



*Metropolitan Water Reclamation District of Greater Chicago
Protecting Our Water Environment*

Odors and Corrosion in Metropolitan Water Reclamation District of Greater Chicago's Sewer Interceptors

**Diurnal and Daily Fluctuations, and the Benefit of
Calcium Nitrate Addition**



***METROPOLITAN WATER RECLAMATION DISTRICT OF
GREATER CHICAGO***

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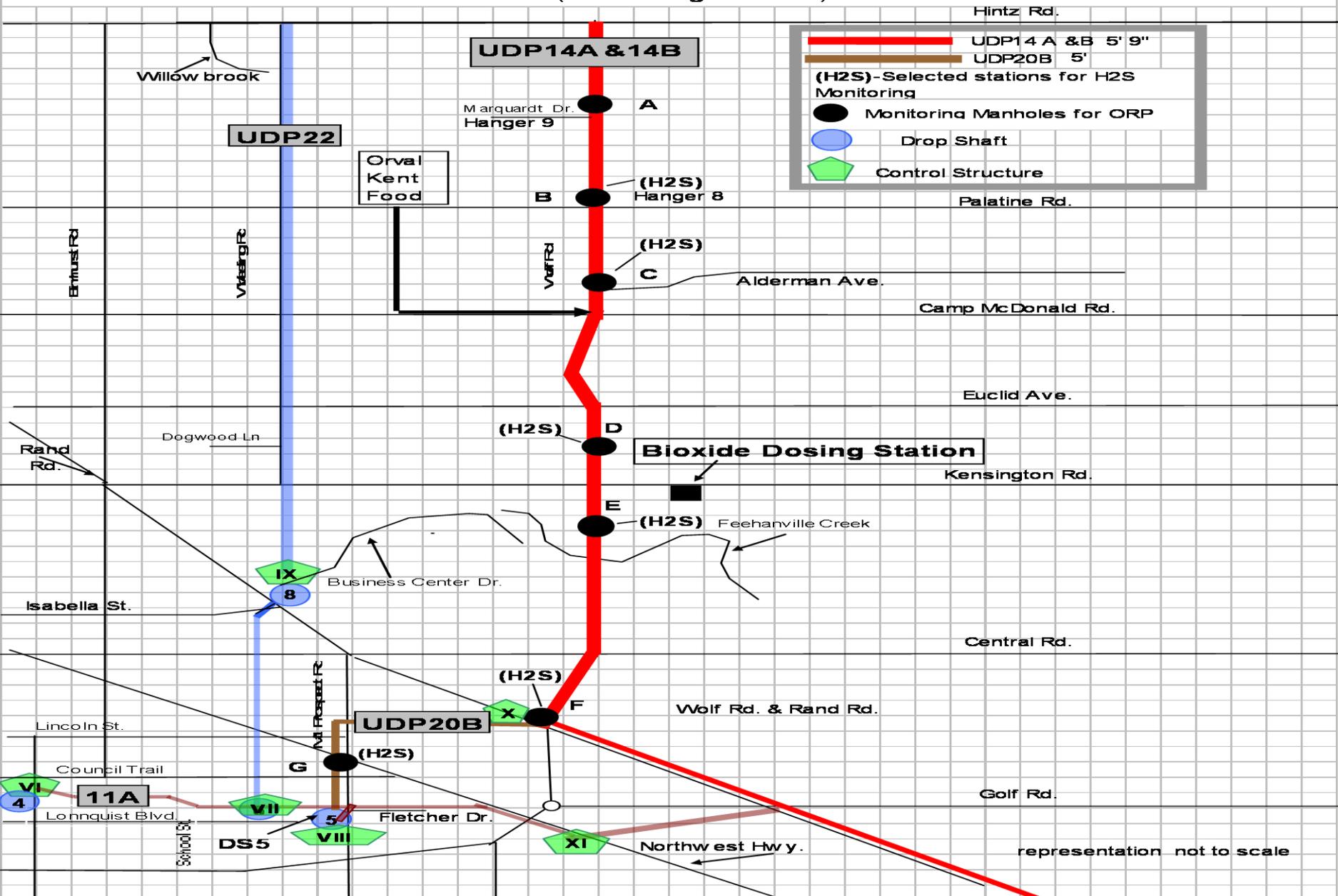
Monitoring and Research Seminar

Why Was The study Initiated?

● **Two main Reasons:**

- Odor issues in the community adjacent to one of the District's Dropshafts
- District's Concern on Corrosion in sewer conduits (interceptors) leading to this Dropshaft

FIGURE 1
 Odor Management and Corrosion Control in select interceptors in the the Kirie Water Reclamation Plant Service Area
 (Monitoring Stations)



Objectives

- TO EVALUATE THE POTENTIAL FOR GENERATION OF H₂S ALONG THE UDP INTERCEPTORS (5 miles of interceptor - conduit diameter of about 5' - mild slope 0.0003 with flow rates ranging from 4-10 MGD)
- To determine the hot spots for H₂S along the UDP 14A & B and UDP 20B, and to Investigate the reason/s for elevated H₂S level at specific location/s
- To find an optimal calcium nitrate (Bioxide) dosage to control the odors and reduce the progression of corrosion
- To curtail the monitoring efforts by developing a reasonable mathematical model to predict the extent of corrosion

Mechanism of Hydrogen Sulfide generation

- Sulfide generation occurs only in the submerged portion of sanitary sewers
- Domestic sewers usually are devoid of sulfides (reduced sulfate), but biological activity quickly kicks off and produces sulfides
- High BOD, High sulfate, Elevated Temperature, High Detention Time, Low DO are few important indicators for septic conditions (presence of sulfides) in a sewer system.

Mechanism of H₂S Generation- (continued)

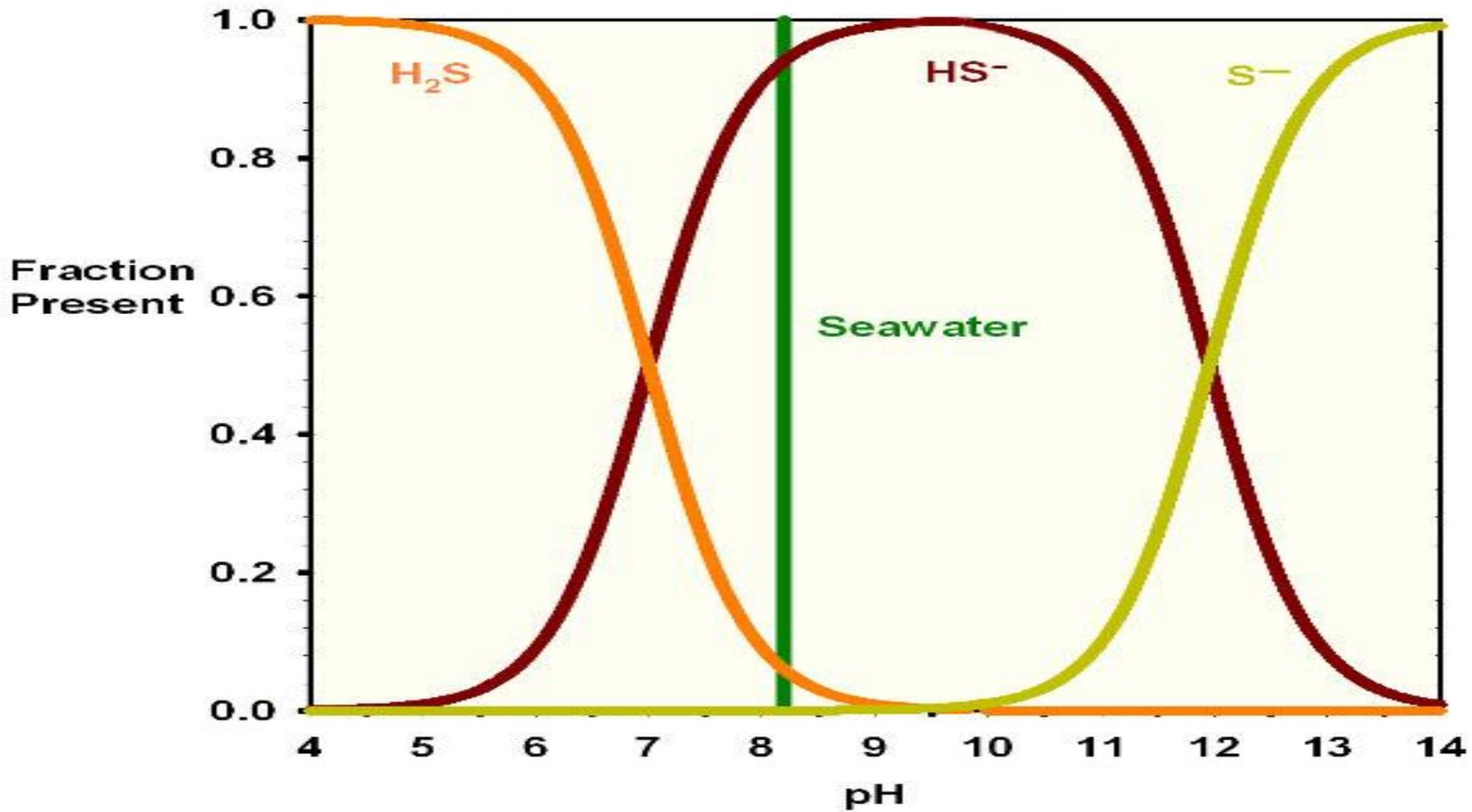
- **Thickened Slime Layer (3 layers)**
 - **Anaerobic, Anoxic and Aerobic layers**
- **Sulfate** (SO₄²⁻) Diffuses to the anoxic zone and utilized by facultative bacteria. It then converted to **sulfide** (S²⁻) and diffuses back to the stream.
- Very little soluble BOD (food) can penetrate all the way to the anaerobic zone (so: **no sulfide generation in this zone**)

Mechanism of H₂S Generation- (Continued)

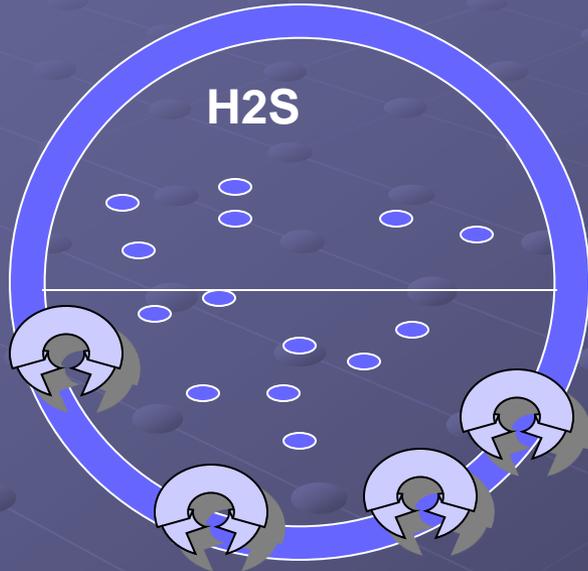
- How the equilibrium is achieved for Sulfate Reduction?
 - Once dissolved sulfide is released into gas phase, bisulfide (HS⁻) is immediately converted to aqueous H₂S to replace the lost gas phase H₂S.
 - Concurrently, S²⁻ is transformed into bisulfide to replace that lost to aqueous H₂S. The equilibrium shift is very rapid, and sensitive to pH.



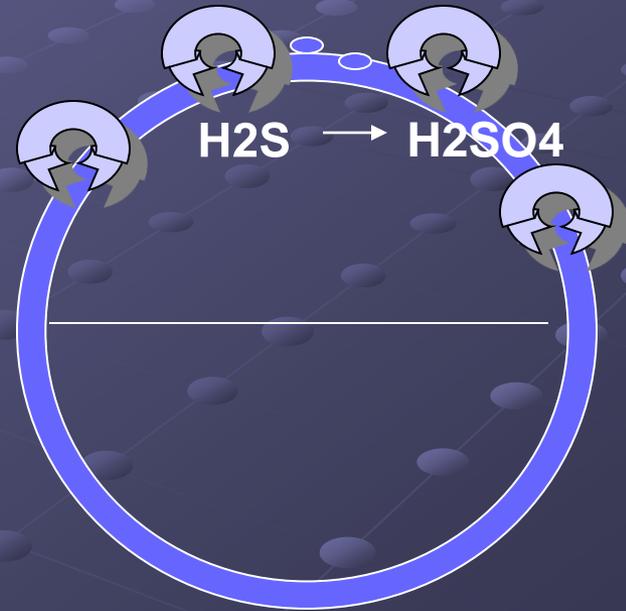
Sulfide Speciation



First Stage: Sulfide Production
By Sulfate Reducing Bacteria
(Desulfobacter/Desulfovibrio)



Second Stage: Sulfate Production
Sulfur Oxidizing Bacteria
(Thiobacillus thiooxidans or
Thiobacillus Concretivorous)



Mechanism of Calcium Nitrate Odor Mitigation by Chemical Reaction

● Prevention:

- Uses oxygen-source substitution to prevent formation of dissolved sulfide.

● BOD is utilized by microorganisms in the presence of sulfate, and dissolved sulfide is produced. If Nitrate is added to wastewater-anoxic denitrification proceeds, and N₂ will be produced NOT Sulfides.



Mechanism of Calcium Nitrate Odor Mitigation (continued)

● Removal:

- Biochemically oxidizing dissolved sulfide in the presence of nitrate



This reaction does not prevent sulfide production in the slime layer. But is intended to oxidize the sulfide via the above reaction.

Why **Nitrate** is Preferred over **Sulfate** By Microorganisms

- Thermodynamically, the microbial reduction of nitrate to nitrite, nitrogen or ammonia provides more Gibbs free energy than the Reduction of Sulfate
 - So nitrate can be a preferred electron acceptor when both anions were potentially available
- Addition of Nitrate leads to the buildup of nitrous oxide which raises the redox potential contributing to long term prevention of sulfide production

Sampling Procedure

- 7 stations along the interceptors were sampled once in the morning, and once in the afternoon for 3 weeks, and were analyzed for wastewater quality parameters
- The samples downstream from calcium nitrate dosing station (station E) were taken before and after injection of the compound.
- Some water quality parameters were measured on-site, and another samples were taken to analytical laboratory for further analysis.

Sampling Procedure (Continued)

- Depth of Flow was measured with a telescopic measuring stick at each location
- Odalogs were installed at a close distance to the water surface to measure the headspace hydrogen sulfide at the interceptors.

Parameters Measured

- HeadSpace H₂S (Odialog)
- pH
- ORP (Redox Potential)
- DO
- Wastewater Temperature
- BOD₅
- TSS
- VSS
- Depth of Water (For Flow Rate calculations)
- Total Sulfide
- Dissolved Sulfide

2-Sep	Calcium Nitrate On						
Monitoring Location	Time	ORP (mv)	Tsulfide (mg/L)	Dsulfide (mg/L)	BOD5 (mg/L)	TSS (mg/L)	Temp (F)
UDP-14 A	9:00 AM	-138	1.74	0.91	210	179	nd
	1:15 PM	-65	0.74	0.17	223	279	nd
UDP-14 B	8:40 AM	-131	1.98	0.95	153	258	70.5
	1:05 PM	-118	1.45	0.71	216	354	70.7
UDP-14 C	8:25 AM	-77	1.05	0.49	305	313	70.5
	12:50 PM	-90	4	0.01	526	483	70.7
UDP-14 D	9:15 AM	-122	2.04	1.53	245	362	nd
	1:35 PM	-123	4.6	0.32	718	321	nd
UDP-14 E	9:30 AM	-110	0.99	0.45	261	163	65.4
	1:45 PM	-104	2.38	0.76	523	354	65.6
UDP-14 F	9:50 AM	-58	0.26	0.1	184	212	64.9
	2:05 PM	-104	2.32	0.74	311	762	65.1
UDP-14 G	8:00 AM	-62	0.43	0.27	153	122	64.7
	12:30 PM	-110	1.54	0.61	373	217	64.5

4-Sep	Calcium Nitrate	f (6:AM-6:47PM)					
	OFF						
Monitoring Location	Time	ORP (mv)	Tsulfide (mg/L)	Dsulfide (mg/L)	BOD5 (mg/L)	TSS (mg/L)	Temp (F)
UDP-14 A	9:10 AM	-125	0.74	0.2	293	550	nd
	1:20 PM	-110	1.29	0.51	260	512	nd
UDP-14 B	8:55 AM	-124	0.36	0.22	419	958	70.8
	1:05 PM	-124	2.28	0.89	302	521	71
UDP-14 C	8:40 AM	-106	1.86	1.42	505	271	71
	12:55 PM	-102	1.54	0.45	480	525	70.7
UDP-14 D	9:25 AM	-136	2.62	2.14	482	258	nd
	1:25 PM	-112	2.62	1.28	371	442	nd
UDP-14 E	9:40 AM	-134	2.18	0.84	302	212	65.8
	1:45 PM	-110	1.96	0.44	314	483	66.2
UDP-14 F	9:50 AM	-113	1.44	0.84	240	329	64.9
	2:05 PM	-108	2.26	0.31	499	425	64.9
UDP-14 G	8:05 AM	-80	5.3	0.98	226	192	65.3
	12:30 PM	-122	4.5	1.2	422	504	66

Summary of Statistical Analysis

Mean H₂S, ppmv

Calcium Nitrate Off

Calcium Nitrate On

P

E	0.3	0.6	0.3278
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F	4.1	0.8	0.0021
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G	4.1	1.3	0.0963
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Statistical Analysis- (Continued)

Mean ORP (mV)

	Calcium Nitrate OFF	Calcium Nitrate ON	P
E	-105.1	-73.2	0.0031
F	-109.6	-67.2	<0.0001
G	-104.1	-76.3	0.0058

ANOVA

Dependency of Total Sulfide on Other

Variables

Type I SS

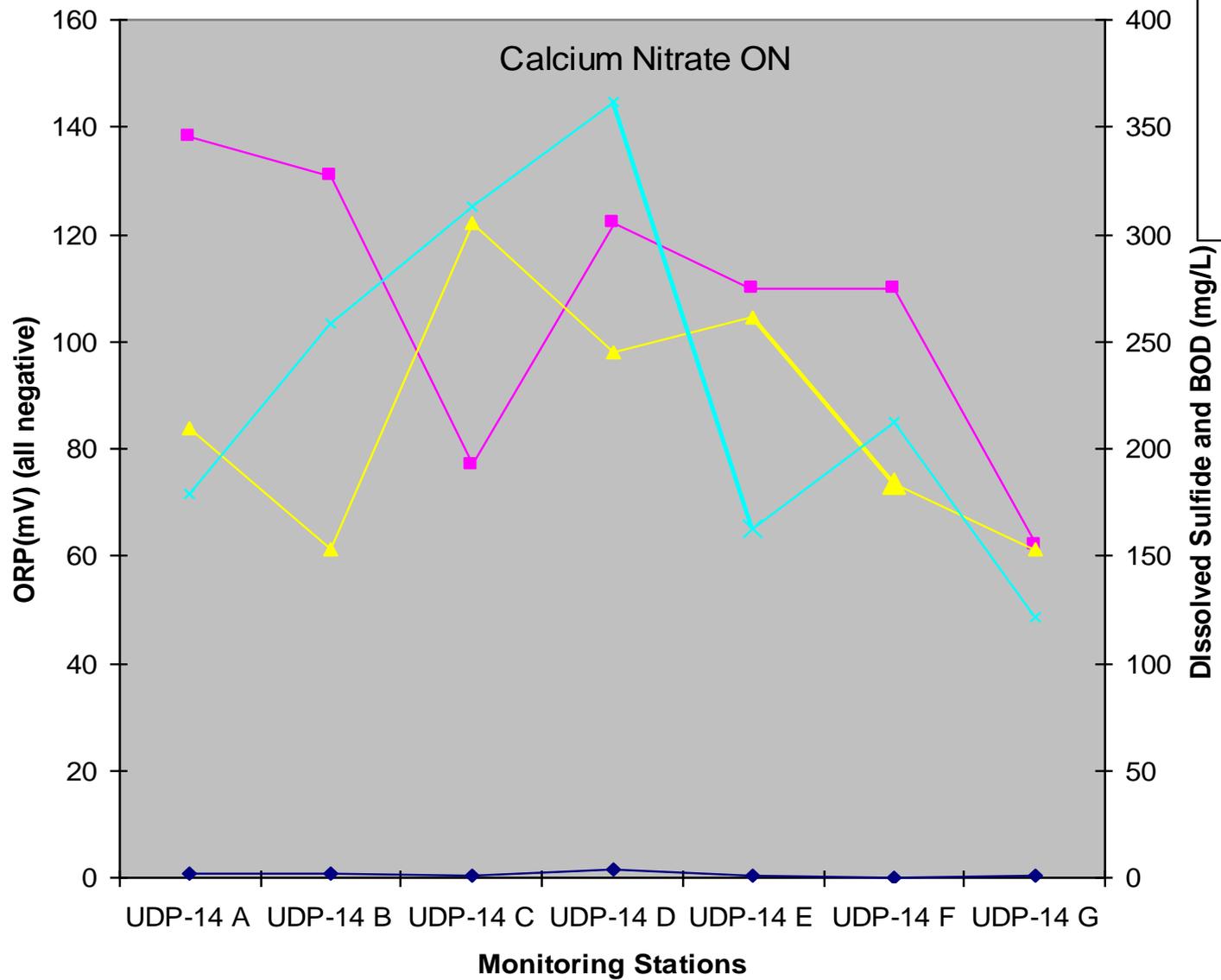
	DF	SS	MS	F value	pr>F
Flow	1	0.892	0.892	1.58	0.2142
BOD5	1	7.422	7.422	13.17	0.0007
Time	1	0.116	0.116	0.21	0.6515
Calcium Nitrate	1	4.335	4.335	7.69	0.0077

Change in BOD

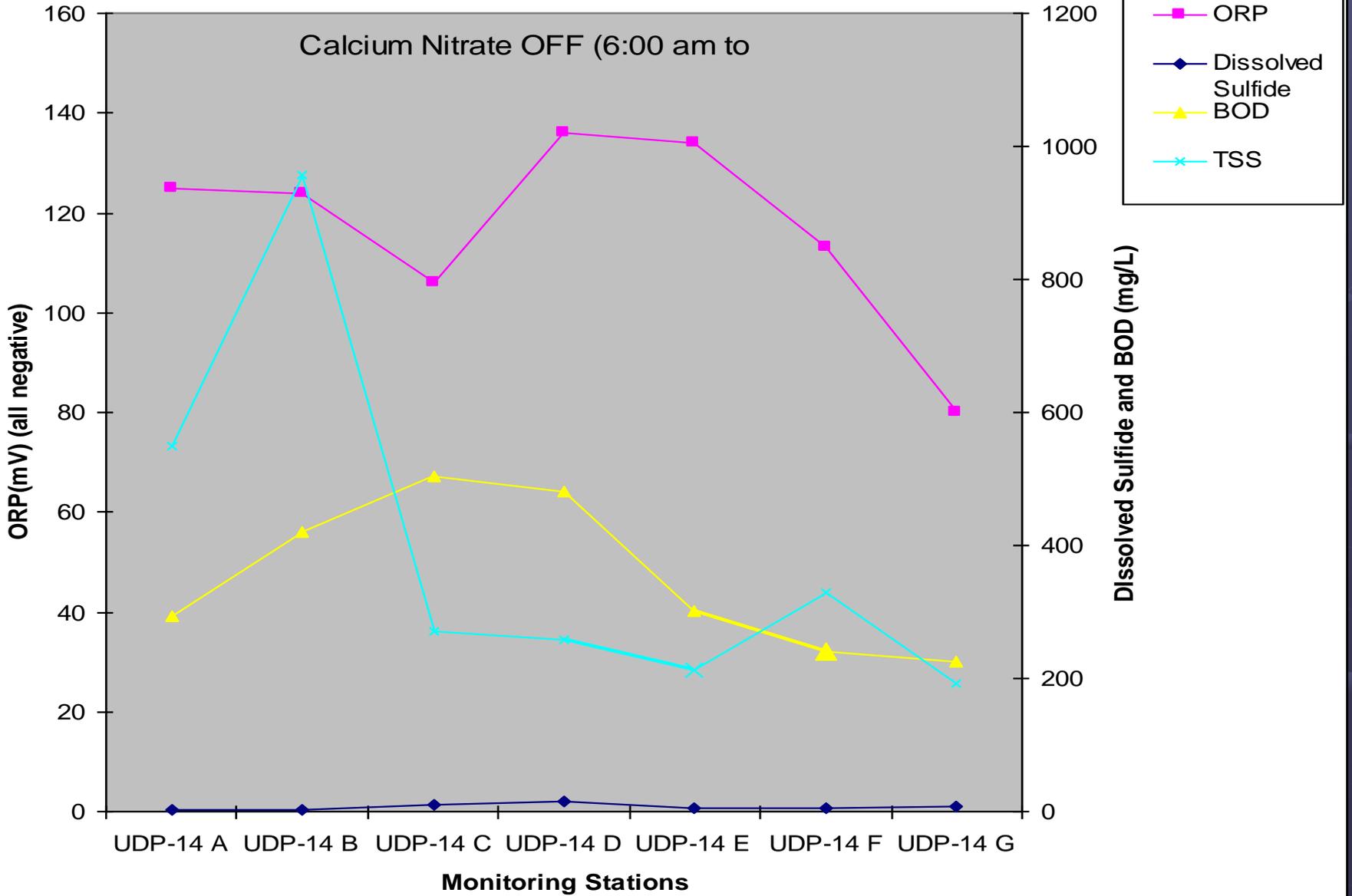
Morning Versus Afternoon sampling

Mean BOD, mg/L

	AM	PM	P
A	241.2	134.4	0.7331
B	242.2	242.0	0.9919
C	353.2	452.3	0.0853
D	312.4	455.4	0.0153
E	248.4	368.9	0.0092
F	249.0	358.2	0.0159
G	328.2	291.2	0.6300

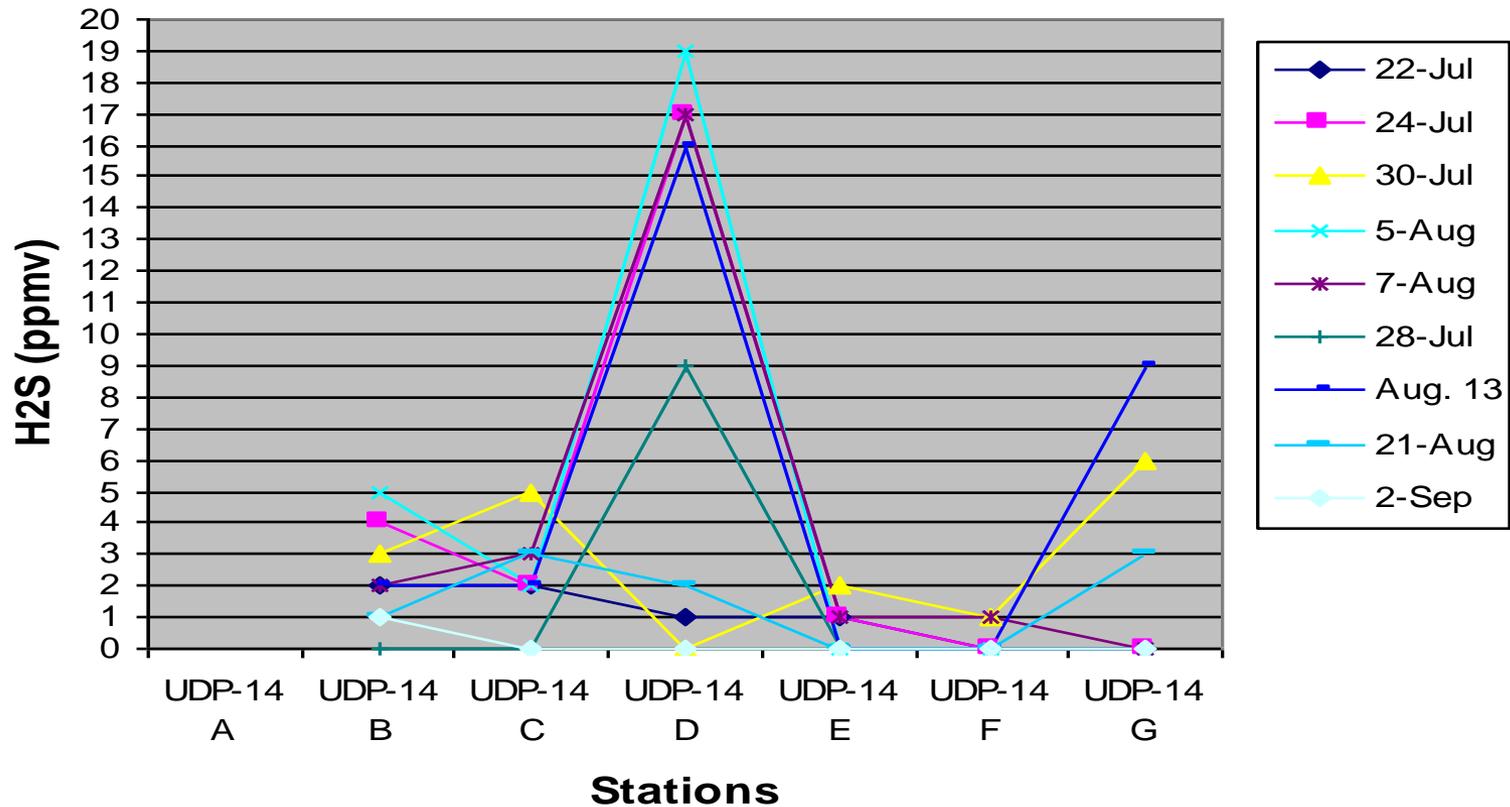


Calcium Nitrate OFF (6:00 am to



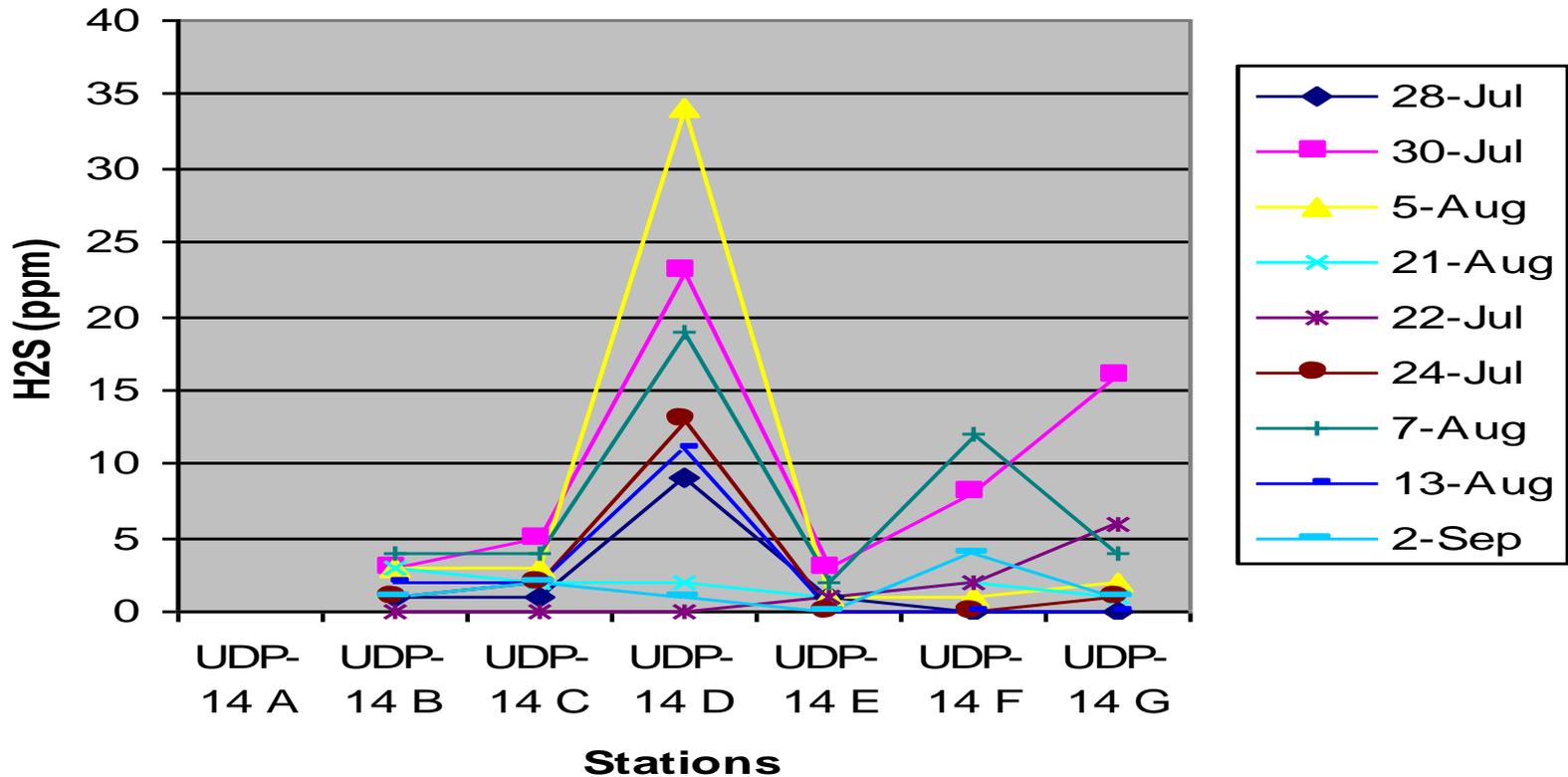
Headspace H₂S at Station D Morning Sampling

Headspace H₂S along the interceptors-Morning
With Calcium Nitrate Injection



Headspace H₂S at Station D Afternoon sampling

Headspace H₂S along the interceptors-Afternoon
With Calcium Nitrate Injection



Summary Results

- H₂S level on average was above **3 ppmv** (potential for corrosion based on **WERF** study)
- ORP level on average was lower than **-50 mV** in many stations (**WERF report** - potential for a reduced environment condition – The system is ready to emit H₂S)
- Strong correlation between the **BOD₅** and **H₂S** level in the interceptors

Summary of Findings

- Odalog data showed that in general the headspace H_2S was higher than **3ppm** in many cases (with and without calcium nitrate), and this is an indication of potential for corrosion.
- The calcium nitrate injection at the present rate (250 gallons/day) **improved the ORP by 20 to 40%**, but this reduction was not sufficient to eliminate the reducing condition in the sewer line (ORP did not fall below **-50mV**)

Calcium Nitrate Effect on H₂S Level

- On average H₂S level was reduced by 30%
- The effect of calcium nitrate solution beyond station F was not clear. Very High Levels of H₂S still persisted in DS5 where UDP 14A and B are leading to, even after calcium nitrate solution injection.

Acknowledgment

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