Wastewater Plant Upset from H2S

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R8PA Conference

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Presentation Overview

Hydrogen sulfide

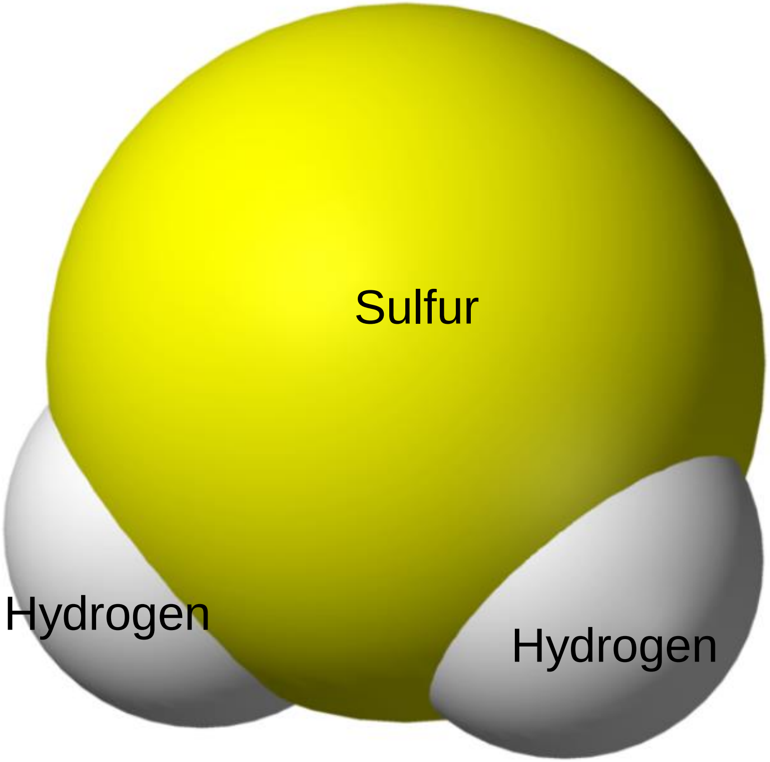
- Causes, detection and safety
- H2S data from the collection system and wastewater treatment plant
- Current treatment conditions at the WWTP
- Liquid stream chemical treatment options
- Vapor phase treatment options
- H2S jar testing and pilot testing
- Cause of plant upset
- Case studies monitoring and reducing H2S

What’s the difference between a Man buying a lottery ticket and a Man arguing with his wife.

The Man buying a lottery ticket actually has a chance to win!

Hydrogen Sulfide

- Colorless gas
- Rotten Egg Odor
- Heavier Than Air
- Toxic
- Corrosive
- Water Soluble



Detection Threshold - concentration of gas odor that can be detected by 50% of the people, 100% of the time.

From Minimization of odors and Corrosion in Collection System WERF 2007

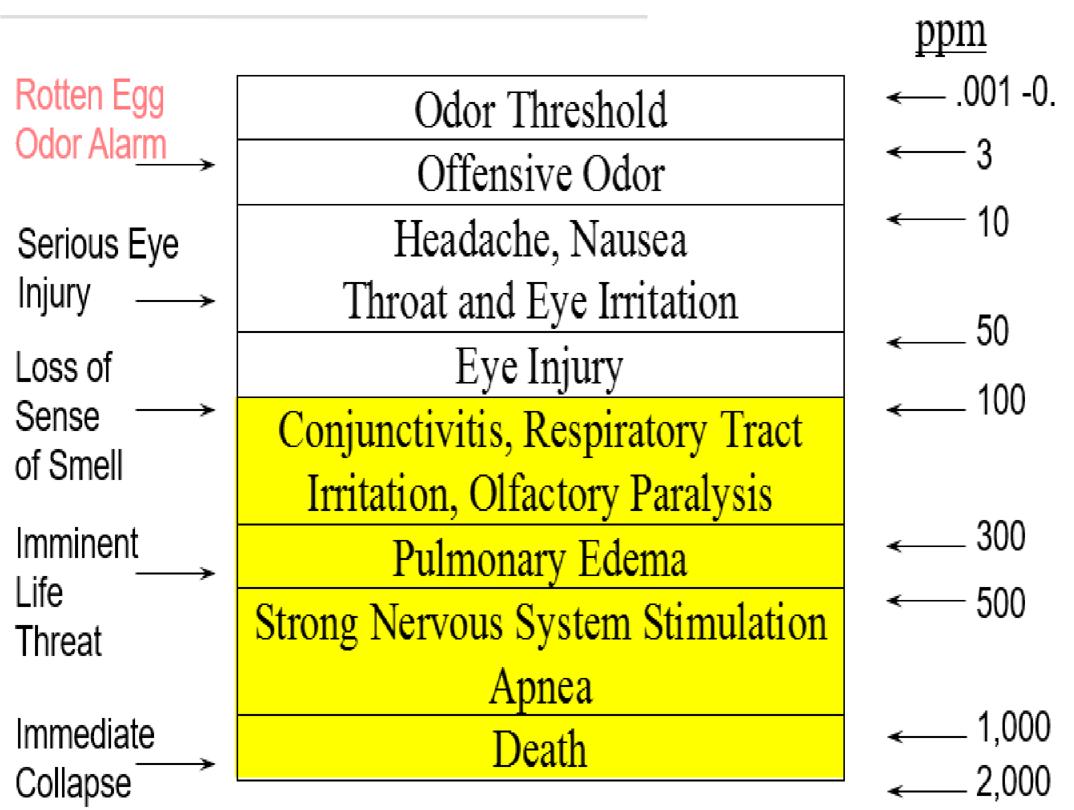
Table 2-1. Odorous Compounds in Wastewater.

Name	Formula	Characteristic Odor	Detection Threshold (ppm)
Hydrogen sulfide	H_2S	Rotten eggs	0.0005
Ammonia	NH_3	Irritating, pungent	17
Skatole	C_9H_9N	Fecal, nauseating	0.001
Indole	$C_6H_4(CH)_2NH$	Fecal, nauseating	0.0001
Methylamine	CH_3NH_2	Putrid, fishy	4.7
Allyl mercaptan	$CH_2{=}CHCH_2SH$	Disagreeable, garlic	0.0001
Amyl mercaptan	$CH_3(CH_2)_4SH$	Unpleasant, putrid	0.0003
Benzyl mercaptan	$C_6H_5CH_2SH$	Unpleasant, strong	0.0002
Ethyl mercaptan	C_2H_5SH	Decayed cabbage	0.0003
Dimethyl sulfide	$(CH_3)_2S$	Decayed cabbage	0.001
Trimethylamine	$(CH_3)_3N$	Pungent, fishy	0.0004
Sulfur dioxide	SO_2	Pungent, irritating	2.7
Methyl mercaptan	CH_3SH	Decayed cabbage	0.0005
Thiocresol	$CH_3C_6H_4SH$	Skunk, irritating	0.0001
Thiobismethane	CH_3SCH_3	Rotting meat	0.0011

Note: Different threshold values are reported in the literature, particularly for hydrogen sulfide and ammonia. Odor thresholds are included here to give the reader a general idea of human sensitivity and odor concentrations which could potentially cause complaints. Ammonia for example is reported in ranges from 2.8 ppm to 17 ppm.

Hydrogen Sulfide

- **Hydrogen Sulfide is Dangerous**
  - **January 2017: 3 collection system workers killed in Key Largo, FL**
- **Hydrogen Sulfide Corrodes Infrastructure**
  - **EPA reports annual rehabilitation costs of $6,000,000,000**
- **Hydrogen Sulfide Reduces Quality of Life in the Community**



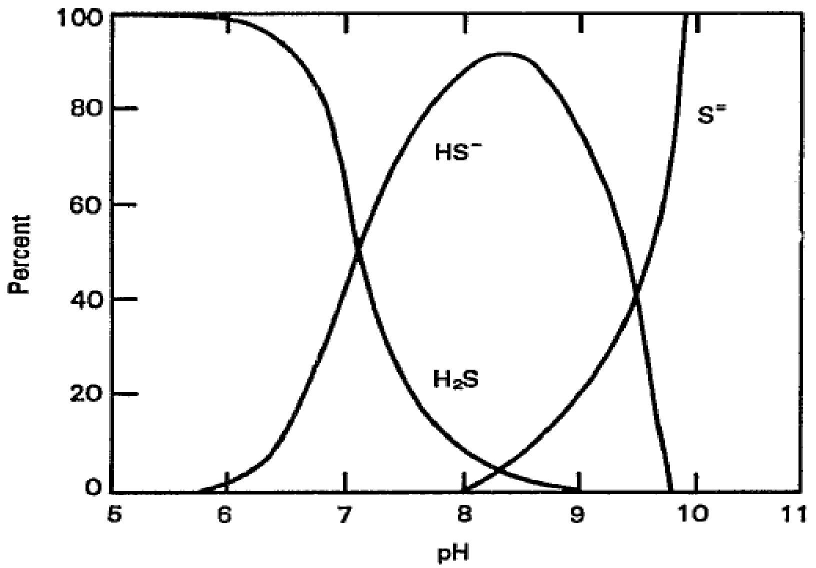
Hydrogen Sulfide Generation and Release

- Factors that influence hydrogen sulfide generation
  - Detention time
  - Temperature
  - Biochemical oxygen demand
  - pH
  - Sulfate concentration
  - Sediment and debris
- Factors that influence hydrogen sulfide release
  - Dissolved hydrogen sulfide concentration
  - Turbulence
  - pH

pH Shift – Chemicals

- Chemicals for pH shift
  - Calcium hydroxide & magnesium Hydroxide
  - Sodium hydroxide & potassium hydroxide
- Excellent at keeping sulfides solubilized
  - Does not remove sulfides, if pH decreases downstream of application, sulfides may still be released.
- Relatively Safe

- Increasing pH, chemicals work by changing the sulfide type to non-volatile.
  - $S^{=}$: non-volatile
  - HS^{-} : non-volatile
  - H_2S : volatile, can off-gas causing corrosion and odors.



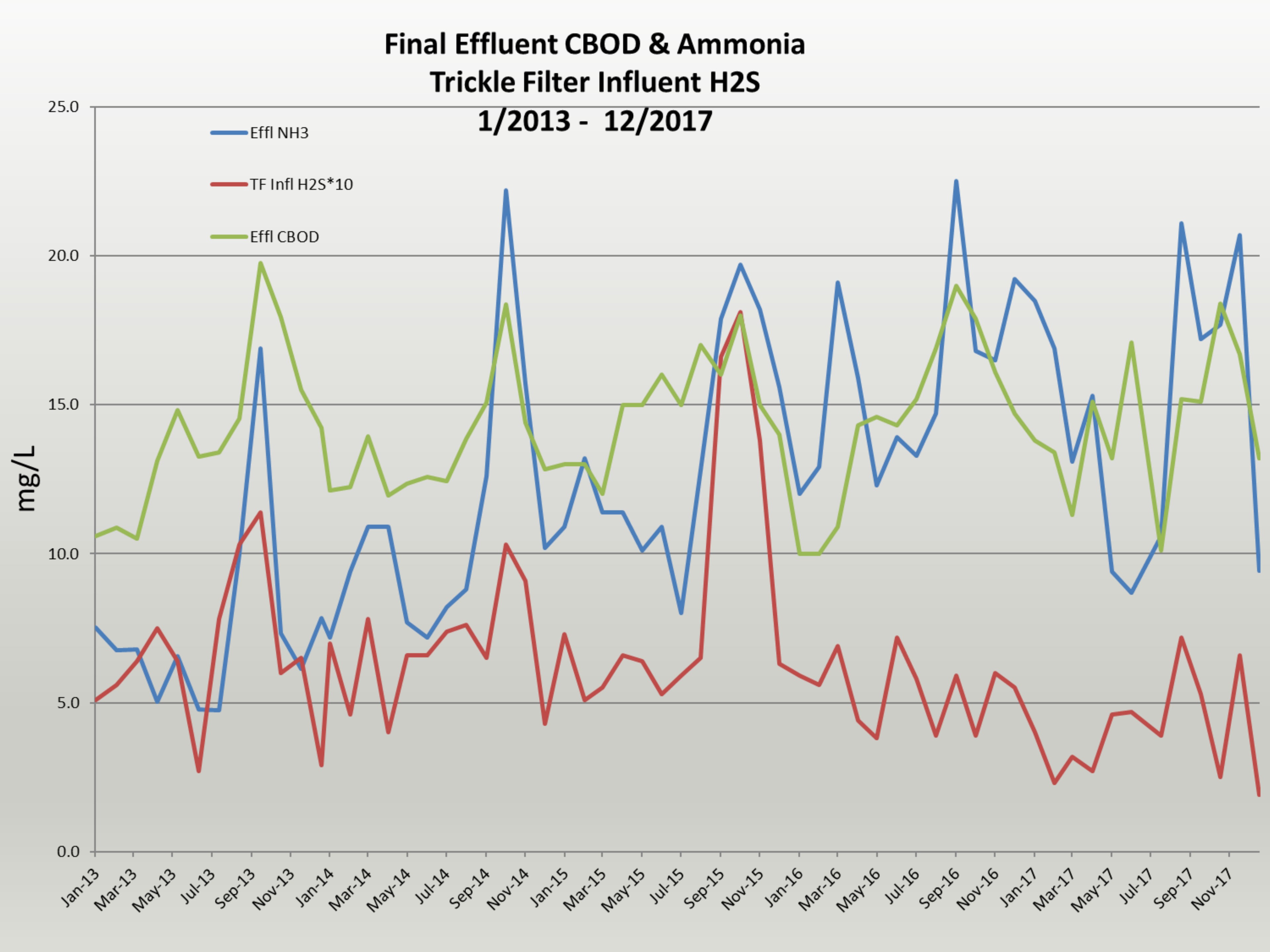
Wastewater Treatment Plant Monthly Average Influent Dissolved H2S Data

	2013	2014	2015	2016	2017	2018	2019		Avg.	Min	Max
January	4.60	5.56	4.27	5.07	5.8	4.35	4.17		4.94	4.27	5.80
February	4.73	2.74	5.86	5.03	4.6	3.84	3.56		4.34	2.74	5.86
March	2.10	2.76	3.29	4.88	2.5	3.20	2.93		3.09	2.10	4.88
April	2.05	3.18	3.40	5.15	3.5	2.06			3.22	2.05	5.15
May	7.26	3.39	3.38	6.01	4.2	3.02			4.54	3.02	7.26
June	7.82	4.86	3.81	7.52	5.1	5.66			5.79	3.81	7.82
July	3.79	5.58	4.81	9.03	5.8	4.14			5.53	3.79	9.03
August	6.09	7.65	7.55	7.57	7.17	6.26			7.05	6.09	7.65
September	5.64	9.45	8.58	9.94	6.40	5.97			7.66	5.64	9.94
October	4.24	10.6	10.3	8.62	8.01	5.33			7.84	4.24	10.57
November	4.47	8.76	7.08	9.47	7.62	4.25			6.94	4.25	9.47
December	3.86	5.38	6.46	8.00	4.89	3.40			5.33	3.40	8.00
							To date				
Yearly average H2S	4.72	5.82	5.73	6.85	5.47	4.29	3.55				
Yearly average Flow	6.83	6.62	6.41	6.37	6.43	6.33	6.34				
Yearly average BOD	260	254	270	281	268	295	327				

Dissolved H2S and BOD data is in mg/L

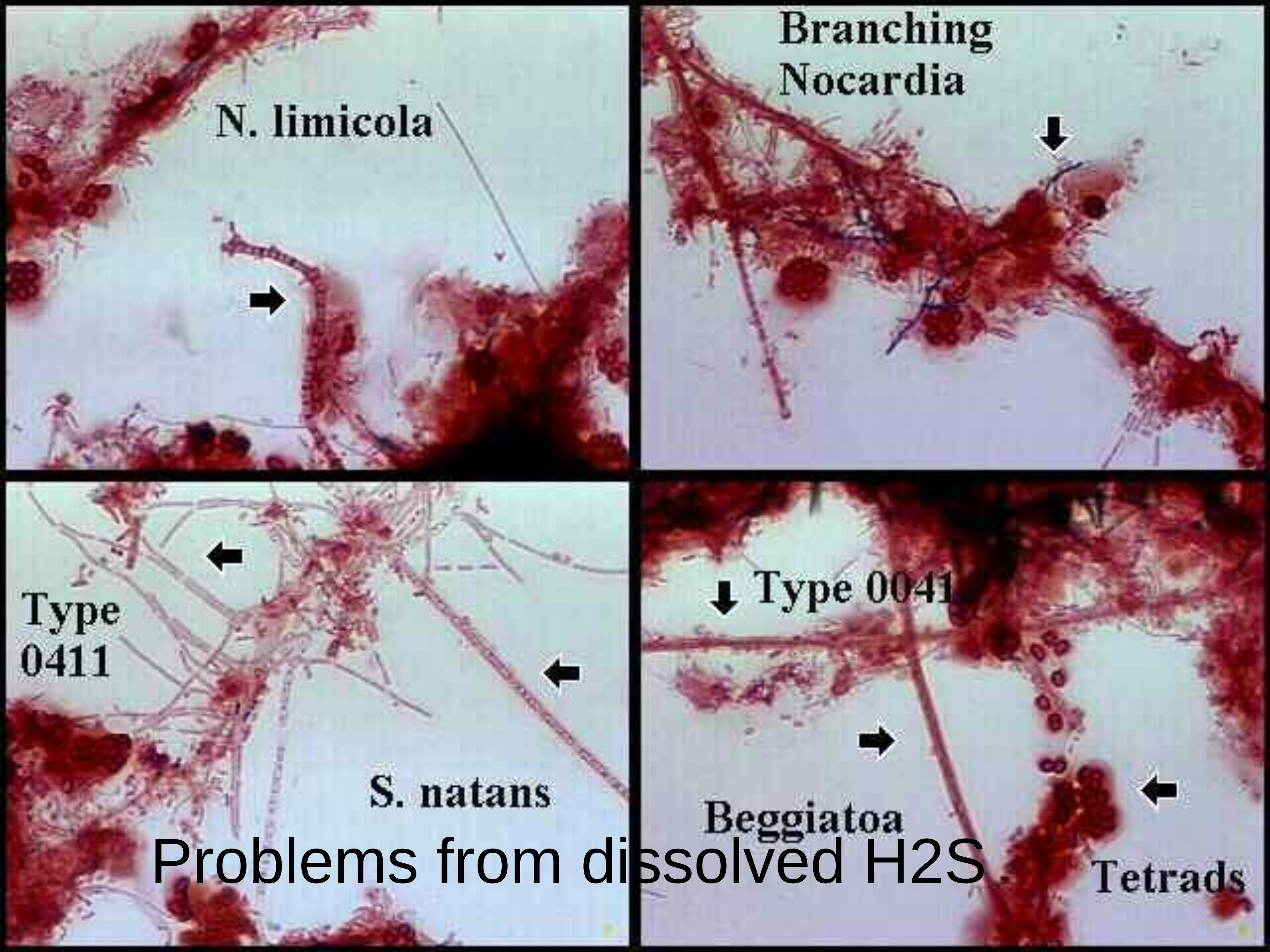
Flow data is in millions gallons per day

BOD - biochemical oxygen demand



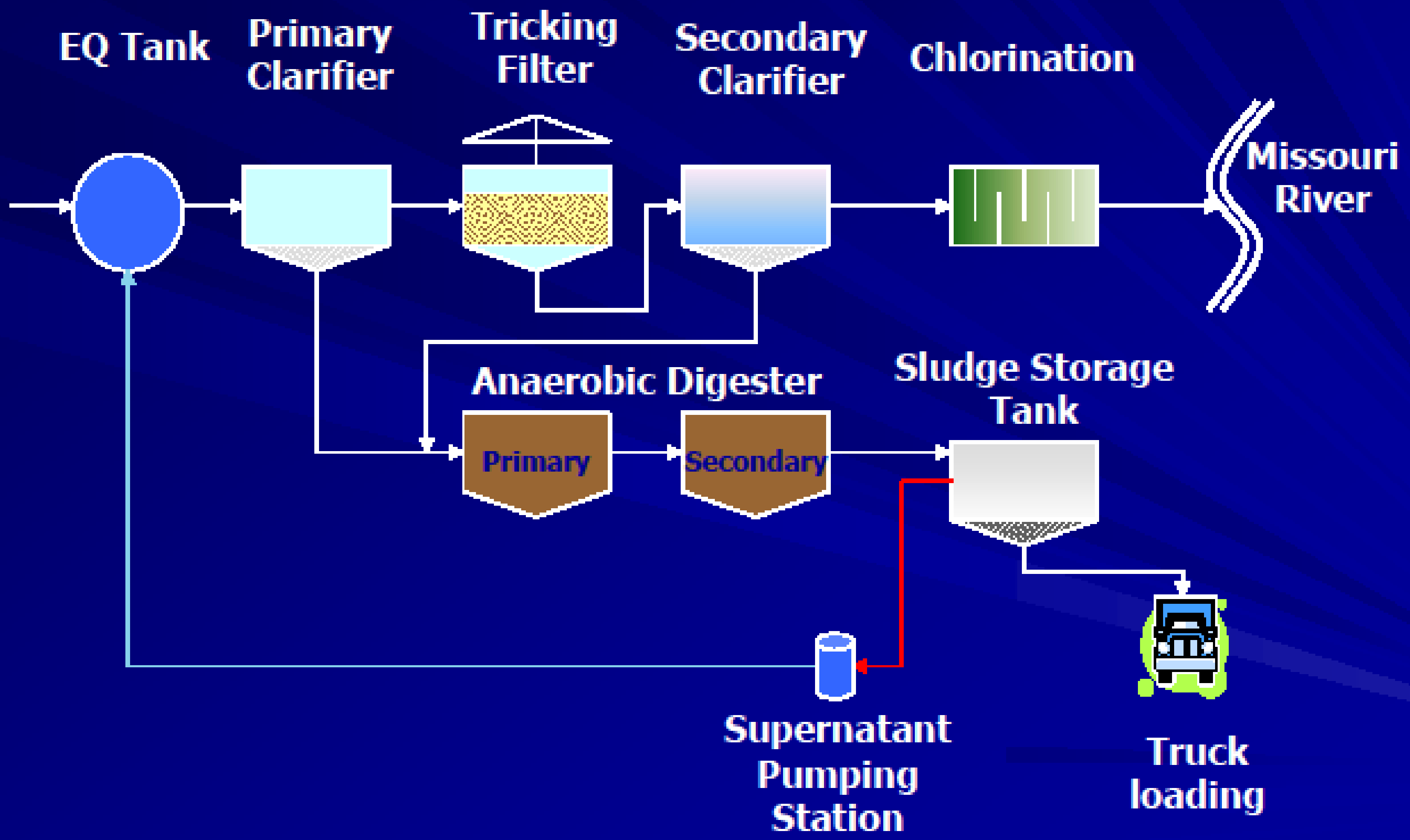
Final Effluent CBOD & Ammonia
Trickle Filter Influent H2S
1/2013 - 12/2017
Effl NH3
TF Infl H2S*10
Effl CBOD
mg/L
25.0
20.0
15.0
10.0
5.0
0.0
Jan-13
Mar-13
May-13
Jul-13
Sep-13
Nov-13
Jan-14
Mar-14
May-14
Jul-14
Sep-14
Nov-14
Jan-15
Mar-15
May-15
Jul-15
Sep-15
Nov-15
Jan-16
Mar-16
May-16
Jul-16
Sep-16
Nov-16
Jan-17
Mar-17
May-17
Jul-17
Sep-17
Nov-17

Problems from dissolved H_2S




Admin
Lab
601
Flow
Equalization
Headworks
LONDON
Final clarifiers
Primary clarifiers
Trickle Filters
PD

Treatment Plant Process diagram



Grease Interceptor Dissolved H2S data									
FSE	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
1	6	5	6	5	6	5	5		2
2		8	12	6	38	20	24		20
3					15	25	45		25
4							50		6
5	10	8	25	25	2	38	50		8
6		19	25	15	20	28	15		10
7								8	39
8		12	15	10		12	25		<1
9							10		10
10									31
11									18
12									25
13			2	8	1		9		<1
14									10
15		12	5	<1	8	<1			12
16		5	5	12	10				16
17			18	10	20	30	<1		20
18		4	5	< 1	2	10	8		10
19							<1		38
20		<1	<1	6	3	15	10		Closed
21		5	6	10	20	20	14		25
22				2	8	< 2	8		3
23		5	8	19	2	2	6		2
24				12		<1	4		3

Grease Interceptor Dissolved H2S data

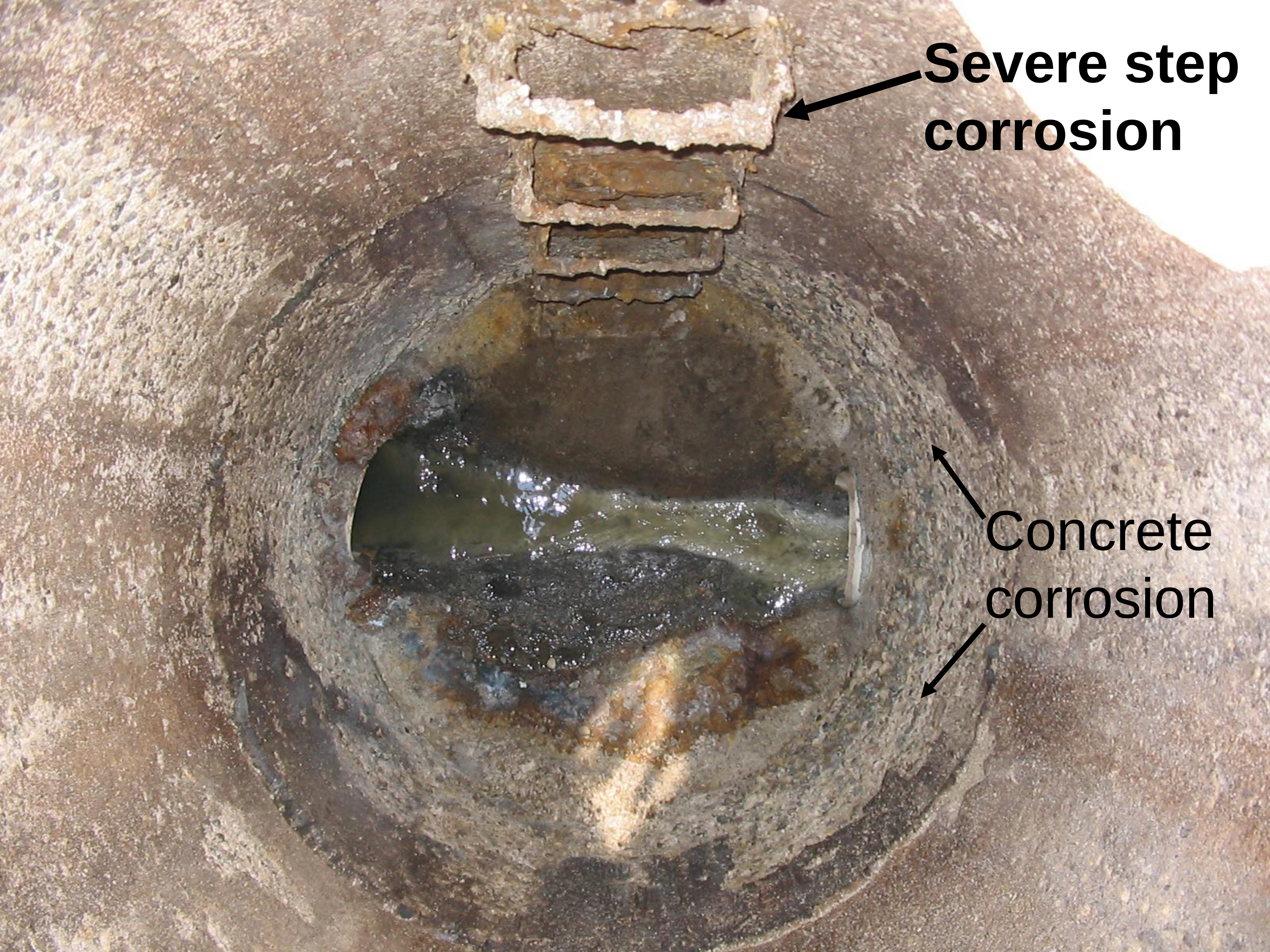
FSE	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
25		12	50	88	55	20			31
26									10
27									2
28					15	10	12		25
29		4	12	10	8	20	10		3
30	12	13	8	12		8	15		6
31		12	12	6	3	8	5		2
32		18	18	7				8	12
33									1
34		21	12	9					25
35		12	15	12	25		25		15
36	3	10	<1	12	20	5	5		10
37		6	2	12	10	8	15		18
38		12	19	25	38				15
39							8		6
40		20	18	12		20	14		21
41		5	6						no data
42		15	12	31	32	20			no data
43		16	12		6	15	25	10	38
44		15	8	6	10	6			6
45			22		9	12			5
46		25	25	12	25	6	32		35
47			8	42	19				44
48		15	8	22	9				20
49	16	12	5	10	15	19	5		2
min	**3**	**4**	**2**	**6**	**3**	**5**	**5**	**8**	**1**
max	16	25	50	88	55	20	32	10	44
avg	10	14	15	22	20	13	15	9	16

Hydrogen Sulfide – Corrosion

- **Hydrogen sulfide gas is corrosive to metals and concrete**
  - **Iron – in air environment**
  - **Copper – electrical wiring**
  - **Other metallic components of wastewater systems**
    - **Structural members, gratings and walkways**
    - **Equipment (grit collectors, bar screens, conveyors, etc.)**
    - **Stainless steel**

Concrete coated ductile iron pipe corrosion at the Bismarck WWTP, due to H2S


Step corrosion



Severe step corrosion
Concrete corrosion


What is left of step


Wastewater Wet Well Corrosion from H2S


APR 11 2008

H_2S Effect on Concrete

H2S (ppm)	Life expectancy (Years) for 3″ diameter pipe, 1″ cover
0.5	>50
1	25 - 50
1.5	25
2	10-25
3	10
4	5-10
7	5
>7	<5

Advanced Oxidation Technology, Buck Cox PhD, February 2004

Barrel Screens –removes large objects, smaller sized inorganics (gravel) and some organics. The high turbulence volatilizes H_2S. Week of October 20, 2017, average H_2S 161 ppm. Peak was at 400 ppm. May 2018 peak was at 1000 ppm.

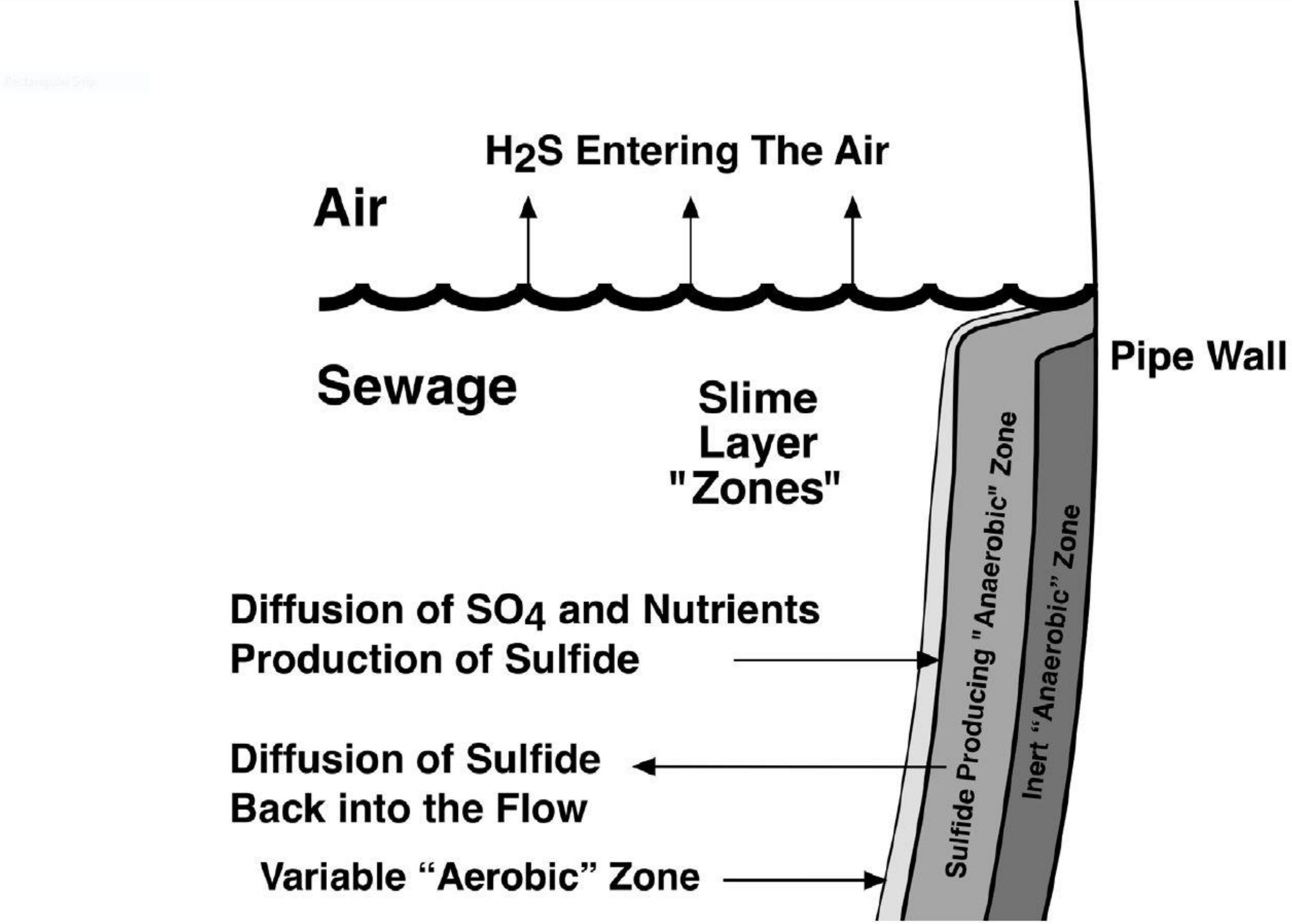


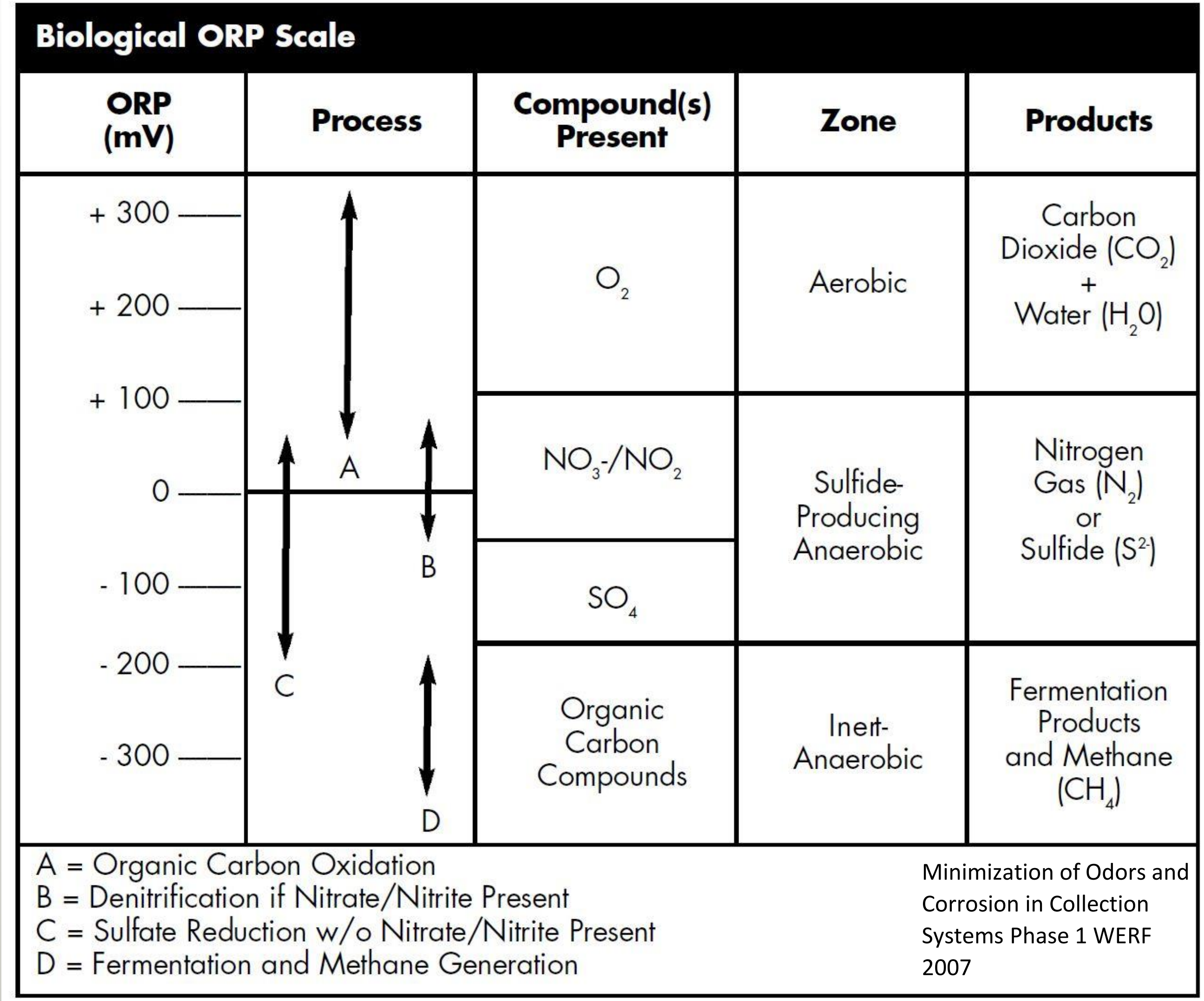
Figure 2-1. Slime Layer Chemistry and Biology Illustration.

A slime layer develops after two weeks in new sewers and becomes permanent.

There are three zones in the gelatinous slime layer

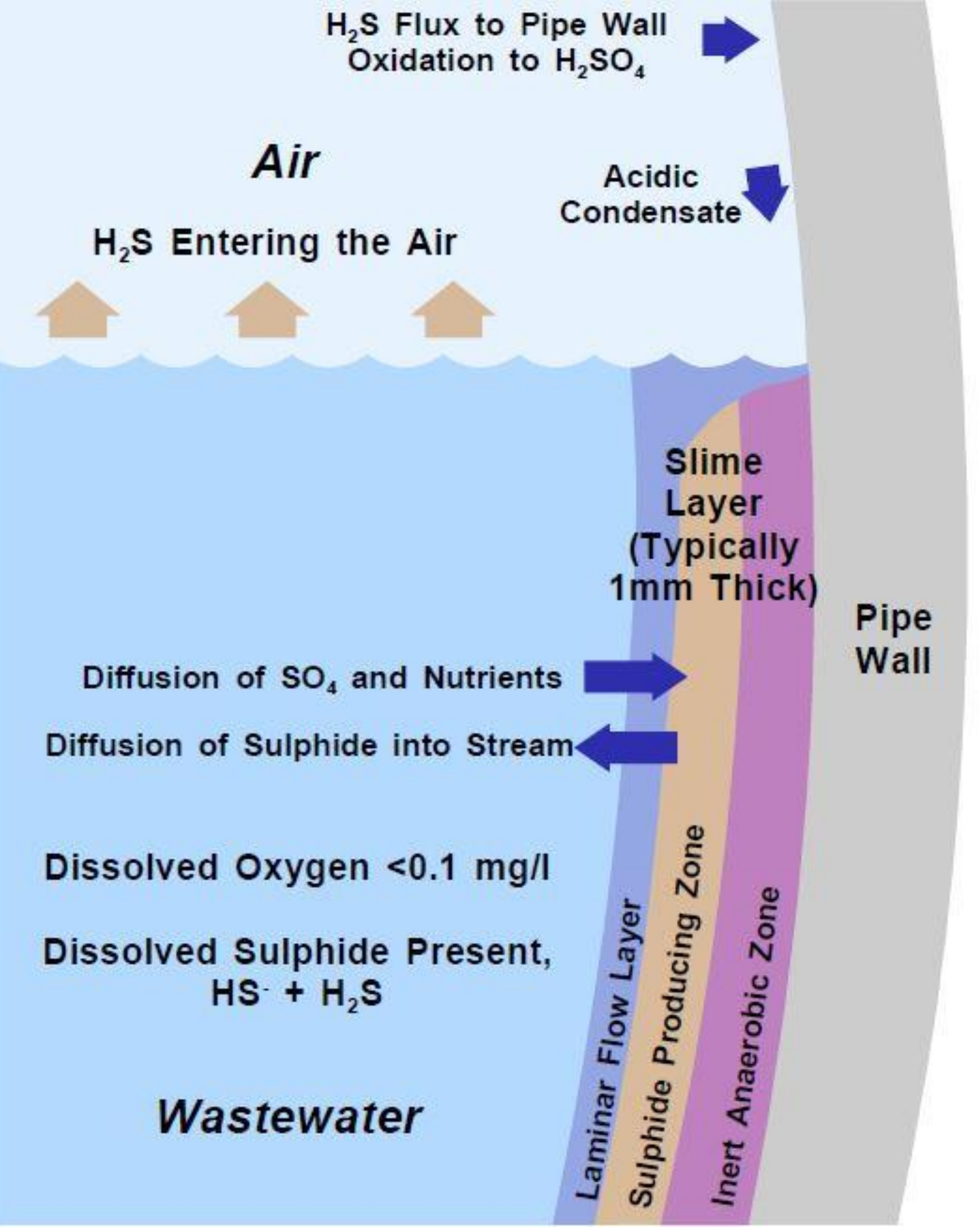
- Variable Aerobic zone,
- Anaerobic zone, H_2S production
- Inert Anaerobic zone, fermentation

Minimization of Odors and Corrosion in Collection Systems Phase 1 WERF 2007



ORP: Oxidation Reduction Potential

- > +50mV, aerobic, bacteria byproducts are CO_2 and water.
- 0 to -50 bacteria use NO3 byproducts are nitrogen gas.
- - 50 to -200 mV, anoxic, SO_4, bacteria convert sulfate to S^{-2} and H_2S.
- < -200mV fermentation. bacteria byproducts are methane and $CO_{2.}$



Minimization of Odors and Corrosion in Collection Systems
Phase 1 WERF 2007


HAVE YOU
EVER NOTICED
THAT A WOMAN'S
"I'LL BE READY
IN 5 MINUTES"
AND A MAN'S
"I'LL BE HOME
IN 5 MINUTES"
ARE EXACTLY THE SAME?

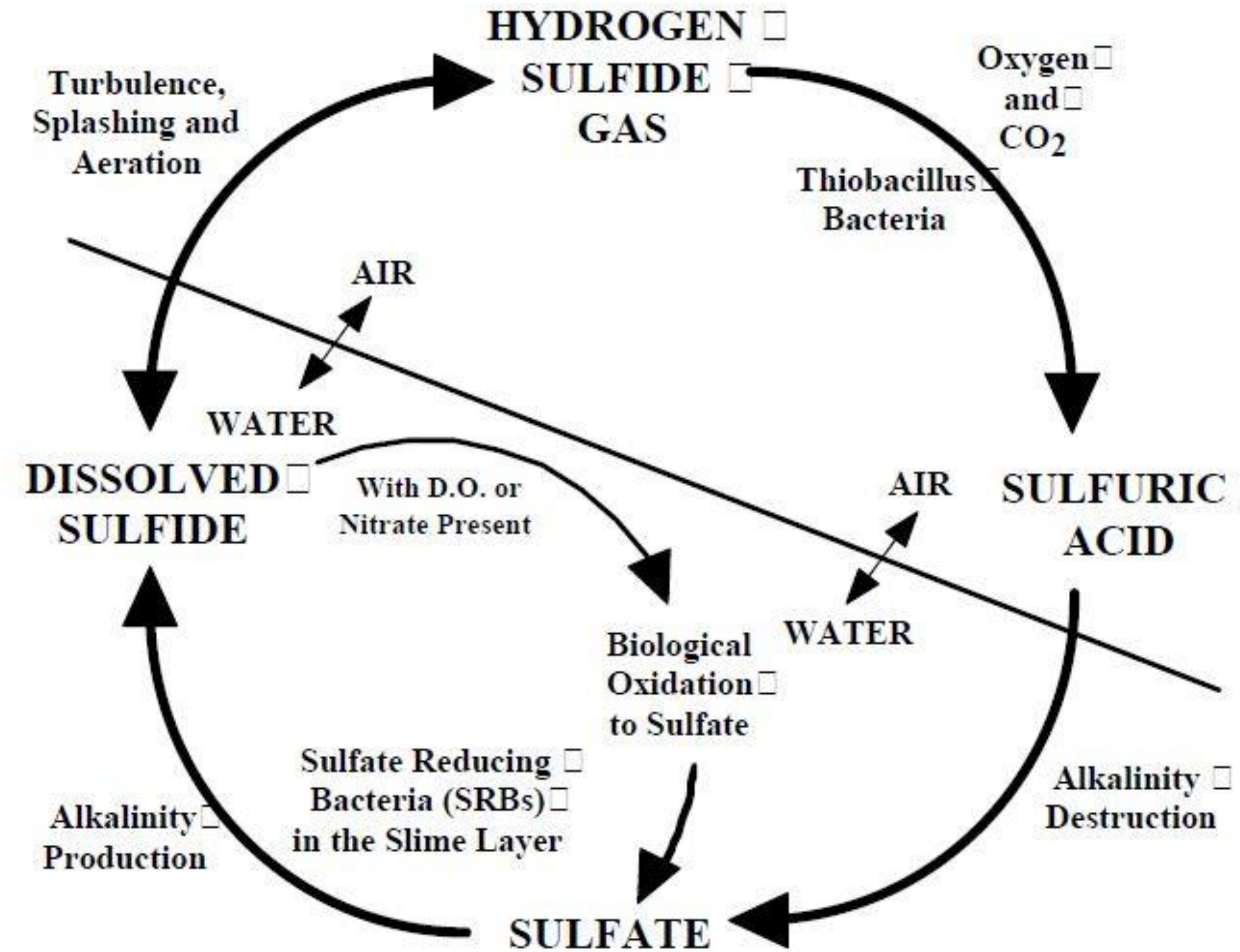


Figure 2-7. The Sewer Sulfide Cycle.

Minimization of Odors and Corrosion in Collection Systems Phase 1 WERF 2007

Sulfide types

Sulfide equilibrium equation, H_2S (g) $\rightleftharpoons$ H_2S (aq) $\rightleftharpoons$ HS^- $\rightleftharpoons$ S^{-2}

1. S^{-2}, sulfide ion, non volatile, does not contribute to odors.
2. HS^-, bisulfide or hydrosulfide ion, can only exist in solution
3. H_2S, hydrogen sulfide, can exist as a gas dissolved in water, can leave water to exist as a free gas. The rate it leaves is governed by Henry's law and is **very dependent upon turbulence and pH**. H2S and corrosion are increased significantly at points or turbulence. When dissolved H_2S is released into the gas phase, the bisulfide ion is immediately transformed into more aqueous H_2S to replace what was lost.

Sulfuric acid is produced by *thiobacillus* bacteria that colonize on the crown of pipes, walls and other surfaces above the water line in wastewater pipes and structures occurs when the air H2S is >2 ppm. Simplified equation, H_2S (g) + $2O_2 \rightarrow H_2SO_4$. The effects on concrete can be devastating. This only occurs under aerobic conditions.

H2S Prevention

1. Preventing the 1st pathway, sulfate to sulfide is difficult, it can be done by pigging to scrape off the soft biological slime layer, using anthroquinone (metabolic inhibitor) and caustic slugs. The slime layer grows back in 3 – 10 days depending on temperature and BOD.

2. Interrupting the 2nd pathway is the most common using chemicals and liquid phase options. Oxygen injection, chemical addition using nitrates, iron salts, peroxide, potassium permanganate and chlorine. Using ferric chloride and ferric sulfate can provide more efficiency. Design drop structures and manholes with drop pipes to reduce turbulence. Discharge force mains below a body of water. Strip the H_2S in a location where facilities have been designed to handle the conditions.

H2S Prevention Continued

3. Interrupting the 3rd pathway, preventing sulfuric acid formation, by surcharging sewers, crown spraying and ventilation.
    - Surcharging sewers “crown cutting” or “crow corrosion” can occur from entrapped air bubbles in the flow that coalesce on the pipe crown in a place where bubbles can remain stationary against hydraulic forces at a high spot or at a joint in reinforced concrete pipe.
    - Ventilation will never be able to stop corrosion, it will help to remove moisture and H2S. Ventilation needs to be done with other measures to be effective.

4. Interrupting the 4th pathway by protecting corrosion prone surfaces.
    - Usage of plastics/glass (PVC, HDPE, PP, PE, Fiberglass and Fiber Reinforced Plastics).
    - Coatings on concrete is the most common, mostly epoxies and resins are used, cast-in-place liners for new concrete pipe and rehabilitation of pipes.

H2S Effect on Concrete

Table 9-1. Concrete Pipeline Corrosion Rates.

	Corrosion Rate, in./yr	
H_2S Concentration, ppm	In Cast Pipe	In Spun Pipe
<1	<0.03	<0.02
1–3	0.03–0.05	0.02–0.03
3–8	0.05–0.08	0.03–0.05
>8	>0.08	>0.05

Minimization of Odors and Corrosion in Collection Systems Phase 1 WERF 2007