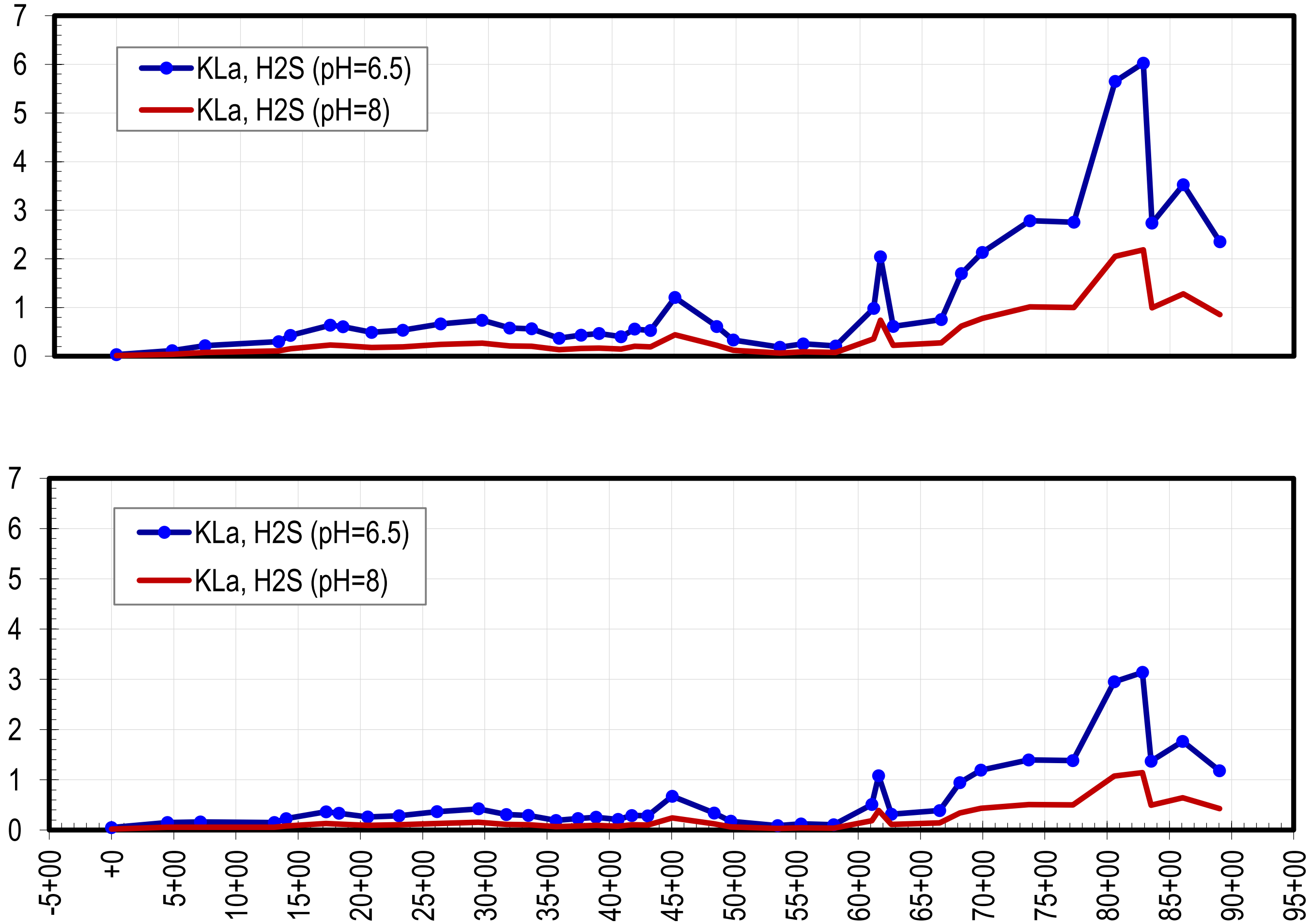
- Hydrogen Sulfide Concentrations More or Less Track Inverse of Diurnal Flow Pattern in Pipe
- Can This be Described by Simplified Model?

Hydraulics Of This Pipe Section Drive Specific Areas Of Concrete Corrosion

0.8 MGD

Modeled K_La for H_2S

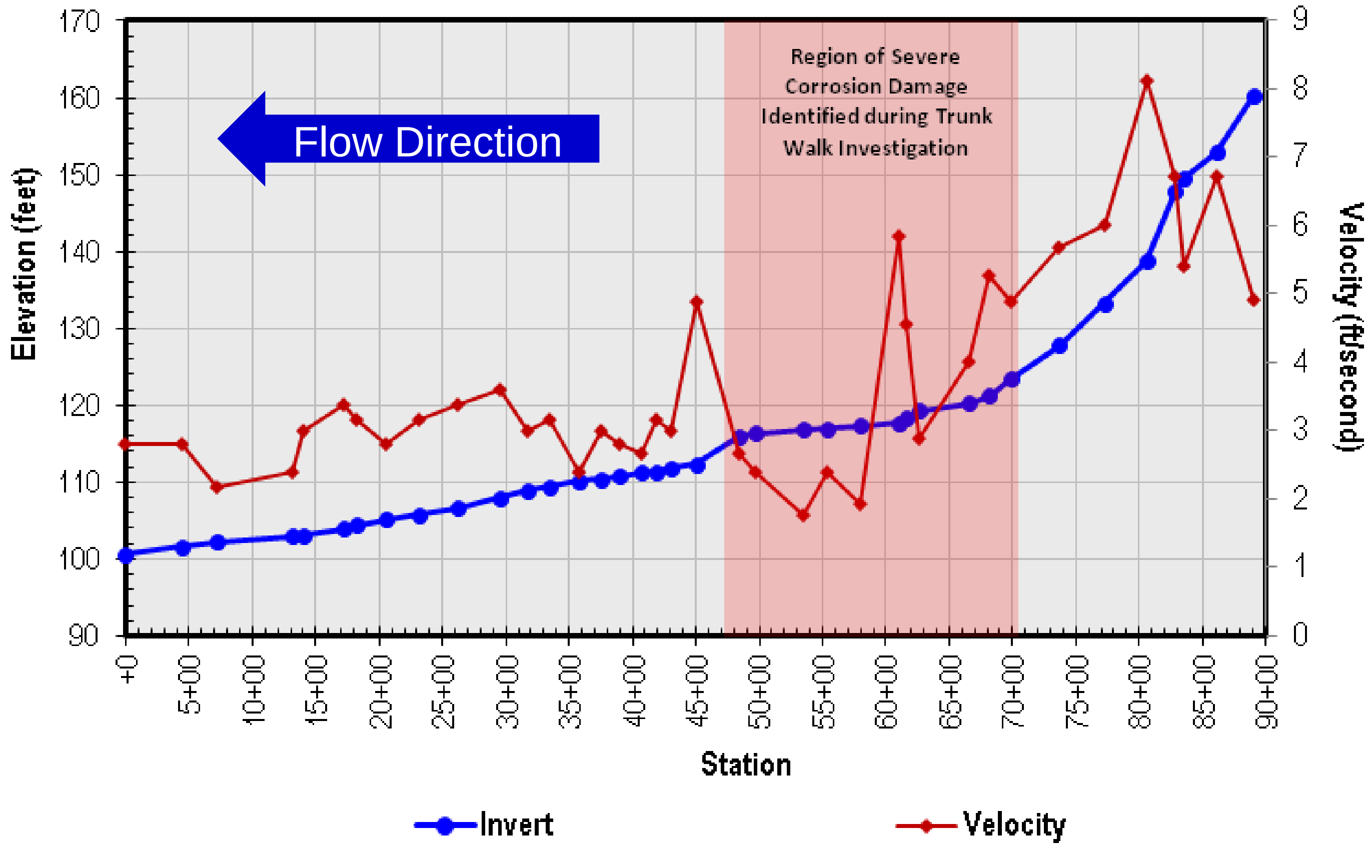
3.0 MGD



Diurnal Patterns Show That Dissolved Sulfide Concentration Is Sufficient To Result In Substantial Flux

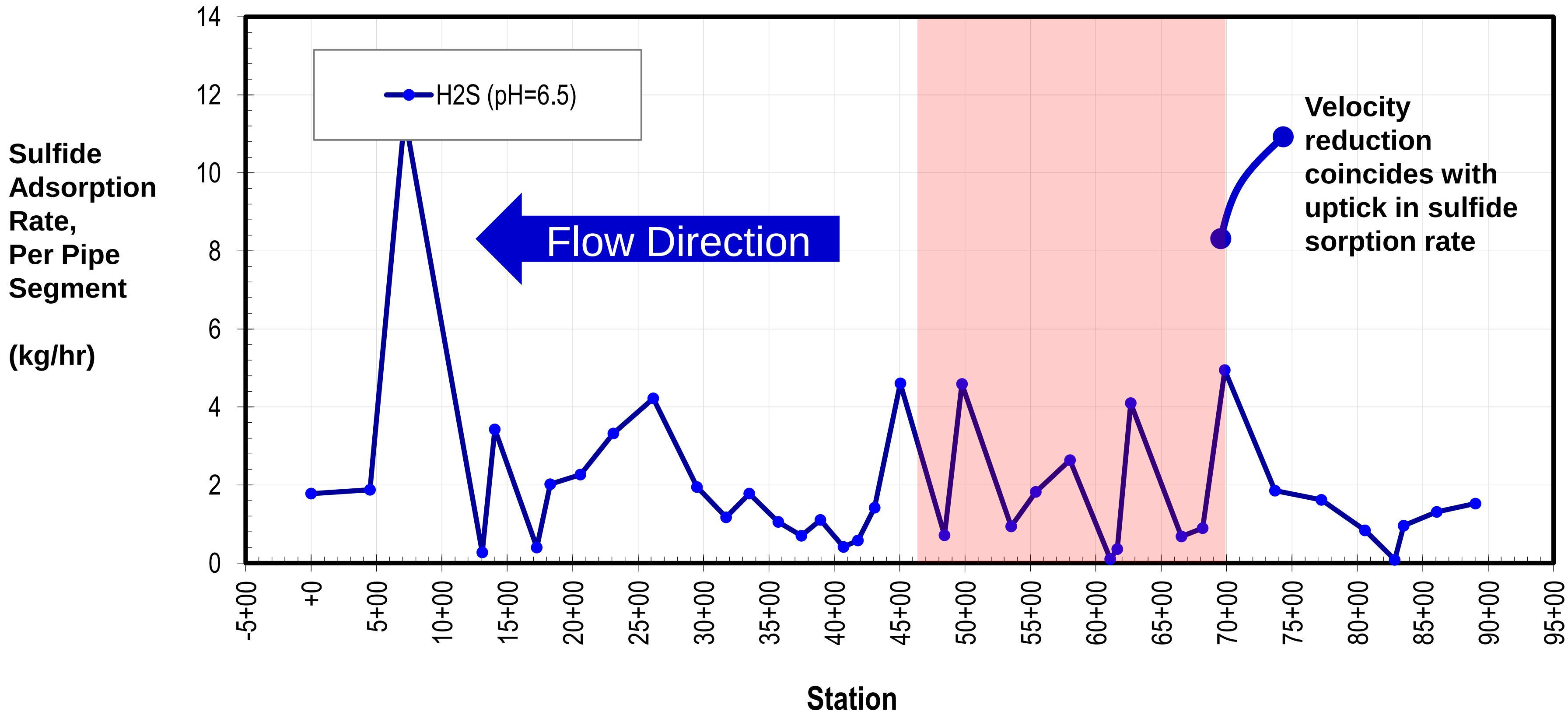
- In this Segment, Low Flows Result in Substantial Flux
  - Increased Flow Criticality Related to Froude Number
  - Froude Number Increases as Flow Depth Lessens at Low Flow Rate
- Sulfide Likely Generated Upstream of this Pipe Segment
  - Retention Time in the Entire Pipe Segment Only 40 Minutes
  - This is Opposite of What Z-Formula Would Predict
    - Z-Formula: Low Velocity = High Sulfide Release

Velocity Profile In Pipe Shows Maximum Corrosion Occurs Where Pipe Flattens And Water Slows Down



Velocity Profile In Pipe Shows Maximum Corrosion Occurs Where Pipe Flattens And Water Slows Down

- Assuming a Non-Limiting Headspace Sulfide Concentration:



Understanding Mechanism Of Sulfide Corrosion Allows You To Develop Strategies To Mitigate It

- In This Case, Sulfide is Transported From Upstream:
  - Alternative Electron Acceptors Will Not Work, e.g. $Ca(NO_3)$
  - Chemical, Enzymatic, and Biological Agents (CEBA) Likely Not Helpful for the Same Reason in This Application
  - pH Adjustment Can Have a Huge Impact, and it Only Needs to be Maintained in Areas With High Flux Rates
  - Potentially, Chemical Precipitation (e.g. ferric salts) or Oxidants Could Work, But You are Treating a Large Mass of Sulfide Rather Than Sequestering a Small Volatized Mass
    - Need to Watch Alkalinity Too!

Take Home: A Simplified Mechanistic Approach Can Provide Useful Prescriptive Information About Sulfide Corrosion

- Sulfide in Itself is Not Evil – It is Ubiquitous
- Sulfide Acts by Volatilizing, Adsorbing, and Oxidizing on the Moist Sewer Wall
- Prior Qualitative Methods of Predicting Corrosion Ignore the Complex Hydraulics of Real Sewer Networks
- Fully Mechanistic Methods Can be Cumbersome
- Useful Information Can be Obtained From a Simplified Method Focusing on the Point of Action of Sulfide
  - Volatilization
  - Adsorption
- Simplified Approach Can be Used for Targeted Field Investigations in Areas With High Headspace Sulfide

GREELEY AND HANSEN

THANK YOU

we do water

mwea