

Accelerated Corrosion of UST Equipment (an ethanol hangover) Inspection Concern to Professional Research

Steve Pollock
EPA Biofuels Series
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**Virginia Department of
Environmental Quality**



An everyday inspection

E-mail to Co-workers

Wed 12/17/2008 4:30 PM – I ran across this mess in a sump today. I've seen similar messes, but this was just a little different. [The environmental consultant I was with] had never seen anything like it either. Kind of mounded, with recently active looking bubbles (Hydrogen gas?) on top. Sort of like the sulfur reducing bacteria crud we sometimes find, but somehow a little more pillowy. [The consultant] knocked it around a little, and I was waiting for the whoosh of rotten egg smell. Instead, it was a **vinegar smell – acetic acid**. Maybe in the presence of E-10, our native soil/water bacteria now prefer to chomp on the ethanol first as Acetobacters or just opportunistic bacteria loving an easier chain (the alcohol) to digest, creating acetic acid. You know, like wine going bad. Or, in the presence of E-10, these are the first bacteria to feast at the buffet, then the vultures, then the oil metabolizers.

Anyway, the acetic acid, bacteria and some funky mold (or yeast?) is tearing up the steel, too. Also note that supposedly the **line leak detector was replaced this past February** ...But if it's new as of Feb '08, it has had a hurting put on it. Oddly, the next door STP sump was also full of water, but not this mess. And it was clear that the LLD had been replaced.





Co-workers' Similar Observations



More than one problem?

Old Familiar Corrosion



Photos prior to E-10; UST's in ground 20 years

Hypothesis

- A new environment primed for biological activity is created
- Acetic acid bacteria use oxygen from the atmosphere to rapidly transform the ethanol to acetic acid:



- **The acetic acid produced by biological degradation of ethanol can facilitate the corrosion of metals.**

Request for Samples

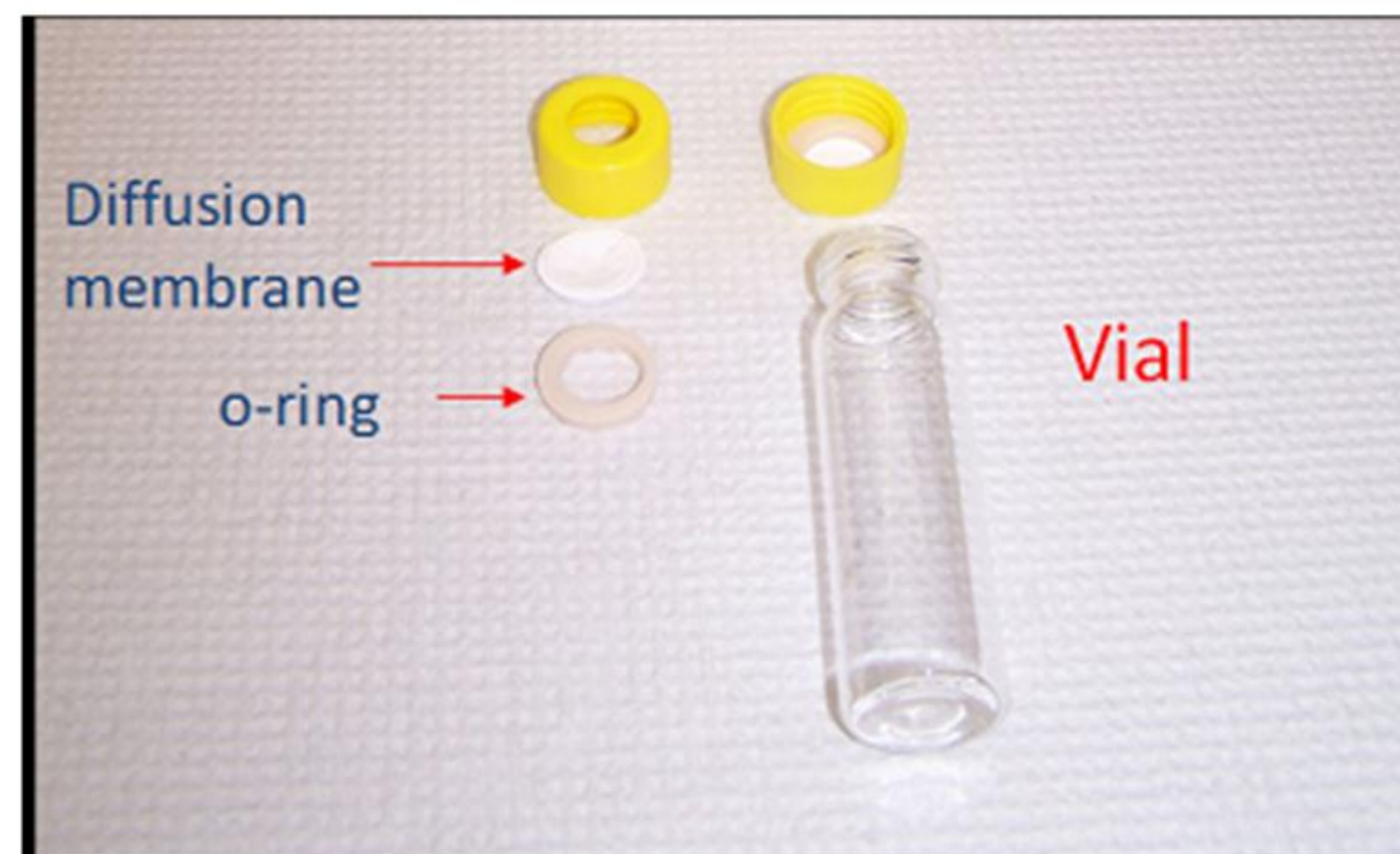
- June 2010: Article asks any inspectors who see this phenomenon to share photos and volunteer their time
- Over the next year, OUST heard back from ~20 inspectors in at least 9 states





Approach

- Volunteers installed **two vapor samplers** under every STP cover at the facility, and left them there for approximately **one month**.



Vapor samplers were 40 mL VOA vials filled with water containing trisodium phosphate (a preservative).

- The vapors enter the sampler by passing through a nylon filter.
- One sampler was kept as a field blank and sent back with the others.
- To test pH of standing water, ORD included pH test strips.
- When possible, a sample of the liquid in the sump was obtained.
- All samples were sent to EPA's Kerr Center in Ada, Oklahoma, for analysis



Photo courtesy: Florida DEP

E10 STP, unknown grade (Florida) – Feb. 2011



Photo courtesy: San Diego County - Dept. of Environmental Health (California)

91 octane STP (California) – August 2010



Photo courtesy: State of Tennessee, TDEC

Premium/E10 STP (Tennessee) – March 2010



Photo courtesy: State of Tennessee, TDEC

Premium/E10 STP (Tennessee) – August 2010

Same sump!



Data

Ample ethanol in vapors
 Water condensing on fixtures
 Ample production of acetic acid
Extensive corrosion

800023 Premium	Sump Water	Vapor Samplers
	(mg/L)	(mg/L)
Ethanol	No Sample	14850
Acetic acid	No Sample	125
Benzene	No Sample	1
Total BTEX	No Sample	21
no standing water, STP 2 years old , pH condensate 5.3		



Data

Minimal ethanol in vapors

Adequate water

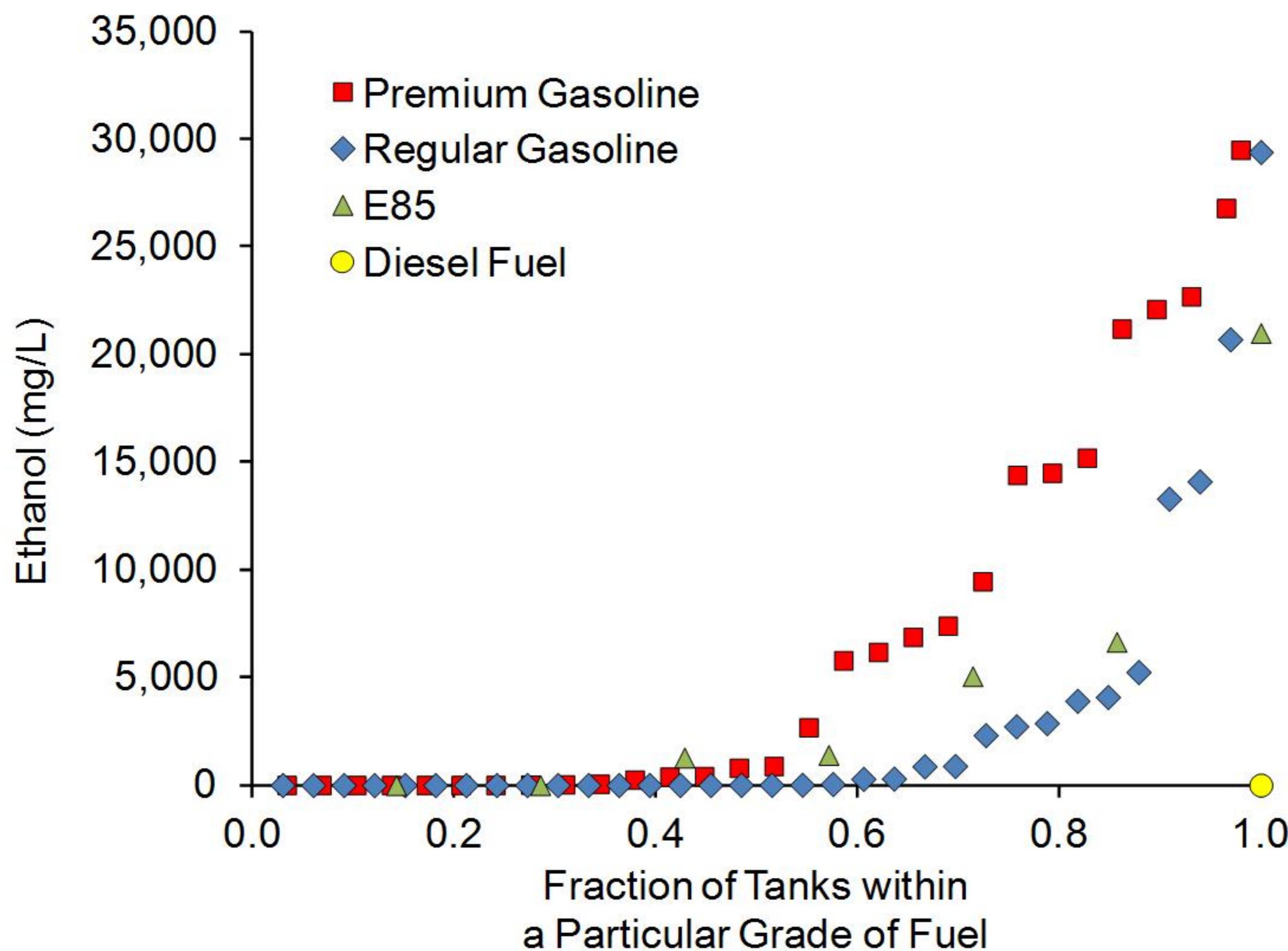
Concentration of acetic acid not above trip blank (0.77 mg/L)

No evidence of corrosion

4-560089 Regular	Sump Water	Vapor Samplers
	(mg/L)	(mg/L)
Ethanol	ND	8.49
Acetate or Acetic acid	0.35	0.99
Benzene	0.09	0.04
Total BTEX	0.98	0.69
19" water, STP 5+ years old , pH 5.3		

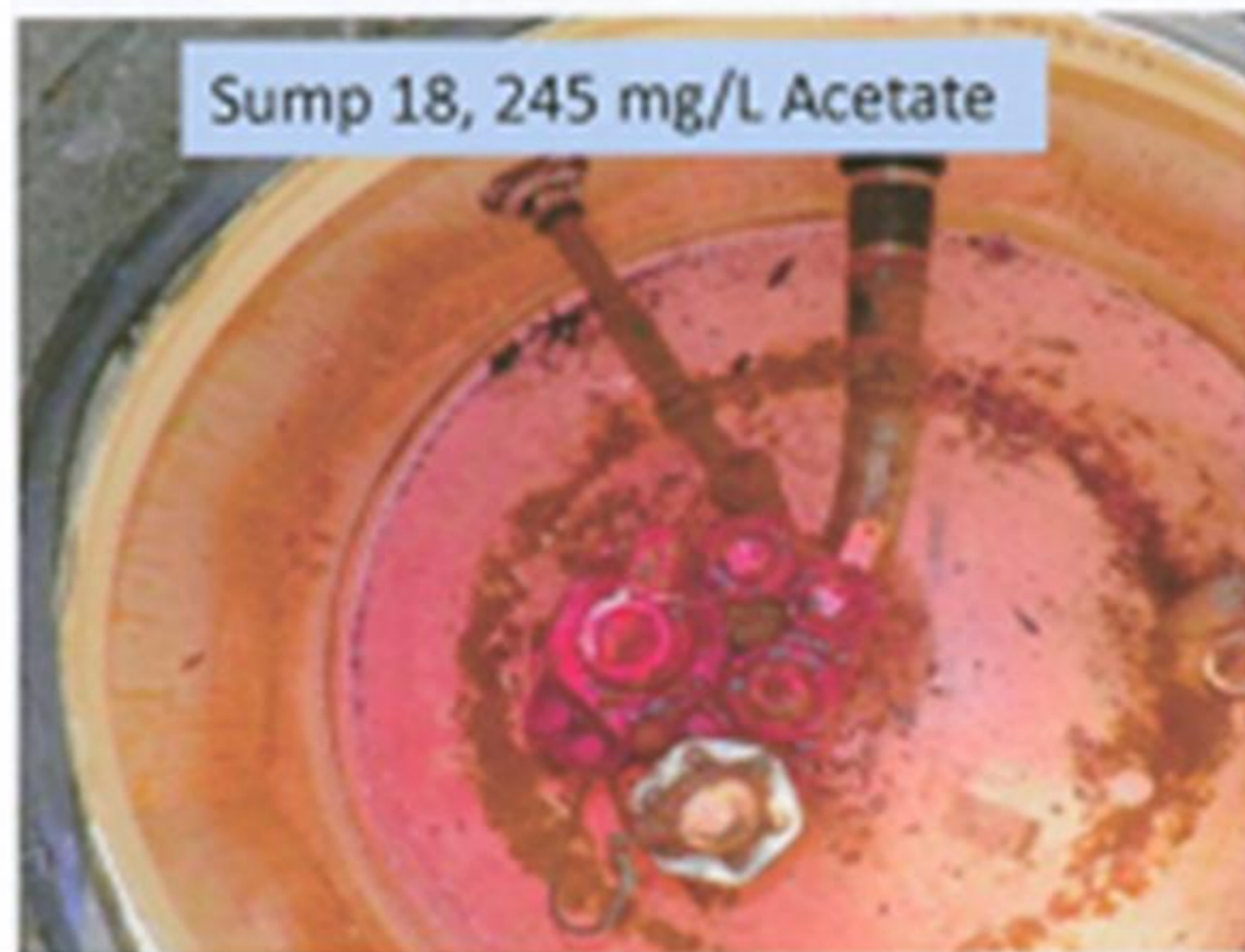
Results

Concentration of ethanol in vapor samplers



- Many sumps had high concentrations of ethanol
- Once the presence of ethanol in the vapor was established, ORD measured acetic acid (in the form of acetate)
- ***New graphs soon!***

Results

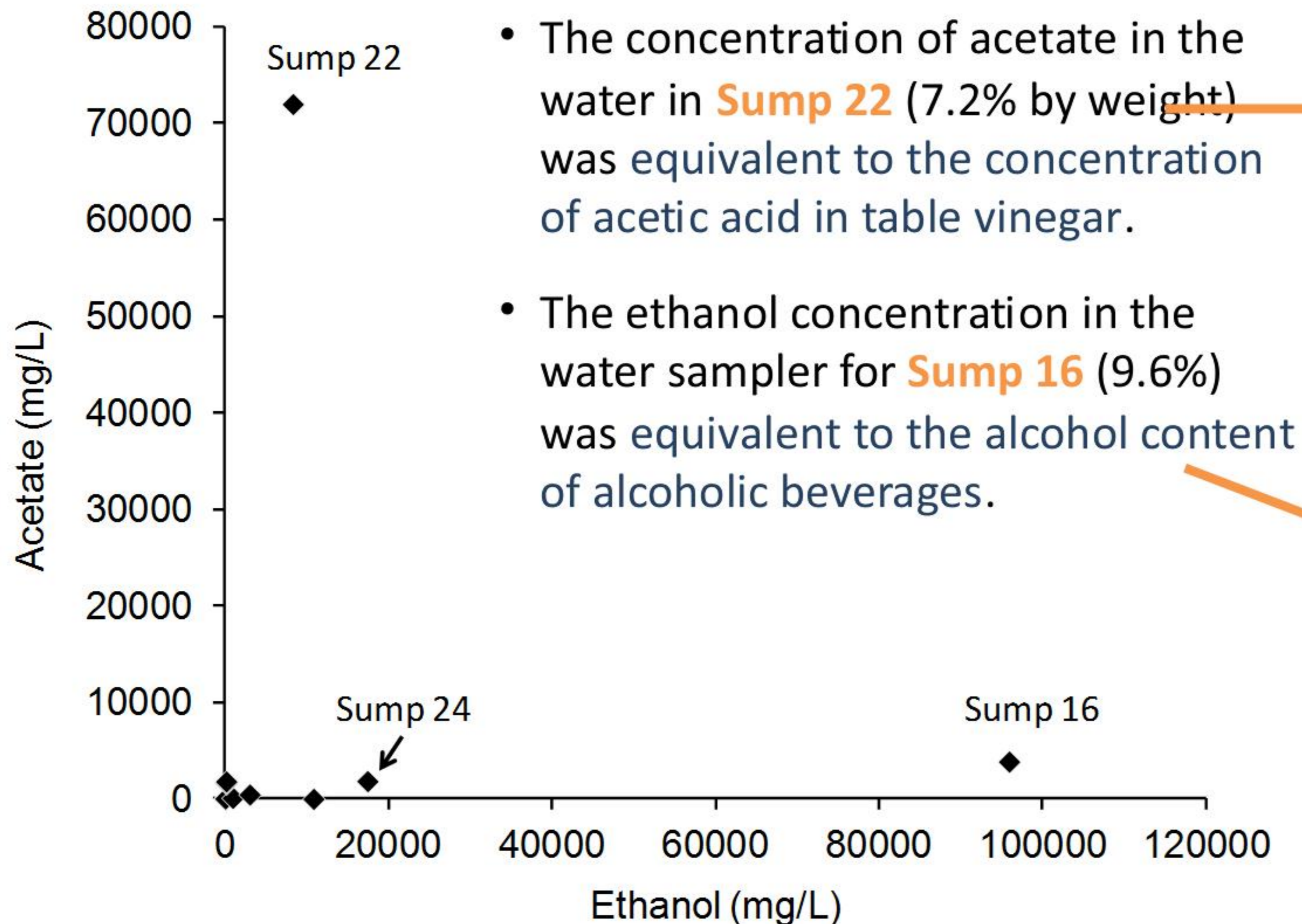


In general, there was more observable corrosion in sumps with high and intermediate concentrations of acetate measured in the vapor samplers.

Results

Concentration of ethanol in sump water

Water in 3 sumps had very high concentrations of either ethanol or acetate. Sumps 22 and 16 are particularly notable because:



Results

Chemical analysis of corrosion products



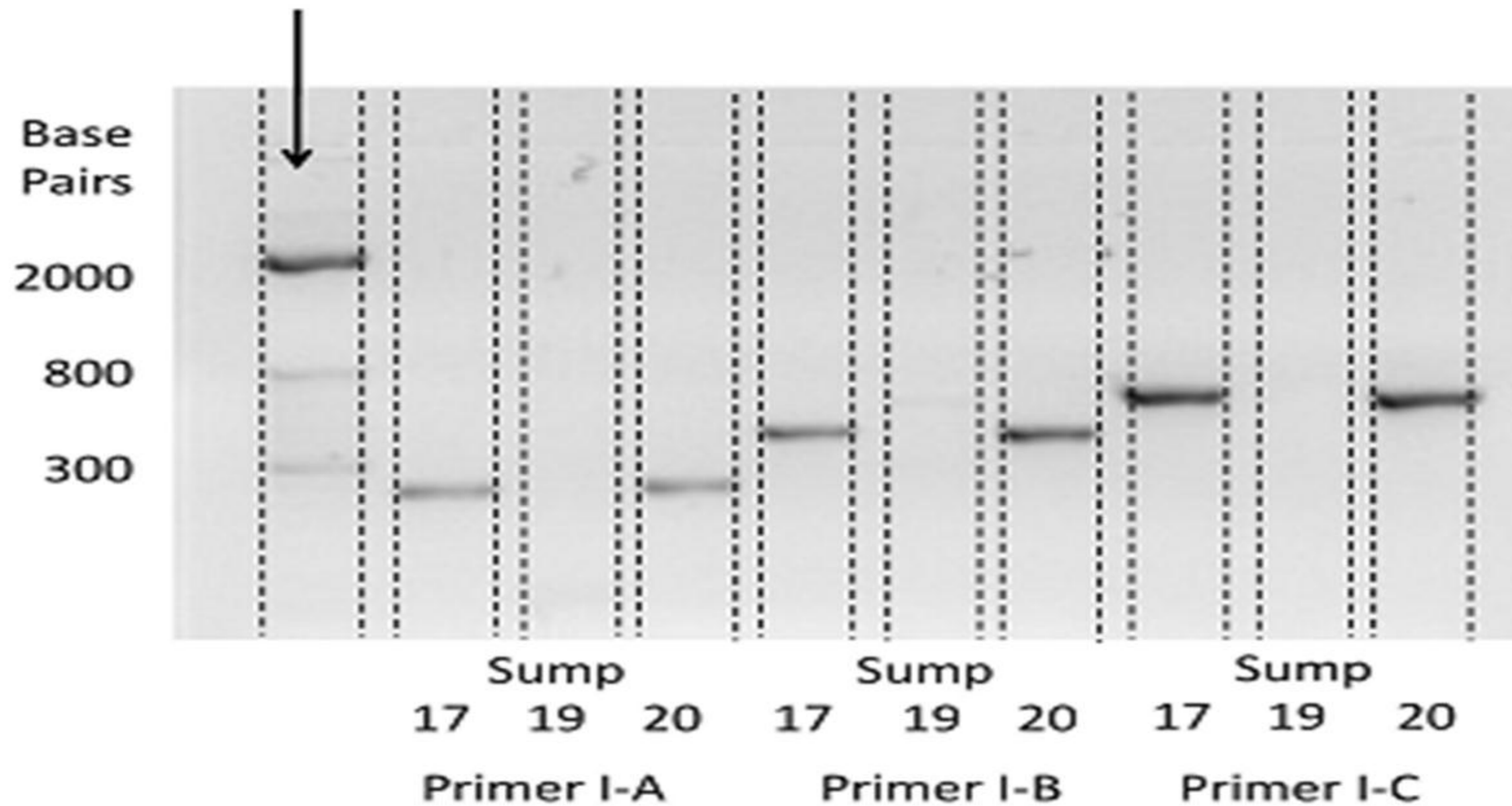
As expected, the red-brown corrosion were iron oxides (rust).

Most of the blue-green corrosion product was copper and acetate.

Results

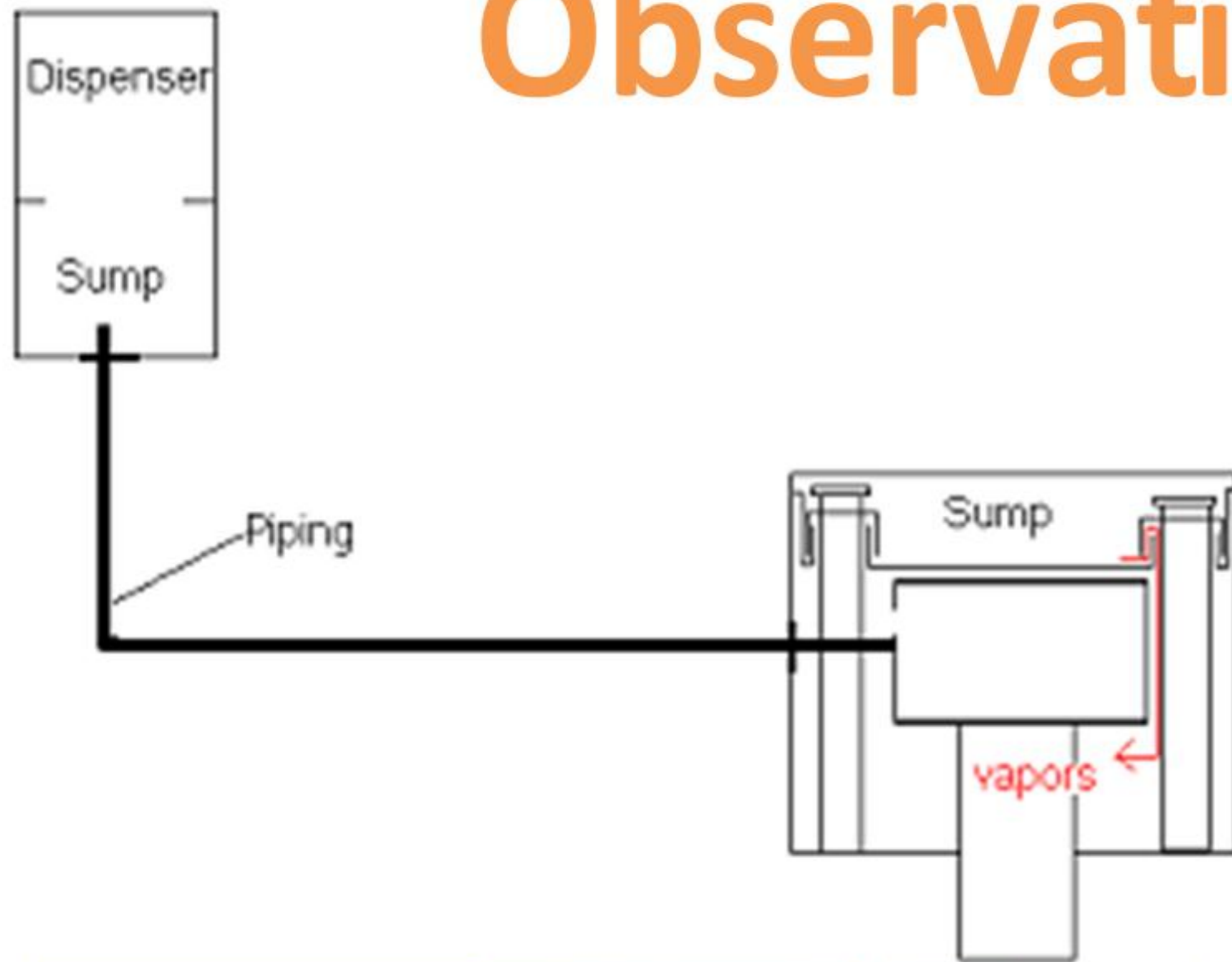
Acetobacter DNA in sump water

DNA to Calibrate the Gel



Sump #	17	19	20
Conc. Acetate	225 mg/L	<0.1 mg/L	30 mg/L
DNA detected?	Yes	No	Yes

Observations from TN



Certain “all-in-one sumps” do not allow vapors to escape and were more likely to have high ethanol vapor concentrations and therefore experience corrosion.

June 2008



November 2010



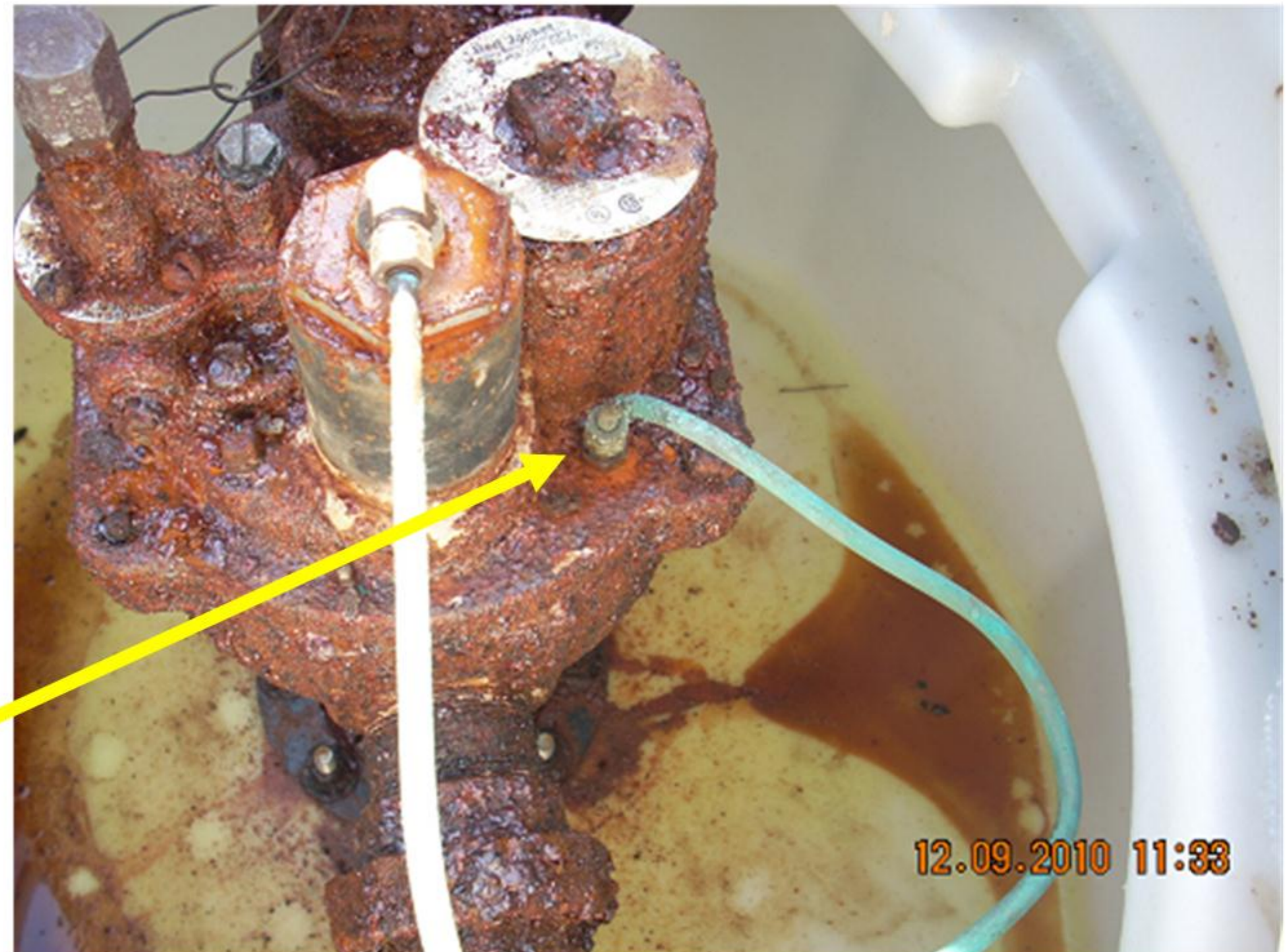
Observations from TN

Fuel can enter the sump from spills; however, there may be other pathways.

TN used an infrared detector to see if there was a detectable vapor leak.



They found a vapor leak here



Stage II

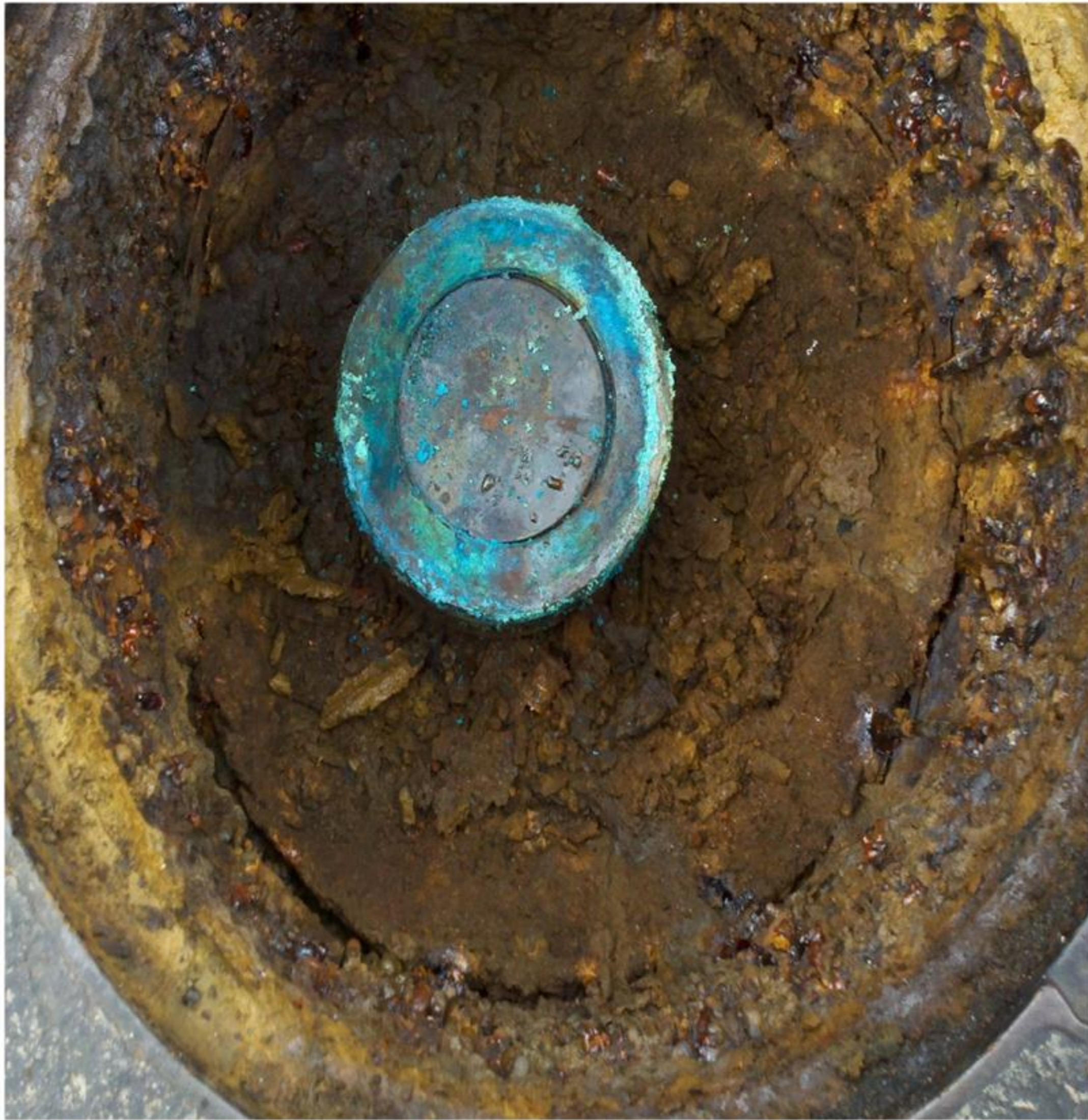


Same Tank Field, Healy
system on left

Fill Risers



Other Risers



Vent Pipes



Real Reason



Summary

- The accelerated corrosion in STP sumps may be explained by biological degradation of fugitive ethanol in vapors to acetic acid in the presence of water
- Take pictures and share with cohorts
- Interact with contractors and testers
- All experience counts

Next Steps (cure the hangover)

- Hair of the Dog
 - E15
- Power through it
 - EPA is working with industry groups to look into this issue, and will consider recommendations or best practices.

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Zhanbei Liang

NRC Postdoctoral Associate, Ada, OK

Edward Fowler

Tennessee Department of Environment & Conservation, Cookeville, TN

Randall Strauss

Pinellas County Health Department, Clearwater, FL

Kathryn West

Florida Department of Environmental Protection, Orlando, FL

John Hickey

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Richard Hansen

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Edwin French

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Erik Humlie

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Joe Owens

Alachua County EPD, Gainesville, FL