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Final Report

Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD), Hypotheses Investigation

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ACRONYMS AND ABBREVIATIONS

ASTM	ASTM International
ATG	automatic tank gauging
bp	base pair
CDFA	Clean Diesel Fuel Alliance
DNA	deoxyribonucleic acid
EPA	U.S. Environmental Protection Agency
GC-MS	gas chromatography-mass spectrometry
IC	ion chromatography
ICP-MS	inductively-coupled plasma mass spectrometry
LSD	low sulfur diesel
MIC	microbial influenced corrosion
NCH	Nationwide Children's Hospital
PCR	polymerase chain reaction
PEI	Petroleum Equipment Institute
ppm	parts per million
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
SOP	standard operating procedure
STI	Steel Tank Institute
STP	submersible turbine pump
TAN	total acid number
taxID	taxonomic identification
ULSD	ultra low sulfur diesel
UST	underground storage tank
UV	ultraviolet
WGA	whole genome amplification
XRD	x-ray diffraction
XRF	x-ray fluorescence

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Executive Summary

Severe and rapid corrosion has been observed in systems storing and dispensing ultra low sulfur diesel (ULSD) since 2007. In addition, the corrosion is coating the majority of metallic equipment in both the wetted and unwetted portions of ULSD underground storage tanks (USTs). To investigate the problem in an objective manner, multiple stakeholders in the diesel industry, through the Clean Diesel Fuel Alliance, funded this research project. The design included the identification of retail fueling sites and the development of an inspection and sampling protocol to ensure uniform and thorough inspections of USTs. Fuel, water bottoms, vapor, bottom sediments, and scrape samples were taken from six sites: one that was not supposed to have symptoms (but did to a much lesser degree) and five that were to have the severe corrosion. Then, samples from the inspections were analyzed for genetic material and chemical characteristics. These data, in combination with information on additives, have allowed Battelle to draw conclusions with respect to three working hypotheses.

Specifically, the hypotheses are:

1) Aerobic and anaerobic microbes are producing by-products that are establishing a corrosive environment in ULSD systems;
2) Aggressive chemical specie(s) (e.g., acetic acid) present in ULSD systems is(are) facilitating aggressive corrosion; and
3) Additives in the fuel are contributing to the corrosive environment in ULSD systems.

All of the sites inspected contained microbes, although at different abundances. The dominant organism identified from three of the sites, *Acetobacter*, has characteristics pertinent to the corrosion observed in all of the sites, such as acetic acid production, ethanol utilization, low pH requirements, and oxygen. Although geographically on opposite sides of the country, from different fuel suppliers, and of relatively new construction materials, the presence of the organisms was relatively uniform. The traditionally expected hydrocarbon degrading organisms were found in insignificant abundances. This indicates that the inspected ULSD USTs are selective environments for these specialized, acetic acid producing organisms.

Of note from the chemical analyses is that acetic acid was found to be ubiquitous (water bottoms, fuel, vapor, and scrapings) in all of the sites inspected. In addition, ethanol was unexpectedly identified and measured at five of the six sites. Components necessary for the organisms identified to proliferate were analytically determined to be present in the majority of the samples: trace amounts of ethanol, low pH, oxygen, and water were present in the diesel USTs inspected. Finally, although additives could play a role in the corrosive environment, it is unlikely that they are the primary cause of the observed corrosion.

This project was designed to objectively investigate multiple hypotheses as to why ULSD USTs have been experiencing severe and rapid corrosion. The in-depth site inspections were performed on a limited number of sites and therefore may not be representative all of systems experiencing this phenomenon. Although it cannot be stated with statistical significance, ingredients necessary for the observed and chemically determined corrosion in this environment were present at the inspected sites. The most obvious issues causing this problem were the focus of this research and the development of corrosion at different sites could also be influenced by other factors (environmental, geographical, seasonal, etc.) not discussed in this report.

The project final hypothesis for this investigation is that corrosion in systems storing and dispensing ULSD is likely due to the dispersal of acetic acid throughout USTs. It is likely produced by *Acetobacter* bacteria feeding on low levels of ethanol contamination. Dispersed into the humid vapor space by the higher vapor pressure (0.5 psi compared to 0.1 psi for ULSD) and by disturbances during fuel deliveries, acetic acid is deposited throughout the system. This results in a cycle of wetting and drying of the equipment concentrating the acetic acid on the metallic equipment and corroding it quite severely and rapidly.

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1. Introduction and Background

To protect public health and the environment, the United States Environmental Protection Agency (EPA) Clean Air Highway Diesel final rule stipulated a 97% reduction in sulfur content of highway diesel fuel beginning in June 2006[1]. Accordingly, diesel fuel was altered so that the sulfur content was reduced from 500 parts-per-million (ppm) in low sulfur diesel (LSD) to 15 ppm normally referred to as ultra low sulfur diesel (ULSD). This rule was implemented with a phased approach where 80% of the change over occurred in 2006 and the remaining 20% occurred by 2010. It was anticipated that the change to ULSD would impact lubricity, energy content, materials compatibility, and microbial growth[2]. However, accelerated and increased corrosion was not foreseen as a likely outcome.

Almost simultaneously, the Renewable Fuel Standard established by the Energy Policy Act of 2005 and amended by the Energy Independence and Security Act of 2007 mandated significant increase in the volume of biofuels production. Subsequently, there was an increase in retail stations storing and dispensing ethanol blends and biodiesel. Since then, over 90% of all gasoline is being sold with 10% ethanol content.

From as early as 2007, the Petroleum Equipment Institute (PEI) started receiving reports of unusually severe and accelerated corrosion of metal parts associated with storage tanks and equipment dispensing ULSD. Reports include observations of a metallic coffee ground type substance clogging the dispenser filters and of corrosion and/or malfunctioning of seals, gaskets, tanks, meters, leak detectors, solenoid valves and riser pipes. These observations were reported to be occurring in as little as 6 months. The corrosion was reported on the unwetted, or ullage, portions of the tanks and equipment in addition to the wetted portions of UST equipment. Figure 1 shows representative pictures of ULSD system components with rust-colored deposits as reported from industry stakeholders and as found at retail sites inspected for this study.

Figure 1. Corroded ULSD equipment: Corroded carbon steel submersible turbine pump (STP) shaft removed from pump housing, CA-1 (left), brass ball float extractor cage plug, NY-2 (middle), aluminum drop tube, NC-1 (right).

By 2009, the Steel Tank Institute (STI) had collected reports and presented the problem at ASTM International (ASTM) meetings to diverse groups of industry stakeholders which included refining, fuel retailing, end-user, petroleum equipment, biodiesel, and fuel additives representatives as well as ASTM and the EPA. As a result of this presentation the need for more information and further investigation was identified. Having many stakeholders with a wide range of interests made developing an objective and inclusive solution imperative to this time sensitive and potentially costly issue.

As an initial step, PEI developed a simple, five-question survey and members distributed it to various parties in the diesel fuel industry and to regulators to screen for issues with systems storing and dispensing ULSD. The survey results showed that problems were reported from all regions of the country (not in refineries, pipelines, and not associated with any individual supplier), the problems were not related to the age of the equipment, corrosion appeared the same in liquid and vapor areas, and there was an undetermined relationship between tank volume, throughput and tank maintenance. After the surveys were returned, the Clean Diesel Fuel Alliance (CDFA) met and a task force was formed which subsequently funded this research project to begin an in-depth investigation into corrosion issues in systems storing and dispensing ULSD. The CDFA Task Force included the Association of American Railroads, American Petroleum Institute, Ford Motor Company, National Association of Convenience Stores, National Association of Truck Stop Operators, Petroleum Equipment Institute, Petroleum Marketers Association of America and Steel Tank Institute.

2. Objective

The objective of the research project was to establish an understanding of factors leading to corrosion of ULSD storage and dispensing systems. For the purpose of this project, the underground storage tanks (USTs), dispensing systems and diesel fuel constitute a “system”. The research was designed to better understand the interconnectedness of the diesel fuel, additives, water (e.g., water bottoms, water emulsion, etc.), polymers and metals as they relate to the material corrosion and degradation issues.

The first phase of this project was a gathering of the anecdotal reports and limited data points (some cultured sample results and chemical analyses) to investigate the feasibility of the approximately 15 hypotheses proposed by the CDFA Task Force. Appendix A presents the (unsubstantiated) information gathered on all of the hypotheses and organizes them in a prioritization decided upon between the CDFA Task Force and Battelle. The output of the first phase was the down-selection to three working hypotheses, based on the discussion of Appendix A. The objective of this second phase was to gather data specific to the chosen three working hypotheses and conclude with a final hypothesis for the problem.

3. Working Hypotheses

Specifically, Phase 2 of the project was designed to investigate the following three working hypotheses.

i. Aerobic and/or anaerobic microbes are producing by-products that are establishing a corrosive environment in ULSD systems;

ii. Aggressive chemical specie(s) (e.g., acetic acid) present in ULSD systems is(are) facilitating aggressive corrosion; and

iii. Additives in the fuel are contributing to the corrosive environment in ULSD systems.

The *first working hypothesis* focused on microbial influenced corrosion (MIC), where microbes are producing metabolites that are corrosive to metals found in fuel storage or dispensing systems (i.e., mild carbon steel). To test this hypothesis, genetic sequencing was used to definitively determine whether microbes are present, which microbes are in the samples from inspected sites, and whether the microbes have metabolites that could contribute to the corrosion.

The *second working hypothesis* focused on chemical corrosion, where specie(s) present in the ULSD are corrosive to the materials found in the fuel dispensing and storage systems. Testing this hypothesis involved analysis of the chemical constituents present in the fuel, water, and headspace vapor within the USTs. These chemical constituents may be corrosive in nature or may contribute to the production of corrosive species, more specifically, acetic acid.

The *third working hypothesis* postulated that additives are contributing to the corrosive environment directly or indirectly as a source of nutrients to microbes that result in corrosive metabolites. The approach for testing this hypothesis focused on gathering information from additives manufacturers, refineries, terminals, stations, and published literature to understand the potential effect of additives on the overall chemical characteristics of the fuel and headspace vapor within USTs.

4. Experimental Methods

The approaches to validate or disprove two of the working hypotheses required knowledge of the contents of the affected UST systems. The research design included the identification of inspection sites to investigate and the development of an inspection and sampling protocol to ensure uniform and thorough inspections of the sites. Samples from the inspections were then analyzed for genetic material and chemical characteristics. These data, in combination with information on additives taken from literature and discussions with suppliers, have allowed Battelle to draw conclusions with respect to the three working hypotheses.

The study allowed for six sites in total to be inspected — one non-symptomatic site and five sites with severe symptoms. The intent was to compare and contrast the characteristics of the sites that have been effected to the characteristics of a site that has not been effected. This was adjusted to an analysis of all six sites to each other, since severe corrosion was identified at all of the sites. The following sections describe the experimental methods used to collect data for this research project.

4.1 Inspection Site Identification

The purpose of this task was to identify, recruit, and coordinate with the inspection sites for this investigation. For all of the sites, it also included phone discussions with the on-site point of contacts, gathering general site information, and coordination of the inspections.

To identify the inspection sites, a communication asking for sites to be volunteered along with a questionnaire regarding general site information was developed by Battelle. The CDFA Task Force approached potential inspection site owners/operators through their networks of association members, and six sites were volunteered. Then the site owner/operators were contacted for follow-up conversations pertaining to the sites volunteered. In doing this, the site owners offered other potential sites to the list. The total number of volunteered sites rose to 12. A subcommittee of the CDFA Task Force was formed to discuss and evaluate the volunteered sites. As a result, the group decided that there would be six (6) site inspections - one (1) site that was not showing symptoms of corrosion and five (5) sites with a history of severe, rapidly induced corrosive symptoms located across the continental United States. Of the 12, two sites were reported as non-symptomatic, one with a fiberglass tank and one with a steel tank. The material of the tanks inspected was also a factor that could be controlled and, therefore it was chosen to be the same material of construction as the first five sites. Six tanks were chosen because they had similar tank size, material, and monthly throughput. They were also chosen for a large range of installation years and for them to be spread across the country geographically, meaning different ages, climates and different supplies of fuel by different routes. It was intended that one of the corroded sites would be replaced with a site from the middle of the country for more geographic diversity. After more searching through known networks of industry representatives, it was decided to move forward with the six chosen sites.

Three months after the site recruitment and just before deployment to the site for the inspection, the non-symptomatic site was inspected by the owner/operator and determined to have corrosion problems. Therefore, another site through one of the already-engaged site owners was identified to be the non-symptomatic site for the study. Once the research team was on site at the non-symptomatic site, it was clear that the site was, in fact, experiencing effects of the problem, just not as severely as the other five sites.

The site inspections entailed documenting the extent of corrosion in the UST systems and the fuel circumstances (inventory volume, water bottom height, temperature, etc.). The specific names and identifying information of the six inspection sites were stripped from the results. The sites inspected were identified by their state and numerically as designated in parentheses below. There was:

- One site from North Carolina (NC-1);
- Two sites from New York (NY-1 the non-symptomatic site and NY-2); and
- Three sites from California (CA-1, CA-2, and CA-3).

4.2 Inspection Procedure and Sample Handling

An inspection procedure and sample handling plan, called the Quality Assurance Project Plan (QAPP), was prepared to ensure the site inspections were conducted in a uniform manner. Battelle and subcontractor field technicians from Tanknology Inc. followed the QAPP to inspect and sample the fuel, water bottom, and vapor from USTs at the inspection sites. One fuel, one water, and two vapor samples from each site were collected, along with scraping or scale samples from various equipment. The inspection steps were followed as described in the QAPP (Appendix B) and briefly described here.

1. Gather printout data from the Automatic Tank Gauging (ATG) system inside retail station.
2. Open and inspect the fill riser pipe and remove the drop tube.
3. Collect vapor samples.
4. Open all other riser pipes (ATG, ball float, etc.), remove equipment where possible, inspect and sample.
5. Collect the fuel sample, consolidate, and split for chemical laboratory analyses. Filter the fuel for biological analysis.
6. Collect the water bottom (and bottom sediment) samples, consolidate, and split for laboratory analyses. Filter the water for biological analysis.
7. Inspect the inside of the UST with a video camera.
8. Inspect the dispensing systems.
9. Reassemble the system and bring the ATG back on line.
10. Ship the samples to respective laboratories.

After collection, the samples were shipped to the appropriate laboratories, and all analysis data were sent to Battelle.

4.2.1 Sample Handling

Samples were collected according to ASTM D6469-11[3] and D7464-08[4]. Filtered samples, scrape samples, and bottom sediment samples were shipped overnight in coolers to Battelle (Columbus, OH) and placed into storage at -80°C in a continuously temperature monitored freezer until use. Liquid samples were shipped by ground to the analytical laboratories directly from the inspection sites. Scrape samples and bottom sediment samples were split and shipped to analytical laboratories once all six inspections were complete. All chain of custody forms were retained by Battelle and are available upon request. It is important to note that the sampling equipment was decontaminated with ethanol at the end of each inspection day and allowed to air dry. The ethanol evaporated before the next use; therefore, it is unlikely that the decontamination process contaminated the collected samples with ethanol. Table 1 summarizes the types of samples acquired during the inspections at each site. A complete list of samples obtained during the inspections is listed in Appendix C.

Table 1. Sample Collection and Handling

Sample Type (Number per site)	Tank Location	Sample Collection and Handling
Vapor (2[a])	Headspace	• 100 L vapor sample on sorbent cartridges for carboxylic acid and formic acid analyses
Vapor (1)	Headspace	• 3 L Tedlar bag for sulfur speciation
Corrosion scrapings (multiple)	Equipment with excessive corrosion	• Sterile 50 mL conical tubes placed in plastic sample bags for fouling analyses
Fuel (1)	Middle of fuel column; Representative sample from multiple risers[b]	• Amber glass bottles for chemical analyses (~4 L total split to multiple bottles) • ~700 to 1000 milliliters (mL) of fuel pulled under vacuum through 0.45 µm filter for biological analysis
Water (1)	Bottom; Consolidated sample from multiple risers and multiple deployments of the thief sampler	• Amber glass bottle for chemical analyses (~1 L total split into multiple bottles) • ~50 to 150 mL of water pulled under vacuum through 0.45 µm filter for biological analysis
Sediment (1- if thief sampler clogged while sampling)	Bottom	• Sterile 50 mL conical tubes placed in plastic sample bags for fouling analyses and biological analysis

[a] Deviation from QAPP. The GC-MS method used for the vapor samples required two sorbent tubes instead of one.

[b] Deviation from QAPP. The fuel volumes were not large enough to collect multiple samples from different horizontal sections of the fuel column.

4.3 Biological Analysis Method

The purpose of the biological sampling and analysis was to determine the types of microbes present, the conditions under which they would be expected to thrive, and their potential to produce metabolites that could lead to the observed corrosion.

4.3.1 DNA Extraction

Frozen samples were thawed and the entire sample was collected in separate 15-mL sterile conical tubes. For solid mass samples (i.e., sediment) Deoxyribonucleic acid (DNA) was extracted via the Ultraclean® Mega Soil DNA Isolation Kit (MO BIO Laboratories, Inc., Carlsbad, CA) using the manufacturer's recommended protocol with modifications for sediment extraction (Battelle Standard Operating Procedure [SOP]). For filtered fuel and water samples, the Meta-G-Nome™ DNA Isolation Kit (Epicentre, Madison, WI) was used according to manufacturer's protocols for direct extraction from biomass captured on nitrocellulose filters. Post-extraction cleanup for all samples was performed using OneStep™ polymerase chain reaction (PCR) Inhibitor Removal Kit (Zymo Research Corp., Irvine, CA). Purified DNA samples were analyzed with an ultraviolet (UV) absorbance (NanoDrop™ 200 spectrophotometer, Thermo Scientific, Waltham, MA), Qubit® dsDNA HS Assay Kit, and SYBR® Gold Nucleic Acid Gel Stain according to manufacturer's protocols (Invitrogen/LifeTechnologies, Grand Island, NY).

4.3.2 Sequencing

Numerically coded aliquots of approximately 0.5 to 1 µg DNA per sample were used to create sequencing libraries. First, genomic DNA was fragmented using a Covaris™ S220 Sonicator (Covaris, Inc., Woburn, MA) to approximately 300 base pairs (bps). Fragmented DNA was used to synthesize indexed sequencing libraries using the TruSeq DNA Sample Prep Kit V2 (Illumina, Inc., San Diego, CA), according to the manufacturer's recommended protocol. Cluster generation was performed on the cBOT using the TruSeq PE Cluster Kit v3 – cBot – HS (Illumina). Libraries were sequenced with an Illumina HiSeq 2000 at Nationwide Children's Hospital (NCH) Biomedical Genomics Core (Columbus, OH) using the TruSeq SBS Kit v3 reagents (Illumina) for paired end sequencing with read lengths of 100 bps (200 cycles). Primary analysis (image analysis and basecalling) was performed using HiSeq Control Software version 1.5.15.1 and Real Time Analysis version 1.13.48. Secondary Analysis (demultiplexing) was performed using Illumina CASAVA Software v1.6 on the NCH compute cluster. Sequence data (.fastq files) and quality control (QC) reports for library construction were delivered to Battelle via an external hard drive.

4.3.2.1 Whole Genome Amplification

DNA extracts with less than suitable yields of DNA for sequencing were subjected to whole genome amplification (WGA) using the Repli-g UltraFast Mini kit (Qiagen, Valencia, CA) according to manufacturer's recommended protocols. For samples with less than the required 10 ng of DNA input, 1 µL of DNA extract was added. Products were evaluated by UV-absorbance measurements and agarose-gel electrophoresis.

4.3.2.2 16S rRNA Gene Analysis

DNA extracts with less than suitable yields of material for sequencing were also subjected to PCR amplification to detect bacterial DNA. Primers 27F (5,-AGAGTTTGATCMTGGCTCAG - 3') and 1492R (5,- GGTTACCTTGTTACGACTT-3') were used to amplify the 16s ribosomal ribonucleic acid (16s rRNA) gene of bacteria using Phusion High fidelity DNA polymerase (New England BioLabs, Ipswich, MA) with parameters of 98°C for 30s, 35 cycles of 98°C for 10s, 56°C for 30s and 72°C for 60s, followed by 72°C for 5 minutes in a PTC-200 thermalcycler (Bio-Rad, Hercules, CA). Products were visualized by agarose-gel electrophoresis.

4.3.3 Bioinformatics

In order to remove poor quality sequencing data (~1% on the Illumina HiSeq), sequence data were quality filtered such that 80% of the bases had a quality of ≥17 (i.e., the probability of a correct base call was ~98%). Following quality filtering, read files were processed using the Battelle Galileo high performance compute cluster and the Basic Local Alignment Search Tool (BLAST®) (National Library of Medicine, Bethesda, MD). Sequences were searched against the entire genomic DNA sequences reported in the *RefSeq* database v. 12/04/2011 (NCBI, Bethesda, MD), which contained entries for 2,059,236 sequences. Search results were filtered for sequences with ≥97% identity and sequence length of ≥80 bps. The output from this search resulted in a list of taxonomic identifications (taxIDs), associated organism names, and number of sequences per taxID for each sample. Krona[5] v. 2.1 was used to create an interactive comparative chart for viewing the relative abundance of organisms in each sample. A final filtering of the results was performed to include only taxa (species) identified by numbers of hits greater than 0.1% (1:1000) of the total representation per sample.

4.3.4 Diversity Analysis

To measure the microbial diversity, the Shannon-Weaver Diversity Index, H^6, was calculated using Equation 1:

$$H = -\sum_{i=1}^{S} p_i \ln p_i$$

Equation 1: Shannon Diversity Index

where p_i is the proportion of identified genetic sequences for each species in the sample and S is the total number of species identified in each sample. In addition, the relative evenness of the identified organisms was measured by Shannon's Equitability $(E_H)^6$ using Equation 2:

$$E_H = H/ln\,S$$

Equation 2: Shannon's Equitability

As H approaches zero, a microbial ecosystem is dominated by fewer species. E_H values range between 0 and 1, with 1 being complete evenness/diversity.

4.4 Chemical Analysis Methods

The purpose of the chemical analysis was to determine the chemical characteristics of the sampled matrices and evaluate the relationships between the chemical analysis results with the biological analysis results for a better understanding of the UST environment that is causing the observed corrosion. Table 2 includes what was measured, the standard method number (if applicable), and matrices associated with the samples taken in this project. The standard methods are very detailed and will not be reiterated in this document.

Elemental and crystallographic structural analysis was performed on a number of scraping, deposit and particulate specimens taken from filters, water samples, and other areas of the system. The objective of these analyses was to determine what the elemental composition and crystalline structures were in different areas of the system and to correlate them with observed corrosion and materials used USTs. The primary modes of analysis used were x-ray diffraction (XRD), x-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). Each technique provides slightly different and complementary information which can be used to piece together the sample components. As such, these methods are designed to analyze for as many elements and chemicals as possible.

The chemical analyses were performed by three members of the CDFA Task Force who have laboratories that regularly perform these analyses and one laboratory that was contracted for vapor analysis. Some methods were performed by more than one lab, resulting in duplicate or triplicate analyses on the liquid samples. Marathon performed analyses on the Tedlar bag vapor, fuel, water, and scrape samples. Chevron analyzed the water and scrape samples. Ford Motor Company analyzed the fuel and water samples. Finally, the contracted laboratory, Columbia Analytical Services, analyzed vapor samples.

Table 2. Analysis Methods by Sample Type

Determination of:	Method Identification Number[a]	Sample Type
Biodiesel by Mid Infrared Spectroscopy	Modified ASTM D7371-07	Fuel
Carbon and Hydrogen	ASTM D5291-10	Fuel
Electrical Conductivity	ASTM D2624-09	Fuel
	EPA 120.2	Water
Density, Relative Density, and API Gravity of Liquids by Digital Density Meter	ASTM D4052-09	Fuel
Sulfur Compounds and Sulfur Selective Detection (hydrogen sulfide, sulfur content, sulfur speciation)	ASTM D5623-94	Headspace vapor
Dissolved Inorganic Anions by Capillary Electrophoresis	Modified ASTM D6508	Water
Corrosive Properties	NACE TM-0172	Fuel
Trace Nitrogen in Liquid Petroleum Hydrocarbons by Boat-Inlet Chemiluminescence	ASTM D5762-10	Fuel
Carboxylic Acids and Formic Acid by Gas Chromatography-Mass Spectrometry	Columbia Method 102	Headspace vapor
Oxygen Concentration by Calculation	Calculation	NA
Particulate Contamination by Laboratory Filtration	ASTM D6217-98	Fuel
Total Acid Number (TAN)	ASTM D664-09a	Fuel
pH by Potentiometric Titration	EPA 150.1	Water
Total Sulfur	ASTM D5453-09	Fuel
Water Content by Coulometric Karl Fischer Titration	ASTM D6304-07	Fuel
Water Content and Temperature	Hygrometer on site	Headspace vapor
Flash Point	ASTM D93	Fuel
Analysis of Solid Corrosive Substrate by XRD, XRF, ICP-MS and IC	Laboratory Fouling Investigation Methods	Scrapings
Determination of Acetate and Formate by Capillary Electrophoresis	Ford Method - SOP CL029-02	Fuel and Water

[a] References for analytical methods are in the QAPP, Appendix B.

4.5 Additives Hypothesis Investigation Approach

The approach for testing this hypothesis focused on gathering information from additives manufacturers and literature to understand the potential effect of additives on the overall chemical characteristics of the fuel and headspace vapor within USTs. Battelle performed literature and internet searches of fuel additives in general and additives important to ULSD service. Also, discussions were held with technical representatives from multiple additive manufacturers. Some discussions were directly related to understanding the data set produced from this research and others were discussing ULSD additives in general.

5. Results

5.1 Inspection Site Descriptions

Site inspections took place from February 8–23, 2012. Four people were at each site to conduct the inspections: the Battelle Project Manager, the Tanknology Vice President of Engineering and Research and Development, a Tanknology Quality Assurance (QA) Manager, and a Tanknology Field Technician. NY-1 was intended to be used as a baseline site that would not have symptoms. However, it did have symptoms but they were much less severe than the other sites; therefore, it could not be considered a truly clean site but is identified as "clean" in the following results tables. Table 3 summarizes some of the site characteristics recorded during the inspections. The complete inspection form data are included in Appendix C.

Table 3. Inspection Site Characteristics

Site ID	NC-1	NY-1 "Clean"[a]	NY-2	CA-1	CA-2	CA-3
Inspection Date (2012)	8-Feb	15-Feb	16-Feb	21-Feb	22-Feb	23-Feb
Tank Year of Installation	1998	2008	1988	1990	1991	1991
Tank Capacity (gallons)	17,265	12,000	6,000	10,000	12,000	6,000
Tank Diameter (inches)	120	120	92	92	120	92
Tank Material	Fiberglass	Fiberglass	Fiberglass	Fiberglass	Fiberglass	Fiberglass
Single/Double Wall	Double	Double	Single	Double	Double	Double
Approximate Monthly Throughput (gal/month)	29,000	18,000	6,500	26,000	20,000	25,000
Filter Date Replaced	24-Jan-12	unknown	Filter not identified	2-Feb-12	13-Jan-12	9-Jan-12
Biocide Treatment History	Dec 2011	unknown	2 times in past year	unknown	none	unknown

[a] Site was affected by corrosion. It was intended to be the non-symptomatic site; therefore clean is in quotations.

5.2 Biological Sample Results

5.2.1 DNA Yield and Amplification Results

Sixteen sediment, filtered fuel, or filtered water samples from five geographically distributed sites were subjected to DNA extraction. Nine samples provided DNA measurable by a high-sensitivity dsDNA method (Table 4). In most cases, the filtered fuel provided little to no measurable DNA, while sediment and filtered water samples had measurable amounts of DNA. All sites yielded DNA, suggesting biomass within the systems, with NC-1 providing the least amount of DNA. Survey reports also showed that NC-1 had received a biocide treatment (December 2011) which could be responsible for the low recovery of DNA.

The sequencing method employed in this study requires at least 400 nanograms of high quality DNA. As seen in Table 4, only four samples met this criterion. WGA was attempted in the samples with lower yield to increase the DNA to quantities suitable for sequencing. A common commercial kit that is based on multiple displacement amplification was used, as discussed in the methods. The products of this procedure were measured for quantity and quality. The results showed that the only samples to yield measurable amounts of product from WGA were the same four samples with high DNA yield (Table 4). Thus, the low DNA samples did not achieve high DNA yields following this method.

A confirmatory test for presence of bacteria was also performed on the DNA extract samples to determine if bacterial DNA was present when total DNA was not measurable by the methods used. PCR amplification of the ubiquitous 16s rRNA gene from bacteria was performed. All but two samples yielded 16s amplification in varying amounts (Table 4 and Figure D5 [Appendix D]) including samples that had less than measurable amounts of DNA following extraction. One sample, 53609-06-09e, had measurable DNA, but gave no 16s rRNA PCR product. This could be due to interferants in the sample that prohibited the PCR reaction. In conclusion, all sites tested displayed presence of bacterial DNA, although at different abundances.

Table 4. DNA Yield, Whole Genome Amplification and 16s rRNA Amplification

Site ID	Sample ID	Description	Purity (Abs 260/280 nm)	Total DNA (ng)	Whole Genome Amplification (WGA)	16s Amplification
NC-1	8Feb12_07c	Filtered Fuel	1.32	Too Low	-	+
NC-1	8Feb12_09	Filtered Water Bottom	1.32	123.9	-	++
NY-1	53609-06-08c	Filtered Fuel	1.24	Too Low	-	++
NY-1	53609-06-09d	Filtered Water Bottom	1.70	463.6	+++	ND
NY-2	53609-08-09e	Bottom Sediment	1.09	75.24	-	-
NY-2	53609-08-08c	Filtered Fuel	1.36	Too Low	-	+
NY-2	53609-08-09d	Filtered Water Bottom	1.50	1353	+++	ND
CA-1	53609-11-11e	Bottom Sediment	1.11	27.36	-	+
CA-1	53609-11-08c	Filtered Fuel	1.18	Too Low	-	-
CA-1	53609-11-11d	Filtered Water Bottom	1.48	Too Low	-	-/+
CA-2	53609-14-09	Bottom Sediment	1.13	7714	+++	ND
CA-2	53609-14-07c	Filtered Fuel	1.56	76.00	-	+
CA-2	53609-14-08d	Filtered Water Bottom	1.72	2584	+++	ND

Table 4. DNA Yield, Whole Genome Amplification and 16s rRNA Amplification (Continued)

Site ID	Sample ID	Description	Purity (Abs 260/280 nm)	Total DNA (ng)	Whole Genome Amplification (WGA)	16s Amplification
CA-3	53609-17-11	Bottom Sediment	1.12	340.1	-	+++
CA-3	53609-17-10c	Filtered Fuel	1.35	Too Low	-	++
CA-3	53609-17-12d	Filtered Water Bottom	1.15	94.24	-	++

Shading indicates samples analyzed by whole metagenome sequencing
ND = not done
- = no product
+, ++, +++ = product and relative amount

5.2.2 Dominant Organisms by Site

Sequencing and bioinformatic analysis was performed on four samples (Table 4). The full results of the analysis are listed in Tables D2-D5 and Figures D1-D4 (Appendix D). Table 5 shows the dominant or most prevalent organisms by site, and Table 6 shows a breakdown of the identified organisms by oxygen requirements. *In general, bacteria of the acetic acid producing family (Acetobacteraceae) were prevalent in all four samples*. These are organisms that characteristically require oxygen and utilize ethanol as an energy source. They do not historically utilize hydrocarbons, such as the components of diesel fuel, for energy. In general, the most abundant organisms identified from the four samples have characteristics that can lead to corrosion of metallic equipment, such as acetic acid production, ethanol utilization, low pH requirements, environmental presence, and oxygen. An expanded list of attributes for the organisms in Table 5 is provided in Appendix E.

Some differences were observed between sites. For example, CA-2 had predominantly *Gluconacetobacer sp*. Over 50% of the DNA identified belonged to this genus. NY-2 had higher levels of *Lactobacillus sp.* compared to NY-1 and CA-2. NY-1 showed higher levels of a fungus, *Zygosaccharomyces*, and bacteriophage (viruses that infect bacteria) compared to the other samples. Very little difference was observed between the filter water and sediment samples in CA-2, suggesting that the same organisms reside in these two sample types within this system. It is interesting to note that although the three geographically separate sites had some observable differences in abundance of select organisms, Table 5 indicates the presence of organisms was relatively uniform. This suggests that the ULSD system is very selective for specialized organisms capable of thriving in these environments, rather than a site specific or environmental effect driving the composition of microbial population.

Table 5. Dominant Organisms by Site

Genera	NY-1 (06-09d)	NY-2 (08-09d)	CA-2 (14-08d)	CA-2 (14-09)
Gluconacetobacter sp.	35%	44%	53%	55%
Acetobacter pastuerianus	33%	23%	24%	19%
Gluconabacter oxydans	4.0%	3.0%	20%	19%
Lactobacillus sp.	1.0%	34%	0.1%	4.0%
Fungi (e.g. Zygosaccharomyces sp)	9.0%	0.3%	0.1%	0.2%
Bacteriophage (virus)	7.0%	2.0%	0.8%	0.7%

Underlined results highlight which samples had the highest percentages of the different genera.

Table 6. Identified Organisms According to Oxygen Needs

Category	NY-1 (06-09d)	NY-2 (08-09d)	CA-2 (14-08d)	CA-2 (14-09)
Strictly aerobic	23%	63%	30%	28%
Strictly anaerobic	1%	6%	0%	0%
Facultative[a]	33%	7%	0%	2%
Viruses and Unknowns	43%	24%	70%	70%

[a] Organisms that survive in both aerobic and anaerobic conditions.

5.2.3 Hydrocarbon Degrading Bacteria

Some species of bacteria contain biochemical pathways to utilize and break down petroleum hydrocarbons of various chemical forms.[7] Although these species identified to date are distributed within several bacterial orders, a majority of hydrocarbon degrading bacteria originate from marine environments and are typically of the class *Gammaproteobacteria*. Common hydrocarbon degrading genera include *Alcanivorax, Marinobacter, Pseudomonas, Shawanella* and *Acinetobacter* species. To evaluate if the bacteria are present with the potential of using diesel fuel as a carbon source, bacteria and genes involved in hydrocarbon utilization were evaluated. Table 7 shows the percentage of positive hits for selected groups of bacteria with the potential to utilize hydrocarbons for each site sampled by metagenomics. In general, the class of bacteria *Gammaproteobacteria* was only a small percentage of the total consortia, ranging from 0.3 to 5% of the identified DNA (Table 7). NY-2 showed that *Pseudomonas sp.* were the major *Gammaproteobacteria* present, while NY-1 showed *Enterobacteriaceae*, an order of non-hydrocarbon utilizers, were the dominant *Gammaproteobacteria*. The two samples from CA-2 showed near limit of detection levels of total *Gammaproteobacteria*. Further, a search of the alkane hydroxylase (alkane-1-monoxygenase) gene, an essential enzyme involved in degradation of n-alkanes (C_{10}-C_{13}), was performed using data for sample 06-09d (NY-1). No positive gene hits were discovered for homologues of the alkane hydroxylase gene in NY-1 (data not shown), suggesting that the pathway to utilize n-alkanes is not present for the species of bacteria sampled at this site. *Thus, based on the current library for metagenomics comparison available, the evaluation of hydrocarbon degradation suggests that the hydrocarbons contained within the diesel fuel may not be the primary carbon source for the consortium of bacteria present.*

Table 7. Percent of DNA Identified for Selected Hydrocarbon Degrading Bacteria

Category	NY-1 (06-09d)	NY-2 (08-09d)	CA-2 (14-08d)	CA-2 (14-09)
Gammaproteobacteria	4%	5%	0.3%	0.3%
Pseudomonas sp.	1%	4%	<LOD	0.1%
Marinobacter sp.	<LOD	<LOD	<LOD	<LOD
Acinetobacter sp.	0.7%	<LOD	<LOD	<LOD
Shawanella sp.	<LOD	<LOD	<LOD	<LOD

< LOD = below threshold for genetic identification, <1:1000 of total data set.

5.2.4 Diversity Assessment

A measurement of microbial diversity was performed to further evaluate the community profiles identified by DNA sequencing. Table 8 shows that overall all four samples have low diversity, as measured by the Shannon Index, compared to environmental sediment samples. This finding suggests that there are both less overall unique organisms present in the community, and of those present, there are limited species that dominate the community within the USTs surveyed. This is further evidence that the conditions of the ULSD USTs are conducive to growth of limited, specialized organisms. Lastly, the NY-1 site had the most diverse microbial community, while the CA-2 site was the least diverse (Table 8).

Table 8. Diversity Assessment

Shannon Index	NY-1 (06-09d)	NY-2 (08-09d)	CA-2 (14-08d)	CA-2 (14-09)	Historical sediment samples[c]
Shannon's diversity (H)[a]	2.6	2.7	1.5	1.7	4.8 - 5.3
Shannon's equitability (E_H)[b]	0.23	0.22	0.13	0.14	0.74 - 0.80

[a] As *H* approaches zero, an ecosystem (microbial) is dominated by very few species.
[b] Equitability assumes a value between 0 and 1, with 1 being complete evenness/diversity.
[c] Previous data from marine sediments (natural environmental samples) from research studies at Battelle using the same genomics methods.

5.3 Chemical Analyses Results

Many analysis methods were performed on the matrices sampled during the inspections. Some of the results that are more relevant to the hypotheses under investigation are presented below in Tables 9 through 11 and all of the results are presented in Appendix F. Table 9 shows results from the analyses performed on the fuel samples taken at each inspection site. Acetate (a form of acetic acid) is not expected in diesel fuel but was measureable in four of the six sampled fuels. Ethanol was also unexpectedly identified; therefore, a separate analysis was conducted to estimate the ethanol concentrations of both fuel and water bottoms. This was accomplished by comparing the instrument response to the responses of fuel spiked with ethanol. These results indicate that ethanol could be contaminating ULSD as four of the six fuels contained it. An acceptable NACE analysis result is a requirement for fuel to be transported via pipeline and is not traditionally performed for fuel transportation via barge, truck, or directly dispensed from a terminal. In this case, three of the six samples failed this test, indicating that the corrosion inhibitor that may have been added at the refinery was consumed by the time the fuel reached the retail sites. According to the Federal Trade Commission requirements and ASTM D975, biodiesel is allowed to be added to ULSD at up to 5% of the composition. These results indicate that two samples had detectable levels of biodiesel, and only one was close to the 5% at 3.55%. This sample was also the only one that contained formate and had the highest composition of water, both of which are related to the presence of biodiesel. This could be due to the degradation of biodiesel. Finally, since the corrosion started to be reported after the lowering of sulfur content, the sulfur results for these sites ranged from 5.9 to 7.7 ppmv, which is well below the 15 ppm maximum.

Table 9. Summary of Fuel Sample Results

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3	Standard$^+$
Acetate mg/kg (ppm)	<0.3	7.7	2.8	2.7	<0.3	5.9	NE
Biodiesel (vol%)	<0.3	3.55	0.40	<0.3	<0.3	<0.3	NE
Conductivity (ps/m @ ambient)	125	1,200	183	30	70	64	minimum 25^1
Ethanol (vol%)*	0.04	0.01	0.17	0.06	ND	ND	NE
Flashpoint, °F	131	130	111	129	135	132	>125
Formate mg/kg (ppm)	<0.3	5.6	<0.3	<0.3	<0.3	<0.3	NE
Fouling GC-MS Scan	trace Ethanol	trace Ethanol	trace Ethanol	trace Ethanol	NTR	NTR	NE
NACE TM-172 Rating	A	A	A	D	C	C	B+^{1}
Particulate (mg/L)	54.5	87.4	91.4	114.8	69	122.2	12^2
Sulfur (ppmw)	7.2	7.7	7.3	5.9	6.4	6.2	15^3
TAN (mg KOH/L)	0.01	0.04	0.02	0.002	0.005	0.006	5.0^4
Water (ppmw)	39	65	46	44	41	29	50^1

*Fouling GC-MS Scan results compared to fuel spiked with ethanol for estimated quantification.
NTR = Nothing to report outside of expected hydrocarbons
NE – not expected
+ Specification standard, according to source or regulation
1. ASTM D975
2. US Federal Specification (VV-F-800C)
3. EPA420-F-06-064, October 2006
4. ASTM D6751-07b – specific to biodiesel

Table 10 presents chemical analyses results on the water bottom samples collected at each inspection site. Acetate was measured in all six water samples at high levels from 9,000 ppm to 22,500 ppm. Glycolate, a related compound to acetic acid, was detected in appreciable amounts at four of the six sites. In addition, ethanol was identified in five of the six water bottoms. Neither acetate nor ethanol were expected to be in these systems and are considered to contribute to corrosivity. Other characteristics of the water that are connected to corrosivity are the conductivity, pH, and chloride concentration. The conductivity of the water was quite high, ranging from 4,000 µS/cm to 21,000 µS/cm, and the pH of the waters were acidic, ranging from 3.6 to 5.3. Chloride and sodium results were especially high for the three east coast sites, possibly indicating the use of road salts during the winter season although another potential source would be refinery salt driers. Chloride is known to adversely affect corrosion resistance of many metallic materials. The GC-MS fouling scans indicated the presence of a variety of compounds, including alcohols, acids, and amines. Although the exact resins that make up the fiberglass tanks are unknown, methyl vinyl ketone has been identified as a chemical that could have leached from the tank shell.

Table 10. Summary of Water Bottom Sample Results

Site ID	*NC-1*	*NY-1*	*NY-2*	*CA-1*	*CA-2*	*CA-3*	*Water*[+]
Acetate (ppm)[a]	16,500	9,000	21,000	22,500	17,500	20,000	295[1]
Ammonium (ppmw)	871	<1	452	30	37	5.2	< 200[2]
Calcium (ppmw)	<1	<1	<1	732	586	242	6.5[3]
Chloride (ppmw)[b]	6,791	3,890	1,978	785	888	394	17[3]
Carbonate (ppmw)	12	57	19	65	72	41	77[3] bicarbonate
Conductivity (µS/cm)	21,000	17,000	12,000	4,000	7,500	8,000	331[3]
Ethanol* (vol%)	3.17	0.66	0.45	0.40	ND	0.04	NA
Fluoride (ppmw)	1,074	1,205	1,796	4,653	4,372	3,595	1.5[4]
Formate (ppm)	78	1,400	69	350	300	280	data not found
Glycolate (ppmw)	<100	4,000	<100	11,000	11,000	5,000	data not found
Magnesium (ppmw)	<1	<1	112	63	614	25	1.1[3]
Nitrate (ppmw)[a]	39	514	60	26	308	27	10[5]
pH[b]	5.3	4.6	4.1	3.6	3.8	3.6	6.7[3]
Potassium (ppmw)	370	639	278	<1	45	51	3[3]
Sodium (ppmw)	6,124	2,291	1,886	581	158	182	37[3]
Sulfate (ppmw)[a]	440	470	312	598	273	376	15[3]

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3	Water$^+$
Fouling GC-MS Scan (identified peaks)	methyl vinyl ketone, acetic acid, ethanol, 1,2-ethane diol propylene glycol, N-butyl-1-butanamine, N-ethyl-cyclohexylamine	methanol ethanol, acetic acid, 1,2-ehthane diol, propylene glycol, N,N-dimethyl formamide, significant N,N-dimethylbenzenemethanamine, unidentified phthalate	ethanol, acetic acid, 2-hexanone	acetic acid, glycol, ethanol	acetic acid, 1,1'-oxybis-2-propanol, traces of glycol and dioxane	acetic acid, traces of dioxane, glycol, and 2,5-dimethyl-1,4-dioxane, very faint trace of ethanol	NA

NA = Not applicable

*Fouling GC-MS Scan results compared to fuel spiked with ethanol for estimated quantification.

[a] Average of 2 independent analyses

[b] Average of 3 independent analyses

Typical concentrations seen in groundwater or surface waters according to source.

1. In surface soil solutions: The Influence of Acetate and Oxalate as Simple Organic Ligands on the Behavior of Palladium in Surface Environments, Wood, S. A and Middlesworth, J. V. The Canadian Mineralogist, Vol 42, pp. 411-421.
2. Guidelines for Drinking-water Quality, 3rd Edition, Volume 1, World Health Organization, 2008. Pp 303-304.
3. Groundwater from volcanic rocks: Natural Variations in the Composition of Groundwater, Nelson, D., Oregon Department of Human Service, November 2002. pp. 3.
4. Water Quality Fact Sheet: Fluoride. British Geological Survey
5. U.S. EPA drinking water MCL

The vapor results are presented in Table 11. The relative humidity of the vapor was high, ranging from 72% to 95%. Given that the acetate was found in the fuel and water, and there were little other organic acids present in the samples (analyzed for 17 other acids, see Appendix F), the determination of acetic acid in the vapor space makes this the suspected chemical corroding ULSD USTs.

Table 11. Summary of Vapor Sample Results

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Average relative humidity (RH%)	90.9[b]	83.3[b]	95.5[c]	73.7[a]	71.8[a]	95.2[b]
Average In tank temp (°F)	57.1[b]	46.8[b]	44.7[c]	61.8[a]	66.4[a]	58.2[b]
Acetic acid (ppbv)	570	1,800	3,600	7,800	9,500	16,000
Formic acid (ppbv)	18	48	110	190	88	72
Propionic acid (Propanoic) (ppbv)	1.6	15	2.3	1.8	1.7	2.0
2-Methylpropanoic acid (Isobutyric) (ppbv)	ND	0.79	ND	ND	ND	ND
Butanoic acid (Butyric) (ppbv)	ND	0.85	ND	ND	ND	ND
Carbonyl sulfide (COS) (ppmw) (Tedlar bag)	0.14	Bag ruptured	0.29	Lost in transport	0.12	0.22
						0.14 (duplicate)

[a] Average of two readings
[b] Average of three readings
[c] Average of four readings
ND – not detected (see Appendix Table F3 for reporting limits)

5.4 Corrosion Sample Results

The sites inspected were chosen because of the corrosion observed by the owners/operators of the sites. The corrosion is severe and according to the owners happened over a relatively short period of time. During the inspections in this project, severe corrosion was observed on a large number of components *within* the USTs and specifically *not* on the outside of the components in the sump pits and the dispensing systems. The corrosion scrape samples taken from the internal components were coated with corrosion. *The scrape sample results support the conclusion that the internal components made up of all different metals are deteriorating in ULSD USTs.*

Since acetic acid and ethanol have been identified as the chemicals most likely contributing to corrosion from the chemical results, it was not surprising that *acetic acid was identified in 75% of the scrape samples.* Ethanol was not measured in the scrape samples as it is believed to be used as an energy source for the biological activity in the USTs. Appendix G includes a detailed discussion and tables of all of the results from the scrape sample analyses performed.

5.5 Additives

Additives for fuel handling, specifically for de-icing or water removal/encapsulation, may contain various concentrations of alcohols and/or glycols. In the fouling gas chromatography-mass spectrometry (GC-MS) scans of water bottom samples, alcohols (specifically methanol, ethanol, and 1,1’-oxybis-2-propanol) were found in all samples. Glycols were found in five of the six samples (not seen in NY-2). Additives for de-icing are not generally added at the refinery or terminal points, and overall, are not typically added to diesel fuel.

Fuel stability additives composed of strongly basic amines are added to react with and eliminate weak acids such as acetic acid and formic acid. Amine compounds were found in two of the sites’ water bottoms, NC-1 and NY-1. Although the specific amines used are unknown, amine compounds are also components in biocide additives, which had been added to the NC-1 site in December 2011. Additives containing amines are generally added to eliminate microbes that can cause corrosion, or as corrosion inhibitors binding corrosive acids. They would unlikely be a factor in the corrosion seen in the USTs inspected.

The sulfur compounds in LSD contribute to increased lubricity when compared to ULSD. In general, ULSD requires a lubricity additive in order to meet lubricity specifications. Mono- and di-acids or ester synthetic additives are commonly added to ULSD to increase the lubricity, although biodiesel is also a lesser utilized lubricity agent. Biodiesel composition of the tested fuel samples showed results below detection (< 0.3 % by volume) for four of the six samples. The NY-1 and NY-2 sites showed 3.55% and 0.40% biodiesel, respectively. Chemical breakdown of these small chain acids or biodiesel generally occurs slowly over time and could potentially produce acetic or formic acids. The rate of this chemical breakdown could be increased by presence of a microbiological component that metabolizes these mono- and di-acids, forming corrosive products. As discussed in Section 5.2.3, these microbes were not found in significant amounts in the sampled matrices from the inspected USTs.

Gaylarde, Bento, and Kelley report that trace nutrients in fuel may be limiting factors for bacterial growth.[8] The authors mention phosphorus as a likely limiting nutrient. In this respect it is noted that some additives may contain phosphorus. Trace elements were determined in the sampled fuels as presented in Appendix F.

5.6 Quality Assurance/Quality Control

Steps were taken to maintain the quality of data collected during this research effort. 100% of the acquired data were reviewed by the Battelle project manager, and a Battelle QA Manager audited at least 25% of the data acquired in this research effort. Finally, a second review performed by the Battelle QA Manager or designee traced the data from initial receipt from the laboratories, through reduction and comparisons, to final presentation in the report. Battelle did not receive or review the QC data from the laboratories (with the exception of the carboxylic acid, formic acid, and genomics data). The laboratories stated that the ASTM methods were followed and the criteria were met for the chemical analyses.

6. Discussion

6.1 Corrosion Inducing Factors

In order to understand why corrosion is occurring, an understanding of the relationships of the factors in the diesel UST environment is needed. Specifically, corrosion inducing factors are: a substrate that corrodes (UST equipment), a corrosive electrolyte, and a mechanism for the electrolyte to be disseminated onto the substrate surface, in addition to being influenced by microbiological activity.

6.1.1 UST Equipment Materials

Fuel storage and dispensing equipment is composed of a combination of materials including a variety of different carbon steels, austenitic stainless steels, ferritic stainless steels, cast irons, brasses, and cast aluminum alloys. The storage tanks are commonly fiberglass – as were all the tanks evaluated in this study – or steel with a small portion being fiberglass coated steel. This study examined fiberglass USTs. Each of these metals has its own distinct electrochemistry and corrosion susceptibility depending on the specifics of the environment. Additionally, some components may receive nickel coatings for corrosion resistance, while others may be coated with various epoxy, enamels, varnish rust inhibitors or lacquer topcoats. However, generally, increased acidity leads to increased corrosion damage accumulation and promotes depassivation of most of the materials used in USTs, see Appendix G.

6.1.2 Ingredients for an aggressive corrosive electrolyte

The ingredients for an aggressive electrolyte exist within the USTs inspected for this study. Namely, available water, oxygen, acids, and aggressive species create an environment that would be expected to attack most of the materials used in USTs. In addition, these environmental characteristics are specific to microbiological organisms that also contribute to the corrosive cycle in ULSD USTs.

Water Content and Availability - In the presence of an aqueous electrolyte, a susceptible metal may corrode. In this instance, water can be present either in solution with the diesel or as “free” water which exists as its own phase.[8] The water existing in solution with the diesel has little impact on corrosion or increasing the chances of MIC[9] - with measured concentrations in this study ranging from 29 to 65 ppm as shown in Table 9. However, the water accumulated at the bottom of storage tanks or in the vapor spaces can have catastrophic effects[7]. At the time of measurement, water existed in significant enough quantities on the tank bottoms to be sampled and the relative humidity of the vapor spaces were found to range from 72% to 95%. The high measured humidity is consistent with the observed corrosion in the vapor regions. It has been found that the time of wetness on a surface can increase significantly, leading to increased corrosion of steel in particular, when the relative humidity is above 80%.[10] Water accumulation and high relative humidity in tanks are common to the UST environment; however, in this case, it enables the acetic acid to sustain contact with the equipment for longer periods.

Water accumulation has been attributed broadly to three different sources: infiltration, temperature affected solubility, and condensation. Infiltration refers to the ingress of water from the outside environment through obvious physical routes, for example rain water entering through an opening to the system, the spill containment bucket being dumped into the tank, or with the fuel load being delivered from the tanker. Temperature and aromatic content are directly related to the amount of water diesel can hold in solution with warmer, more aromatic rich fuel being capable of holding higher concentrations of water. When the fuel is cooled, water in excess of the solubility limit will drop out of solution. Finally, condensation is considered to be a primary source of moisture in fuel storage tanks, which are vented to the atmosphere with condensate forming any time the temperature falls below the dew point. Although temperature fluctuations are relatively mild for USTs and the frequency of this happening would be related to the climate and season, the possibility for condensate still exists. The introduction of water into the system can occur any time warm fuel is added to a cooler tank – i.e., the transfer of fuel from a truck on a warm day to a UST.

The water samples were highly conductive ranging from 4,000 to 21,000 µS/cm, which is close to brackish water at approximately ~27,000 µS/cm. To cause corrosion, conductivity is needed to complete the circuit with aqueous electrolytes; however, measurements in line with ground water would have enough conductivity to do so (~300 µS/cm). Therefore, it is possible to have the observed corrosion in the ULSD USTs without having the high levels of conductivity found in the inspected USTs.

Oxygen - Based on actual oxygen solubility data for some model hydrocarbons, the solubility of oxygen gas in diesel fuel is estimated to be 200 to 300 mg/L.[11] This could be significant for supplying oxygen to aerobic bacteria. The dissolved oxygen could be, at least partially, replenished in the new loads of fuel. Each delivery requires the tank to be opened and fuel to be added. This churns the fuel in the storage tank and introduces air into the tank. The added fuel can bring with it a fresh supply of dissolved oxygen and dissolved water.

Acid Content – The presence of acids can accelerate corrosion and depassivate normally passive materials (in this case, the primary acids of concern were acetic and formic acids). Acetic acid appears to be the dominant acid species present among those species which were analyzed for and will be the focus of subsequent discussions. However, the concentration of acetic acid varied widely depending on whether considering the diesel fuel, water bottom, or vapor phase. In the fuel phase, acetate was detected to be between 2.7 and 7.7 ppm among the four sites in which acetate was present in detectable quantities – two locations were below the detection limit. Acetate/acetic acid values are summarized in Table 12. Additionally, although not a required test for ULSD specification, a gauge of diesel acidity was measured via TAN values, which were found to vary from 0.006 to 0.04 mg KOH/L.

Significantly larger concentrations of acetate were found to exist in the water bottoms as compared to the diesel fuel as summarized in Table 12. Depending on the site, acetate was found to exist in the water bottoms in concentrations ranging from approximately 9,000 to 22,500 ppm. pH values were also determined for each site and found to range from approximately 3.5 to 5.3.

Table 12. Summary of Acetic Acid/Acetate and Ethanol Concentrations in UST Systems Inspected

Acetic Acid/Acetate	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Fuel Ethanol (vol%)	0.04	0.01	0.17	0.06	ND	ND
Water Ethanol (vol%)	3.17	0.66	0.45	0.40	ND	0.04
Vapor Acetic Acid (ppmv)	0.57	1.8	3.6	7.8	9.5	16
Fuel Acetate (ppm)	<0.3	7.7	2.8	2.7	<0.3	5.9
Water Average Acetate (ppm)[a]	16,500	9,000	21,000	22,500	17,500	20,000

[a] average of 2 results from different laboratories
ND = Not detected

Aggressive Species – The presence of aggressive anionic species such as chlorides is also detrimental from a corrosion perspective. These species not only increase the conductivity of the solution but can act directly in breaking down passivity and passive films. In microenvironments, free hydrogen protons (H^+) can combine with available anions (Cl^-, NO_3^{-2}, SO_4^{-2}) to form strong acids that are also corrosive. High conductivity values and appreciable quantities of fluoride, chloride, and sulfate were observed at all locations in the water bottom samples and are summarized in Table 10. Additionally, nitrates, phosphates, and ammonium were observed at some but not all locations.

6.1.3 Electrolyte Distribution

The distribution of the electrolyte and the mode of contact between a metal and its environment have direct bearing on corrosion. Generically, within this case, three distinct regions exist in the storage tanks and along the STP. Depending on the region of the tank, materials could be constantly exposed to a bulk aqueous electrolyte, thin electrolyte layers, experience wetting and drying cycles, or periodic “washing” as the tank is emptied and refilled. The vapor space at the top of the tank theoretically does not see liquid fuel but exists at relatively high humidity. The tank bottom is constantly submerged unless drained off and would contain any water that drops out of the fuel. Finally, an intermediate region, which depending on tank fuel level, can either be submerged or exist in the vapor space.

Each region will experience a different set of conditions that will directly influence the type and extent of attack. In the vapor space corrosion could occur under thin electrolyte layers from a high relative ambient humidity or the condensate, readily available oxygen, and the presence of acetic acid in the vapor space. If these regions experience wetting and drying cycles, there is the potential to significantly concentrate aggressive anions and acidic species leading to much more corrosive conditions than experienced or measured in the bulk water bottoms. The intermediate region would effectively experience “washing” during tank filling. As the diesel level drops, these regions become exposed in a similar fashion as the vapor phase and it is plausible that residue and contaminants are left behind.

6.1.4 Microbial Presence

Microbial contamination of hydrocarbon-based fuels has been a well known problem for nearly half a century.[12] MIC is not in itself a distinct kind of corrosion, but rather a change to physical or chemical conditions that often accelerate other types of corrosion brought about by local environmental changes induced through microbial activity often associated with bacteria, algae, and fungi.[9,13] Microorganisms can produce and consume species involved in corrosion as well as produce a physical bio-film barrier which either directly or indirectly results in the formation of a bio-film composed of extracellular polymeric material, which causes heterogeneities on the surface and can lead to differential aeration and oxygen depleted zones, differences in diffusion, and concentration gradients of other chemical species.[9,13]

Generically, differences in aeration, diffusion, pH, or concentration gradients of other types can lead to a separation of anodic and cathodic reactions on a surface, which leads to aggressive localized pitting at the anode; this kind of pitting attack is classically associated with MIC on iron (Fe)-based alloys. Once the pit is established and if chlorides are present, the pit will grow independent of microbial activity through autocatalytic processes.[9] In these cases, insoluble $Fe(OH)_2$ corrosion products can combine with the bio-film to form a tubercule which itself can trap electrolytes and subsequently can become highly acidic or combine with chloride from the surrounding environment to form an aggressive ferric chloride solution.[13]

In this case, *Acetobactor* has been identified in the samples and need water, oxygen, and a energy source (ethanol) to thrive and to consequently produce acetic acid. The results from the chemical analyses show that all three components are present in the UST environment. In addition, even though *Acetobacter* are commonly found in the environment, the ULSD UST environment is selective for them. The amount of water needed for microbial proliferation is small and generally the growth of aerobic bacteria and fungi which are likely at play in this instance grow at the interface between the fuel and water.[12] The final component is if ethanol is readily contaminating diesel fuel and whether there is enough ethanol to produce the abundant acetic acid to cause the severe and rapid corrosion.

Ethanol contamination – Fuel distribution systems supply and handle other fuels in addition to diesel, such as gasoline, jet fuel, and ethanol. Diesel fuel is shipped in the same pipelines as gasoline and jet fuel. More importantly, ethanol is specifically kept separate from gasoline until blended in the tanker trucks. Since trucks may transport and switch between all fuels from 0 to 100 percent ethanol, it is possible that there be some cross contamination from the fuels and vapors. Because nearly all gasoline sold in the U.S. now contains 10 percent ethanol, it is not surprising that small amounts of ethanol were found in most of the diesel fuel and subsequent water bottom samples as shown in Table 12. However, further study is required to establish this causal link.

Another source of potential ethanol contamination is through common manifolded ventilation systems. At times, gasoline USTs are converted to diesel service with ventilation systems still connected to other gasoline USTs on site. Ethanol and gasoline have higher vapor pressures than diesel; therefore, vapors may collect in the ullage of the gasoline tanks and be forced back into the ULSD tank contaminating the system.

As mentioned earlier, ethanol was used to decontaminate the sampling equipment at the end of each inspection. It was rinsed and allowed to dry before the next inspection. Throughout the six inspections, the fuel sample was taken from the center of the fuel column then the water sample was taken from different riser pipes of the tank. The concentrations indicate that there was a higher percentage of ethanol in the water samples than in the respective fuel samples. The likelihood of ethanol contamination from the sampling process is low.

Ethanol has an affinity to water; therefore, if the fuel is being dropped with some contamination, the ethanol will migrate into the water bottom. This is also indicated by the ethanol concentrations measured in this study. Site NC-1 received a biocide treatment soon before the inspection. The DNA yields for the genomic analysis were low, as expected. In addition, the ethanol concentration in the water bottom was much higher than the others (~3%). Presumably, the ethanol is collecting in the water bottom to be metabolized if the tank becomes contaminated with *Acetobacter* again. Inversely, the CA-2 had the most measureable amounts of *Acetobacter* and ethanol was not detected in the fuel or water. Understanding how ethanol contamination is happening and what levels are occurring in the USTs of ULSD is a topic for further research.

Feasibility-The presence of acetic acid in high concentration in the vapor sampled from the tanks, as well as the concentration of acetate in the water bottoms, suggest that acetic acid may be reacting with the iron to produce the scale and corrosion. This section will examine whether it is possible for the corrosion product to have resulted from the reaction of steel or iron with the acetic acid in the tank. This requires determining whether it is possible to create enough acetic acid to cause the corrosion, and whether this amount of acetic acid can be created in a timeframe consistent with the observations.

Analysis of the scale sampled from the tanks showed the likely presence of multiple compounds. One compound that was identified in scale samples is iron acetate, which is formed by the reaction of acetic acid with iron, although iron acetate is not the only product resulting from the reaction of acetic acid with iron or steel. To set an upper bound on the amount of acetic acid required, it is assumed there is 1 kg of scale or corrosion in the tank and that the scale is composed solely of iron(III) acetate, $[Fe_3O(OAc)_6(H_2O)_3]^+ OAc^-$. The molecular weight of iron(III) acetate is 650 g/mol, so 1 kg would equal 1.54 mole. Formation of 1.54 mole of iron(III) acetate would require 10.8 mol or 650 g of acetic acid (MW=60 g/mol).

The presence of *Acetobacter* in the tank samples suggests that ethanol is being converted to acetic acid. One of the most common reaction pathways for acetic acid production requires one mole of ethanol per mole of acetic acid. The 10.8 mol of ethanol equates to about 500 g (46 g/mol), and at a density of 0.789 g/cm^3, this is about 0.63 liter of ethanol. Assuming a 5000 gallon diesel tank (18,950 liter), this is equivalent to an ethanol concentration of 0.0033% by volume or 33 ppmv. The ethanol contamination measured in the water bottoms was higher than this calculated concentration, ranging from 0.04 % to 3.17%.

The above discussion shows it is feasible for the corrosion to be formed from acetic acid reacting with the iron or steel surface, if the acetic acid can be generated rapidly enough by the *Acetobacter*. A previously published paper measured the acetic acid production by *Acetobacter* in the presence of ethanol.[14] The acetic acid production rate was controlled by the O_2 concentration in the reactor, as the primary mechanism is the reaction of ethanol and oxygen to produce acetic acid and water.

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$$

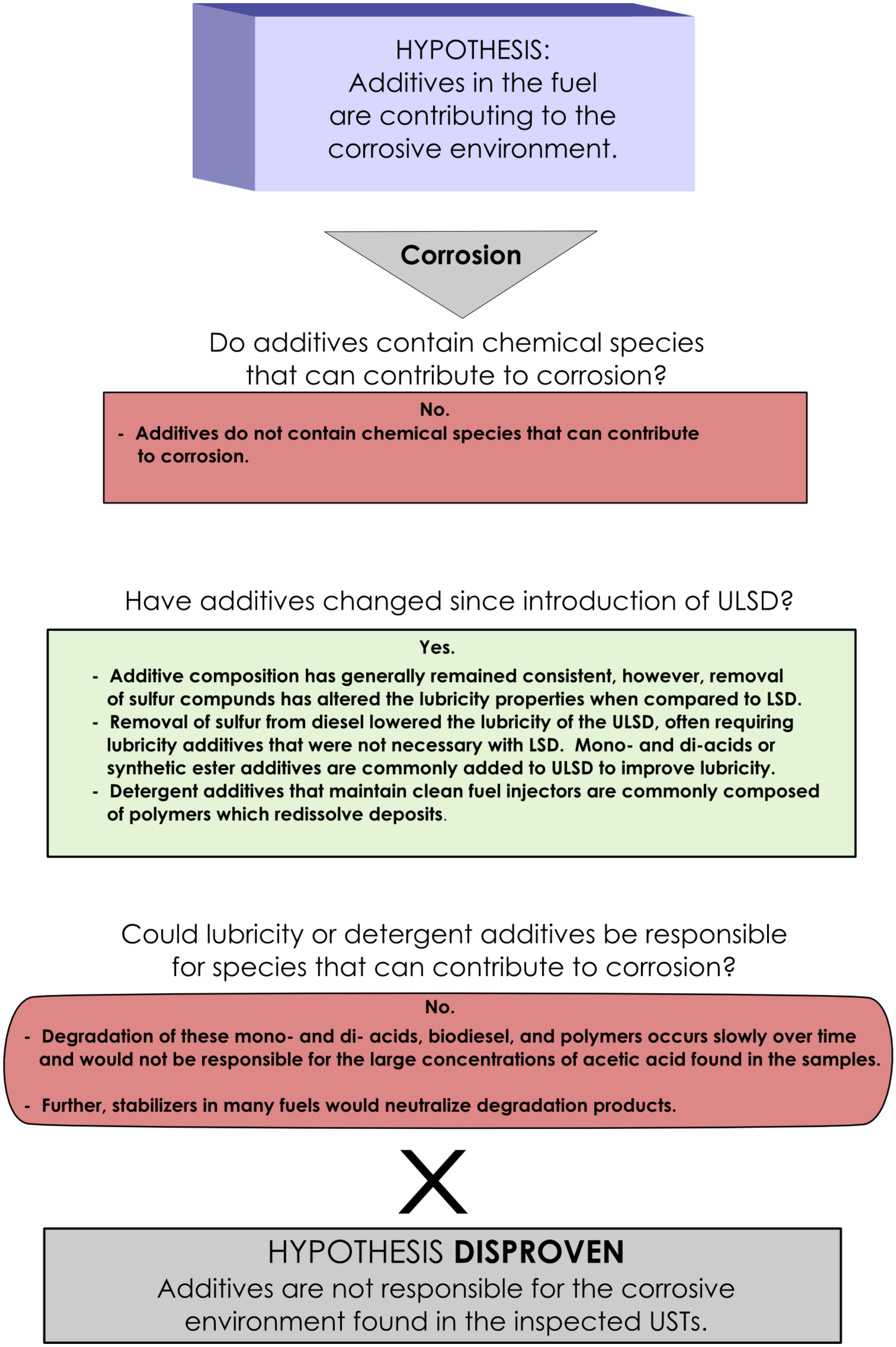
The paper reported the acetic acid production was steady at 4.55 g/Lh for 27 g (dry weight) of *Acetobacter* in a 1-L reactor. Based on this performance, producing 600 g of acetic in the course of one week (144 hours) would require less than 27 g dry weight of *Acetobacter*, if there is sufficient O_2 and ethanol. *Therefore, with the low levels of ethanol contamination and given enough oxygen, it is feasible for the equipment to be corroding as severely and rapidly as observed and reported.*

6.2 Hypotheses Evaluations

6.2.1 Additive Hypothesis Evaluation

One of the three working hypotheses stated that additives in the diesel fuel were causing the corrosion observed in UST systems. The analysis of the fuel and water bottoms showed the presence of some of the classes of chemicals associated with the additives present in ULSD.

The analysis of the fuel, water bottoms, and vapor phase also showed the presence of acetic acid in large quantities. From the literature search and discussions with additive manufacturers, there is no reason for acetic acid to purposely be added to diesel fuel. To be present in the tank at the concentrations measured, the acetic acid would have to be a significant component (or reaction product) of the fuel additive. There is minimal use of ethanol in additives and they are not widely or consistently used. For these reasons, the additives hypothesis is not believed to cause the severe and rapid corrosion occurring in UST systems storing and dispensing ULSD (Figure 2).



HYPOTHESIS:
Additives in the fuel
are contributing to the
corrosive environment.

Corrosion

Do additives contain chemical species
that can contribute to corrosion?

No.

- **Additives do not contain chemical species that can contribute to corrosion.**

Have additives changed since introduction of ULSD?

Yes.

- **Additive composition has generally remained consistent, however, removal of sulfur compunds has altered the lubricity properties when compared to LSD.**
- **Removal of sulfur from diesel lowered the lubricity of the ULSD, often requiring lubricity additives that were not necessary with LSD. Mono- and di-acids or synthetic ester additives are commonly added to ULSD to improve lubricity.**
- **Detergent additives that maintain clean fuel injectors are commonly composed of polymers which redissolve deposits**.

Could lubricity or detergent additives be responsible
for species that can contribute to corrosion?

No.

- **Degradation of these mono- and di- acids, biodiesel, and polymers occurs slowly over time and would not be responsible for the large concentrations of acetic acid found in the samples.**
- **Further, stabilizers in many fuels would neutralize degradation products.**

X

HYPOTHESIS **DISPROVEN**
Additives are not responsible for the corrosive
environment found in the inspected USTs.

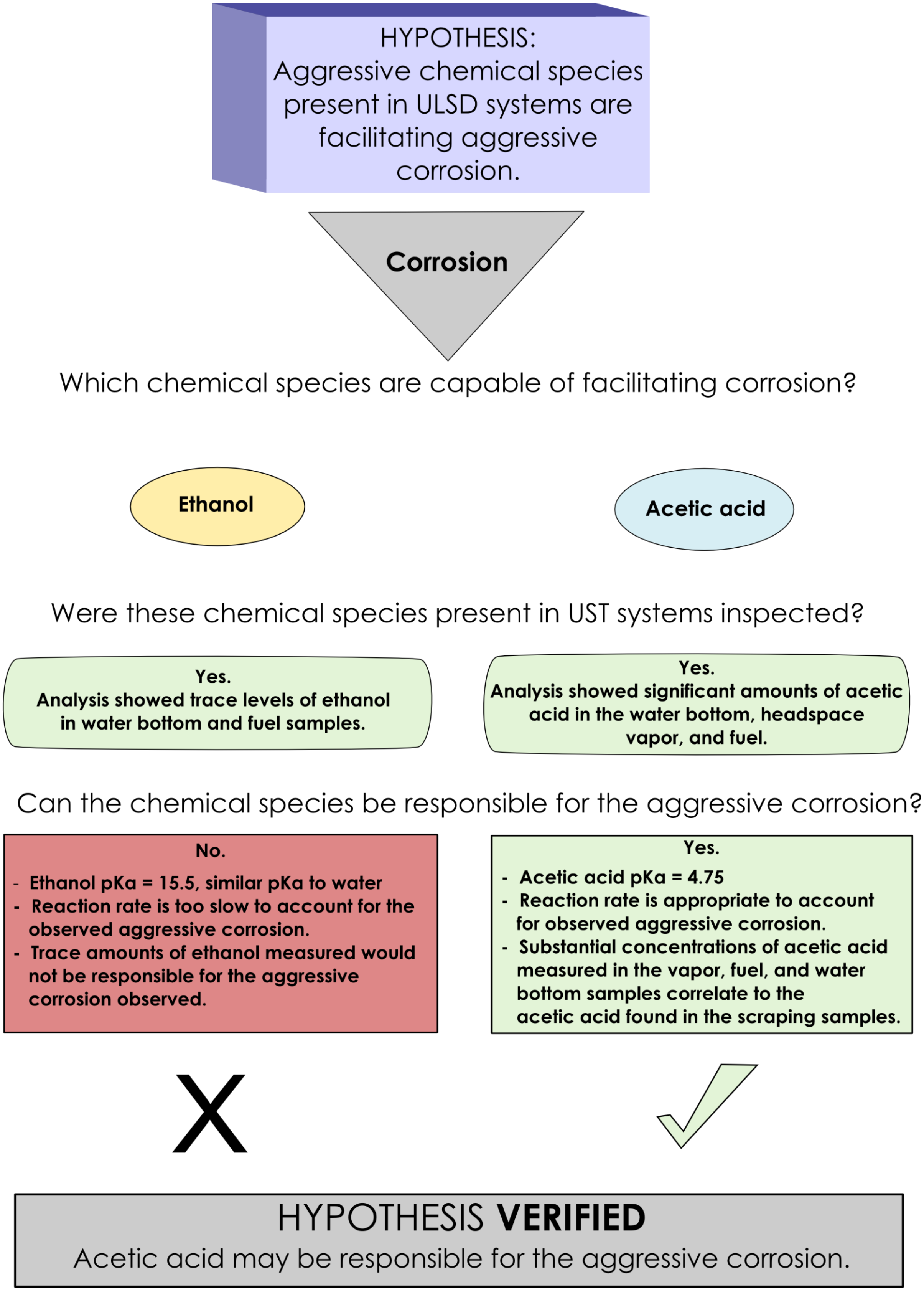
Figure 2. Additives Hypothesis Evaluation

6.2.2 Chemical Species Hypothesis Evaluation

Ethanol and acetic acid were the two potential agents identified in the samples from the site inspections as possibly being responsible for the severe and rapid corrosion.

Ethanol is known to influence corrosion to many of the materials used in fuel delivery infrastructure especially in the presence of water, oxygen and aggressive ions. For this reason, it is blended with other fuels downstream to avoid concerns of possible corrosion during transport through pipelines. Detectable quantities of ethanol were determined in the majority of the liquid samples from this study, and may contribute to the corrosion; however, in this case, any contribution is believed to be minimal for two reasons. In gasoline systems, ethanol is present in significant quantities of 5, 10, or even 85 percent total volume as compared to being available in ppm-type concentrations in the diesel USTs. Second, the pKa of ethanol is ~15.5 and is significantly smaller than the pKa of some of the other aggressive species such as acetic acid (discussed below) with a pKa of ~4.75, which are more likely reasons for the corrosion.[18] Although not the only factor in terms of acidifying the solution and corrosion, other species play a much larger role than ethanol potentially does.

As previously discussed in Section 6.1.2, acetic acid was found in the majority of the samples at all of the inspection sites. With the low pKa, the disassociation of the acid is at a rate that could account for the aggressive corrosion. For these reasons, the chemical hypothesis is accepted with respect to acetic acid and not accepted with respect to ethanol (Figure 3).



HYPOTHESIS:
Aggressive chemical species present in ULSD systems are facilitating aggressive corrosion.

Corrosion

Which chemical species are capable of facilitating corrosion?

Ethanol

Acetic acid

Were these chemical species present in UST systems inspected?

Yes.
Analysis showed trace levels of ethanol in water bottom and fuel samples.

Yes.
Analysis showed significant amounts of acetic acid in the water bottom, headspace vapor, and fuel.

Can the chemical species be responsible for the aggressive corrosion?

No.

- **Ethanol pKa = 15.5, similar pKa to water**
- **Reaction rate is too slow to account for the observed aggressive corrosion.**
- **Trace amounts of ethanol measured would not be responsible for the aggressive corrosion observed.**

Yes.

- **Acetic acid pKa = 4.75**
- **Reaction rate is appropriate to account for observed aggressive corrosion.**
- **Substantial concentrations of acetic acid measured in the vapor, fuel, and water bottom samples correlate to the acetic acid found in the scraping samples.**

X

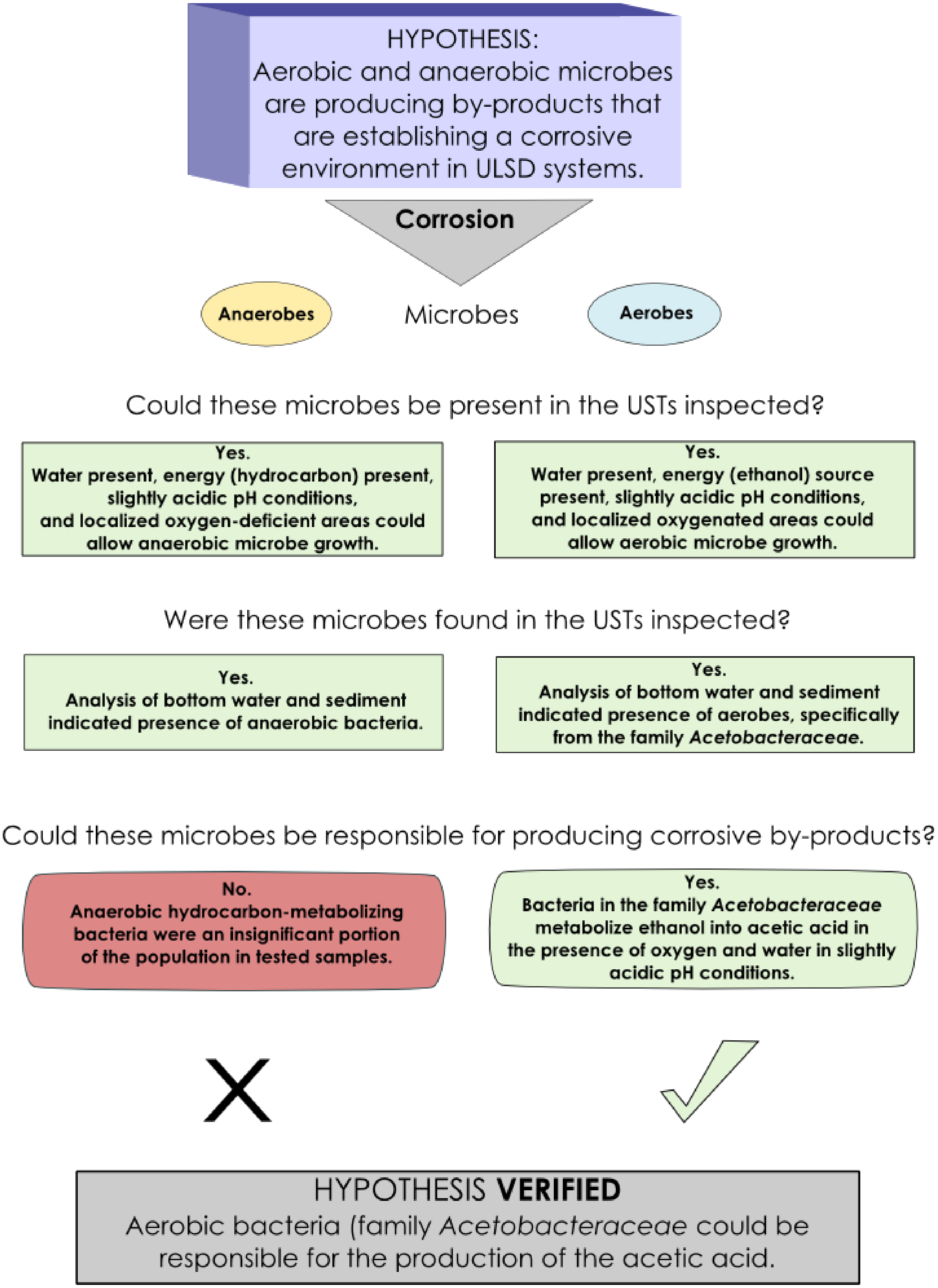
✓

HYPOTHESIS **VERIFIED**
Acetic acid may be responsible for the aggressive corrosion.

Figure 3. Aggressive Chemical Species Hypothesis Evaluation

6.2.3 Microbial Hypothesis Evaluation

All of the sites inspected in this research project contained microbes, although at different abundances. The dominant organisms identified from three of the sites have characteristics pertinent to the corrosion observed in all of the sites, such as acetic acid production, ethanol utilization, low pH requirements, environmental presence, and oxygen. Although geographically on opposite sides of the country, with different fuel supplies and from relatively new construction materials, the presence of the organisms was relatively uniform. The traditionally expected organisms were found in insignificant abundances. Anaerobic organisms ranged from 0% to 6% and hydrocarbon degrading organisms from the *Gammaproteobacteria* class ranged from 0.3% to 5% in the samples analyzed. This indicates that ULSD USTs are selective environments for these specialized, acetic acid producing organisms. Therefore, as shown in Figure 4, the microbial hypothesis is accepted with respect to aerobic microbes but rejected with respect to anaerobic microbes.



HYPOTHESIS:
Aerobic and anaerobic microbes are producing by-products that are establishing a corrosive environment in ULSD systems.

Could these microbes be present in the USTs inspected?

Yes.
Water present, energy (hydrocarbon) present, slightly acidic pH conditions, and localized oxygen-deficient areas could allow anaerobic microbe growth.

Yes.
Water present, energy (ethanol) source present, slightly acidic pH conditions, and localized oxygenated areas could allow aerobic microbe growth.

Were these microbes found in the USTs inspected?

Yes.
Analysis of bottom water and sediment indicated presence of anaerobic bacteria.

Yes.
Analysis of bottom water and sediment indicated presence of aerobes, specifically from the family *Acetobacteraceae*.

Could these microbes be responsible for producing corrosive by-products?

No.
Anaerobic hydrocarbon-metabolizing bacteria were an insignificant portion of the population in tested samples.

Yes.
Bacteria in the family *Acetobacteraceae* metabolize ethanol into acetic acid in the presence of oxygen and water in slightly acidic pH conditions.

HYPOTHESIS **VERIFIED**
Aerobic bacteria (family *Acetobacteraceae* could be responsible for the production of the acetic acid.

Figure 4. MIC Hypothesis Evaluation

7. Conclusions

From this hypotheses evaluation, the following has been concluded:

- Bacteria of the acetic acid producing family (*Acetobacteraceae*) were prevalent at three inspection sites. These are organisms that characteristically require oxygen and utilize ethanol as an energy source. Oxygen and ethanol were identified in the USTs inspected.
- The evaluation of hydrocarbon degradation suggests that the hydrocarbons contained within the diesel fuel may not be the primary carbon source for the consortium of bacteria present (0.3% to 5%).
- There are both less overall unique organisms present in the community and, of those present, there are limited species that dominate the community within the USTs surveyed. This is further evidence that the conditions of the ULSD tanks are conducive to growth of limited, specialized organisms.
- Geographically separate sites had some observable differences in abundance of select organisms and the presence of organisms was relatively uniform. This suggests that the ULSD system is selective for specialized organisms capable of thriving in these environments, rather than a site specific or environmental effect driving the composition of microbial population.
- Acetic acid appears to be the dominant acid species. It was measured in all vapor samples. Acetate was measured in all water samples and four of six fuel samples.
- Acetic acid was identified in 75% of the scrape samples. The scrape sample results support the conclusion that the internal components made up of different metals are deteriorating in ULSD USTs.
- In general, the *Acetobacteraceae* organisms typed from the four samples (from three of the sites) have characteristics pertinent to the corrosion formation, such as acetic acid production, ethanol utilization, low pH requirements, environmental presence, and oxygen.
- Ethanol was unexpectedly identified and measured in four of the six fuel samples and five of the six water samples, suggesting ethanol is contaminating the fuel.
- The source of ethanol is unknown; however, diesel fuel is often delivered in the same trucks as ethanol-blended gasoline. Also, ULSD USTs that have been converted from a gasoline tank could have manifolded ventilation systems with gasoline tanks. Thus, it is possible that there be some cross contamination of ethanol into ULSD.
- With the low levels of ethanol contamination and given enough oxygen, it is feasible for the equipment to be corroding as severely and rapidly as observed in this study and reported from industry representatives.
- Materials could be constantly exposed to a bulk aqueous electrolyte, thin electrolyte layers, experience wetting and drying cycles, or periodic “washing” as the tank is emptied and refilled.

This project was designed to objectively investigate multiple hypotheses as to why ULSD USTs have been experiencing severe and rapid corrosion. The in-depth site inspections were performed on a limited number of sites and therefore may not be representative all of systems experiencing this phenomenon. Although it cannot be stated with statistical significance, ingredients necessary for the observed and chemically determined corrosion in this environment were present at the inspected sites. The above conclusions and Figure 5 summarize the supporting evidence and the final hypothesis for this project. The most obvious issues causing this problem were the focus of this research and the development of corrosion at different sites could also be influenced by other factors (environmental, geographical, seasonal, etc.) not discussed in this report.

Battelle recommends continued research into this issue. The hypothesis derived in this study should be investigated with a larger and more diverse sample set and should use a longitudinal design (where sites would be sampled multiple times over a period of time). In particular, steel USTs and tanks without issue should be investigated. This study could not compare the findings to a non-symptomatic site due to the difficulty finding one. Also, the source and magnitude of ethanol contamination should be determined.

In conclusion, the project final hypothesis is that corrosion in systems storing and dispensing ULSD is likely due to the dispersal of acetic acid throughout USTs. It is likely produced by *Acetobacter* bacteria feeding on low levels of ethanol contamination. Dispersed into the humid vapor space by the higher vapor pressure and by disturbances during fuel deliveries, acetic acid is deposited throughout the system. This results in a cycle of wetting and drying of the equipment concentrating the acetic acid on the metallic equipment and corroding it quite severely and rapidly.

FINAL HYPOTHESIS:
Aerobic microbes are producing acetic acid which is being dispersed into the humid vapor space coating and re-coating the UST equipment. This process concentrates the acetic acid on the equipment, resulting in severe and rapid corrosion.

Acetic acid is a corrosive species found in appreciable concentrations in vapor, fuel, and water bottom samples from the inspected USTs. Further, it was found in the chemical analysis of the corrosion scraping samples.

Did conditions exist for aerobic microbes that produce acetic acid?

Yes.
Oxygenated areas, water, and slightly acidic pH conditions were in all USTs inspected.
Ethanol (energy source) was found in 5 of 6 USTs inspected.

Were these microbes found in the USTs inspected?

Yes.
Analysis of water bottoms with sufficient extractable DNA indicated presence of aerobes, specifically from the family *Acetobacteraceae*.

Could these microbes be responsible for the acetic acid and corrosion?

Yes.
Research conducted by Ghommidh, Navarro, and Durand indicates that with sufficient ethanol and oxygen, approximately 27 grams of Acetobacter can produce approximately 600 grams of acetic acid in one week. This quantity of acetic acid is sufficient to form approximately 920 grams of iron (III) acetate (corrosion).

Are USTs suitable environments for these microbes?

Yes.
The low diversity of microbes seen in the collected samples indicates the UST diesel environment is selective for the microbes given the energy source (ethanol), oxygen, and water.

- ***Ethanol* could enter the UST in diesel fuel that has come in contact with fuels containing ethanol. Shipping tankers commonly carry ethanol fuels, jet fuels, and diesel fuels, where cross-contamination of fuel and vapor is possible. Common manifolded ventilation systems could also force gasoline and ethanol vapors into ULSD tanks.**

- ***Oxygen* enters the UST environment during fuel deliveries and as ambient air displaces fuel during fuel dispensing. Solubility of oxygen in water at 20°C is approximately 9.0 mg/L and in diesel fuel is estimated to be 200-300 mg/L.**

- ***Water* can enter the UST environment via condensation from air displacing fuel removed during dispensing, dissolved in the fuel, or from surface water entering the UST.**

Is there a mechanism to disperse the acetic acid to the vapor phase?

Yes.
- **Turbulence in the UST liquids (fuel and water bottom) during fuel delivery can mix and splash water containing acetic acid to the vapor portion of the UST.**
- **Acetic acid produced in the water layer has a higher vapor pressure than diesel fuel and can migrate through the fuel into the vapor phase.**

Figure 5. Final Hypothesis

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Appendix A

Phase 1 Hypotheses Evaluation Table

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Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD)

Working Hypotheses Prioritization Table

May 20, 2011

NOTE: This table shows the discussion and prioritization of the initial hypotheses posed by the industry representatives. The information has not been verified.

Hypotheses	Supporting Discussion	Recommendations for Investigation
Keep These Hypotheses for Further Investigation		
Aerobic and anaerobic microbes producing corrosive byproducts	• Anaerobic and aerobic microbes have been identified in ULSD fuel samples from an affected tank. • Bacteria were determined by Deoxyribonucleic acid (DNA) sequences (genetic signatures). The Lactobacillus (anaerobic microbe) was identified in this sample as a minor contributor at 2% of the sample and Acetobacter (aerobic microbe) which produces acetic acid represents 91% of the sample. • Lactobacillus has been able to be cultured repeatedly from fuel samples. • Evidence of micro-crystalline structures suggests that there is a cycle between aerobic and anaerobic environments in the storage tanks. • The aerobic strain of Acetobacter converts free ethanol into acetic acid as part of its metabolic cycle. • Fuel throughput/fuel delivery frequency is suspected to be related to corrosion. Tanks with too few (less chance for contamination) or too many (less chance for blooms) fuel drops would not be as affected, as tanks with fuel throughput in an unknown range in the middle could be ideal for microbial growth and/or contamination. • The fuel drops within an unknown fuel drop frequency range could disturb the fuel by aerating and/or mixing the fuel (and possibly water) producing an environment that would help or hinder microbial growth. • Fuel drops can change the temperature of the fuel that could increase or decrease microbial metabolism. • Throughput was loosely connected to tank capacity in the statistical analysis of the Tanknology data. Although this may not be the best surrogate variable to use for throughput, increasing tank capacity was determined to be statistically significant in the probability of line leak detector failures. • Sulfur reducing bacteria (SRB) are known to inhabit fuel and be present with other aerobic bacteria by forming an encasement as protection in aerobic environments. SRB are known to be extremely corrosive and aggressive.	This hypothesis is considered a working hypothesis to be further investigated. • Identify bacteria through laboratory analysis in fuel samples from affected tanks, specifically Lactobacillus, Acetobacter, and SRB. • Investigate the potential food sources of the bacteria suspected to be related to the cause of the corrosion. • Survey operators/owners of sampled sites to gather data relative to microbial contamination, for example the progression/symptoms and rate of the corrosion, fuel throughput and drop frequency, corrective action taken and water bottom history. • Follow-on sampling and questioning of all or a subset of sites. • Investigate the life cycle of bacteria identified in the fuel using literature, survey results, and other site inspection data that would characterize the corrosive environment.

Hypotheses	Supporting Discussion	Recommendations for Investigation
		• Design and perform bench experiments to investigate conclusions from the above bullets.
Microbiological corrosion for unknown reasons	• Vehicle tank data are directly related to ULSD corrosion outcomes and concluded that the eastern portion of the United States has a higher ratio of replacement parts due to corrosion per capita. (Is vehicle data robust enough for this comparison and are data still being collected?) • Anti-microbial solutions have been reported to be used to minimize the corrosive effects once the coffee-ground like substance clogs the filters.	This is a broad hypothesis that is focused to microbes producing corrosive byproducts. • If the data are robust enough, further analysis of vehicle tank data and validation of assumptions.
Acetic acid has been shown to be present in fuel, but not known why	• Acetic acid has been determined from service station fuel samples by standard analytical methods to range from 1.5 ppm to 18 ppm. • Acetic acid has been determined from vehicle fuel tank samples by standard analytical methods from 19 to 24 ppm. • The source of acetic acid is unknown, but supplier testing has shown that acetic acid will corrode vehicle fuel tanks. • Microbes (specifically Acetobacter) can produce acetic acid as a by-product of their metabolism. • It has been reported that the unwetted portions of the tank and equipment are affected by corrosion before the wetted portions of the tanks and equipment. • Acetic acid has a high vapor pressure, especially relative to the components in diesel fuel. Therefore, the acetic acid would be more highly concentrated into the vapor phase and become a form of acetic acid/water solution. The unwetted portions of tanks and components are exposed to this corrosive vapor. • The tanks are usually vented to the atmosphere. The time the corrosive vapors remain in the headspace could alter the concentration of the vapors and could be related to the fuel throughput. • Many underground tanks are constructed of fiberglass or of steel lined internally with fiberglass. Some unlined steel tanks contain fiberglass patches to repair leaks. Water often is present at the bottom of some retail diesel storage tanks (we know of some cases where for various reasons that water has remained for long periods of time). Numerous reports[1-5] for other industries describe the penetration of fiberglass by water, and some of these show a consequential release of acetic acid into the water. This has been an issue in various industries, including boating[1,4]. Possible mechanisms proposed for production of acetic acid include the hydrolysis of ethyl acetate, which is used as a binder for glass fibers and also a sizing material in the resin.	This hypothesis is considered a working hypothesis to be further investigated. • Definitively identify and determine range of concentrations of acetic acid in fuel and in fuel head space by sampling tanks with corrosion issues. • Survey operators/owners of sampled sites to gather data relative to potential sources of acetic acid, for example the progression/symptoms and rate of the corrosion, fuel throughput and drop frequency, corrective action taken, and water bottom history. • Follow-on sampling and questioning of all or a subset of sites. • Perform literature search for potential sources of acetic acid in ULSD distribution and storing systems. • Design and perform bench experiments using data gathered from literature search and field sampling.

Hypotheses	Supporting Discussion	Recommendations for Investigation
	- In cases where unusual diesel equipment corrosion or fouling was observed, the fouling deposits consisted of a mixture of rust and ferric acetate. Acetic acid was confirmed in tank water bottoms; the pH varied from 3 to 6. Ferric acetate was found in the water bottoms, together with glycols that could not be traced back to the terminals or refineries but are known to be present in some types of fiberglass resin (either as free glycol or bound in a hydrolysable ester). Other materials found were various minerals, sometimes at unusual levels, which we think may have come from the action of acetic acid on glass fibers, fillers and other components of the laminate. Significant microbial activity has been observed at pH 5-6, but only a negligible amount has been observed below a pH of 4.5. At the lowest pHs the environment was absent of microbial activity.	- Design and perform bench experiments to investigate the interaction of water with fiberglass laminate as a source of acetic acid.
Fuel additive causing an unexpected reaction	- The compositional difference between low sulfur diesel (LSD) and ULSD lies in the removal of some specific sulfur-containing compounds from the refining stream, not the intentional inclusion of any new categories of molecules. So any unexpected reaction between a fuel additive and ULSD could also have occurred previously between the fuel additive and LSD. - Overall, different additives are being used for lubricity, conductivity, and corrosion inhibition in ULSD that were not needed in LSD. - Alkali ions in corrosion inhibitors used in LSD have become ineffective and have been reformulated for ULSD. - ULSD has lower solubility with the corrosion inhibitors used with LSD. These were reformulated. - Overdosing of corrosion inhibitor could cause corrosion.	This hypothesis is considered a working hypothesis to be further investigated. - Perform literature search for similar and different additives between LSD and ULSD. - Design and perform bench experiments with common equipment pieces exposed to ULSD with suspect additives identified in the literature searches or in fuel samples.
Possibly Keep These Hypotheses for Further Investigation		
Decreased sulfur content allowed increased growth of microbes	- Lower sulfur content may contribute to a more conducive environment for microbial growth, but this would be secondary to the main working hypothesis as it does not introduce a food source for microbes or a microbe contamination source. - SRB is known to be present in sulfur containing fuel. It is unknown whether the reduced amount of sulfur in ULSD is enough of a food source to cause the corrosion issues.	- Bulk storage tanks for heating oil (either above or underground) could be investigated as a tank population that could elucidate the differences between LSD and ULSD.
Hydrogen Sulfide present in fuel in extremely small quantities	- Hydrogen sulfide has been identified in ULSD in very low amounts. - The hydrogen sulfide must obtain a sulfur atom from the small amounts of sulfur present in ULSD. Hydrogen sulfide is produced, and it has a high vapor pressure that condenses into the vapor phase of the storage vessel. This vapor is more concentrated and corrosive in the vapor phase, which could lead to accelerated corrosion. - The differences in processing and additives between ULSD and LSD might have masked issues with corrosive hydrogen sulfide with LSD. - Hydrogen sulfide is a product of the hydrotreating process. It is removed/stripped from the fuel but could remain at ppm levels. Tested with the commonly used copper strip test.	- Identify and determine the range of concentrations of hydrogen sulfide in fuel and in head space by sampling of tanks with corrosion issues. - Survey operators/owners of sampled sites to gather data relative to potential sources of hydrogen sulfide, for example the

Hypotheses	Supporting Discussion	Recommendations for Investigation
	• If the fuel passes National Association of Corrosion Engineers (NACE) corrosion test, it should not be corrosive, but could contain low levels of sulfur as a source of food for SRB.	progression/symptoms and rate of the corrosion, fuel throughput and drop frequency, corrective action taken and water bottom history. • Possibly, the same samples for the acetic acid investigation could be used for this analysis and extra questions could be added to the survey to collect these data.
Do Not Keep These Hypotheses for Further Investigation		
Reaction of biodiesel (up to 5%) added to ULSD produces acetic and formic acids	• The inclusion of biodiesel as a means to enhance the lubricity could lead to many of the corrosion and filter clogging issues reported since the introduction of ULSD. • Biodiesel is also known to have less oxidative and thermal stability than conventional diesel. There are several ways in which the FAME or FAEE can react to form other molecules. In the presence of a free alcohol, the methyl ester can participate in a transesterification reaction, to yield free methanol or ethanol. This reaction can be catalyzed by acid. • The FAME or FAEE can also undergo hydrolysis in the presence of water. This hydrolysis reaction leads to the production of methanol or ethanol, and free acid, which can act to further catalyze the hydrolysis reaction. The rate for the hydrolysis reaction can be increased by elevated temperature or the presence of catalysts, such as acids. In the case of FAME, the decomposition product is formic acid, while in the case of FAEE, the decomposition product is acetic acid. • A third possible reaction involving FAME or FAEE utilizes O_2 from the ambient environment to form reactive intermediates	This hypothesis is viewed as unlikely and will not be investigated at this time. • Investigate the reactions that could produce corrosive acids. • Investigate the prevalence of biodiesel in ULSD, or whether there are regional differences in the loading.
Diesel fuel not properly processed	• It is possible to envision cases when there would be improper processing of the diesel, or there was a contaminant introduced at some point in the processing that was carried along. Improper processing would be a localized to a single refinery, and likely localized in time. The analysis of the data in Section 5 of the Phase 1 report, along with the general feedback, provides some indication that the leak detector failures are tied to geographical regions; however, with respect to pre and post introduction of ULSD, there is a 1% increased probability for equipment failure before the introduction of ULSD. If there were issues with processing or contamination, there we would expect a stronger indication of a more affected region and a higher probability of failure post 2006. • The general process for refining ULSD is similar to the process for refining diesel. The major differences center on the reactor conditions or amount of catalyst used during the hydrotreating steps. However, the general hydrotreatment step is already part of the process used in creating	This hypothesis is viewed as unlikely and will not be investigated at this time.

Hypotheses	Supporting Discussion	Recommendations for Investigation
	LSD.	
Corrosive carryover when refining fuel	Same as: Diesel fuel not properly processed	This hypothesis is viewed as unlikely and will not be investigated at this time.
Galvanic reaction from dissimilar metals	• Although there will be corrosion at any junction between two dissimilar metals, there is nothing in the compositional difference between LSD and ULSD that would hasten this galvanic reaction. • The fuel additive or the incorporation of biodiesel into the ULSD could provide a means to enhance this galvanic reaction by providing materials that could act as an electrolyte. In both these cases, this reaction would be viewed as a secondary, not primary, cause of the degradation.	This hypothesis is viewed as unlikely and will not be investigated at this time. • Differences in conductivity and water solubility can be determined when examining the suitability of ULSD for microbial growth.
Dispenser grounding issues	• The inherent compositional difference between LSD and ULSD by itself would not change any problems caused by improperly grounding a tank; however, the fuel additive or the incorporation of biodiesel into the ULSD could provide a means to enhance this effect.	This hypothesis is viewed as unlikely and will not be investigated at this time. • Differences in conductivity and water solubility can be determined when examining the suitability of ULSD for microbial growth.
Increased water bottoms due to ULSD	• An increased water bottom could enhance the conditions for bacterial growth and could lead to enhanced corrosion at the tank bottom, but would likely not directly cause most of the reported issues as they are not focused on the bottom of the tank. • This could be a condition enhancing one of the other hypotheses, but is likely not the primary origin of the corrosion and equipment issues.	This hypothesis is viewed as unlikely and will not be investigated at this time.

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Appendix B

Inspection and Sample Handling Protocol

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Quality Assurance Project Plan

Investigation of Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel

Prepared for
Clean Diesel Fuel Alliance

American Petroleum Institute Contract 2011-105589

Prepared by
Battelle Memorial Institute

January 18, 2012

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A1 TITLE AND APPROVAL PAGE

Quality Assurance Project Plan
for
Investigation of Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel

1-24-12

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A3 LIST OF ABBREVIATIONS/ACRONYMS

ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	ASTM (American Society for Testing and Materials) International
CDFA	Clean Diesel Fuel Alliance
COC	Chain of Custody
DQO	Data Quality Objective
EPA	Environmental Protection Agency
L	liter
Lpm	liters per minute
LRB	Laboratory Record Book
LSD	Low Sulfur Diesel
mL	milliliter
NACE	National Association of Corrosion Engineers
NIST	National Institute of Standards and Technology
PEI	Petroleum Equipment Institute
PM	Project Manager
ppm	parts per million
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RMO	Records Management Office
SOP	Standard Operating Procedure
ULSD	Ultra Low Sulfur Diesel
UST	Underground Storage Tank

A4 DISTRIBUTION LIST

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A5 PROJECT ORGANIZATION

Battelle will perform this project under the direction of the Clean Diesel Fuel Alliance (CDFA) through American Petroleum Institute's (API) Contract 2011-105589. The organization chart in Figure 1 shows the individuals from Battelle and API who will have responsibilities during this project. The specific responsibilities of these individuals are summarized below.

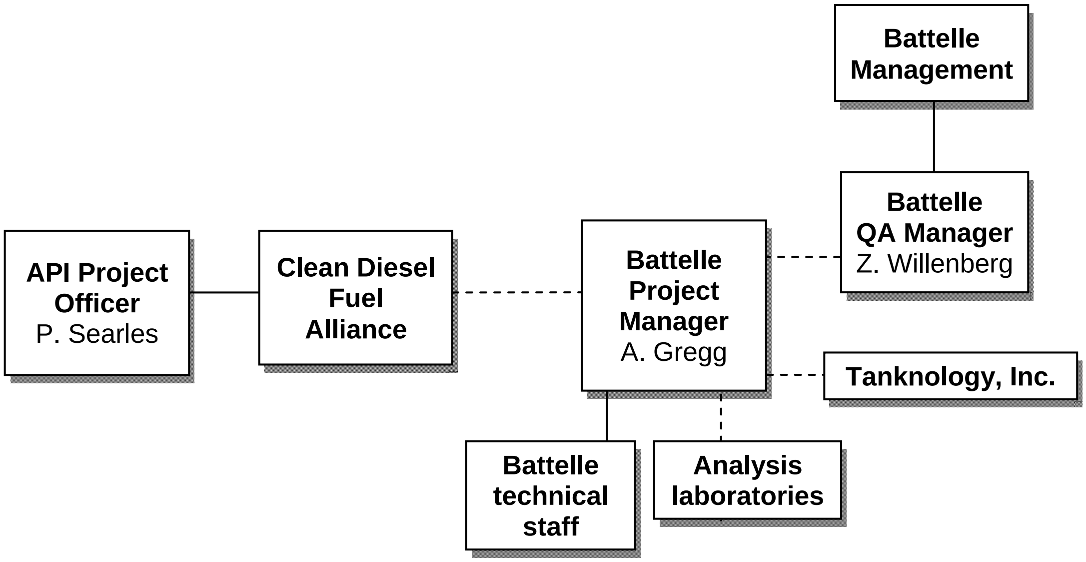


Figure 1. Project organizational chart.

A5.1 Battelle

Ms. Anne Marie Gregg, Battelle's Project Manager (PM) for this project, will:

- Prepare the draft quality assurance project plan (QAPP) and a draft results report, revise the draft QAPP and the draft results report in response to reviewers' comments;
- Establish a budget and schedule for this project and direct the effort to ensure that the budget and schedule are met;
- Have responsibility for ensuring that this QAPP is followed;
- Arrange for use of required facilities/laboratories;
- Arrange for the availability of qualified staff to conduct this project;
- Collect and review data generated during the project;

- Respond to any issues raised throughout project, including instituting corrective action as necessary;
- Coordinate distribution of the final QAPP and results report; and
- Maintain communication with the API project officer throughout the project.

Mr. Zachary Willenberg is Battelle's QA Manager. As such, Mr. Willenberg will:

- Review and approve the draft and final QAPP;
- Audit at least 10% of the project data against QAPP requirements;
- Prepare and distribute an assessment report for the audit;
- Verify implementation of any necessary corrective action;
- Provide a summary of the QA/quality control (QC) activities and results for the results report; and
- Review the draft results report.

Several Battelle technical staff will support Ms. Gregg throughout this project. They will:

- Assist the PM in developing a schedule for the project;
- Assist the PM in the preparation of the QAPP and all versions of the results report; and
- Work to carry out the test procedures specified in this QAPP.

A5.2 Tanknology, Inc.

Tanknology, Inc. is an underground storage tank (UST) inspection and testing company that will support Battelle in providing the UST site inspection and fuel and water sampling services during this project. Mr. Brad Hoffman is the engineer that will be overseeing the site inspection process for Tanknology and will:

- Assist the PM in developing a schedule for the project;
- Assist the PM in the preparation of the QAPP and all versions of the results report; and

- Work to carry out the test procedures specified in this QAPP.

A5.3 API

Mr. Prentiss Searles, the API project officer for this project will:

- Have overall responsibility for directing the project;
- Communicate with the PM regularly to receive updates on the status of the project;
- Review the draft QAPP, distribute the QAPP to the CDFA for review and comment, and review and approve the final QAPP;
- Coordinate involvement of the CDFA;
- Review all versions of the results report and technical brief; and
- Oversee the CDFA review process on the draft QAPP and draft results report.

A5.4 Clean Diesel Fuel Alliance

The CDFA is a consortium of organizations (government, engine and vehicle manufacturers, diesel marketers, diesel refiners, and diesel equipment producers) which have a vested interest in identifying and resolving the severe accelerated corrosion of mild carbon steel in fuel systems that store ultra low sulfur diesel (ULSD). The CDFA, under the organization and coordination of API, is funding this work and will serve in an advisory role. Collectively, they will:

- Review the draft QAPP and review and approve the final QAPP before site inspections or sampling begins and
- Provide in-kind support to Battelle in the form of inspection/sampling site selection and chemical analyses.

A5.5 Subcontracted and In-kind Analysis Laboratories

External laboratories (Marathon Petroleum, Chevron, and Columbia Analytical Services) will be used to provide chemical measurements that are defined later in this QAPP. All participating laboratories will be required to meet the minimum requirements of the applicable standard methods.

A6 PROBLEM DEFINITION/BACKGROUND

To protect public health and the environment, the United States Environmental Protection Agency (EPA) Clean Air Highway Diesel final rule stipulated a 97% reduction in sulfur content of highway diesel fuel beginning in June 2006. Accordingly, diesel fuel was altered so that the sulfur content was reduced from 500 parts-per-million (ppm) in low sulfur diesel (LSD) to 15 ppm, thereby being considered ULSD. From as early as 2007, the Petroleum Equipment Institute (PEI) started receiving reports of severe and accelerated corrosion in storage and dispensing equipment using ULSD. Reports include observations of a metallic coffee ground-type substance clogging filters and of corrosion and/or malfunctioning of seals, gaskets, tanks, meters, leak detectors, solenoid valves, and riser pipes (see Figure 2). What made this problem so unique is that corrosion was observed not only in the wetted areas but also the unwetted, or ullage, portions of the tanks and equipment. Whereas, prior to the roll out of ULSD in mid 2006, corrosion of metal surfaces in fuel systems storing and dispensing diesel fuel primarily occurred at or below the waterline of the tank. In January 2010, the PEI chaired a meeting of stakeholders to discuss the issue.

The result of that meeting was the development of a screening survey for industry and state inspectors, designed to capture the extent of corrosion in underground storage tanks and dispensing systems storing ULSD. The month-long screening survey was hosted by PEI and sent to North American tank owners, fuel suppliers, service providers, equipment manufacturers, tank/equipment regulators, cargo tank motor vehicle owners, and others, between March and April of 2010. The respondents to the screening survey identified many difficulties that may be related to the change to ULSD. Some of these included: filters

Figure 2. Example of observed corrosion.

clogging/requiring more frequent replacement, seal/gasket/O-ring deterioration, tanks rusting/leaking (includes tanks on vehicles), meter failure, pipe failure, etc. The screening survey results indicate that more work is needed to understand if any of these issues may be associated with the storage and dispensing of ULSD.

A7 PROJECT DESCRIPTION

The objective of this project is to evaluate three main working hypotheses identified in the first phase of this project which was completed in April 2011. The overall approach to testing these hypotheses is to develop and implement a procedure for inspecting and sampling ULSD systems (this QAPP document). This ensures uniform and thorough inspections of six pilot sites in which underground storage tanks (UST) containing ULSD reside. Five will have corrosive symptoms and one will not. Following site inspection the fuel, headspace, corrosion substrate (if present), and bottom water (if present) will be sampled and analyzed for biological and/or chemical parameters. Information on additive use will also be gathered. It is expected that analysis of the resulting data set will allow conclusions to be drawn with respect to the working hypotheses, which are as follows:

- Hypothesis 1. Aerobic and anaerobic microbes are producing metabolic by-products that are establishing a corrosive environment in ULSD systems;
- Hypothesis 2. One or more aggressive chemical species (e.g., acetic acid) present in ULSD systems are facilitating aggressive corrosion; and
- Hypothesis 3. Additives in the fuel are contributing to the corrosive environment in ULSD systems.

The first working hypothesis is focused on microbial-induced corrosion, where microbes are producing metabolites that are corrosive to metals found in fuel storage or dispensing systems (i.e., mild carbon steel). To test this hypothesis, genetic sequencing will be used to definitively determine whether microbes are present and which microbes are in the samples from the pilot sites. Since some microbes are known to be present in fuel, the identified microbes will be characterized as expected (known) and unexpected (new). This information will guide the understanding of the corrosive environment of the UST and provide data about microbe presence that can be more thoroughly investigated in the future.

Testing the second working hypothesis involves analysis of the chemical constituents present in the fuel, water, and headspace vapor within the USTs. These chemical constituents may be corrosive in nature or may contribute to the production of corrosive species, more specifically, acetic acid. The approach will focus on comparisons of chemical constituents of the fuel and vapor samples from the pilot sites with and without corrosive symptoms. The identification of the chemical constituents that are present only in pilot sites with corrosive symptoms will add to the understanding of the corrosive environment in USTs.

The third working hypothesis postulates that additives are contributing to the corrosive environment directly or indirectly as a source of nutrients to microbes that result in corrosive metabolites. The approach for testing this hypothesis will be focused on gathering information from additives manufacturers, refineries, terminals, stations, and published literature to understand the potential effect of additive on the overall chemical characteristics of the fuel and headspace vapor within USTs. While not an experimental approach, the gathered information will indicate whether additives are a plausible cause for the corrosive symptoms the USTs.

A8 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

This project will include three major components that involve making measurements: 1) sampling of fuel, headspace vapor, corrosion substrate (if present), and water (if present) from USTs, 2) chemical and biological measurements/analyses that will be performed on those samples, and 3) analysis of the resulting data to identify correlations between objective measurement data and corrosion of USTs. Most of the measurements will follow standard analytical methods that has been published and accepted by either ASTM International (ASTM), American National Standards Institute (ANSI), NACE International (NACE), or the EPA. Detailed QC requirements are provided in Section B5 and in each applicable standard method. Method specific data quality objectives (DQO) are listed in Table 4.

A9 SPECIAL TRAINING NEEDS/CERTIFICATION

The Tanknology, Inc. staff who will be performing the site inspections and fuel and water sampling will have documented training pertinent to their function in the inspection and sampling process. Prior to inspection/sampling, each staff member will be required to review the applicable ASTM sampling methods and have experience or become adequately trained with the required sampling equipment. This training/experience will be documented in the project records. Analysis laboratories will be required to provide documented support for their proficiency in performing the required analyses in a thorough and safe manner with proper attention to QC samples and waste disposal. Laboratory compliance with the DQOs will be demonstrated by QC data provided by the laboratories performing analyses.

A10 DOCUMENTS AND RECORDS

Project staff (Battelle, Tanknology, analysis laboratories) will record all relevant aspects of this project in laboratory record books (LRBs), electronic files (both raw data produced by applicable analytical method and spreadsheets containing various statistical calculations), audit reports, and other project reports. Table 1 includes the records that each organization will include in their project records to be submitted to the PM. The PM will review all of these records within seven days of receipt and maintain them in his office during the project. At the conclusion of the project, the Battelle PM will transfer the records to permanent storage at Battelle's Records Management Office (RMO). The Battelle QA Manager will maintain all quality records. All Battelle LRBs are stored indefinitely by Battelle's RMO. The PM will distribute the final QAPP and any revisions to the distribution list given in Section A4. Section B10 further details the data recording practices and responsibilities.

Table 1. Project Records Submitted to PM

Organization	Records	Submission Deadline
Battelle	LRBs, result raw data spreadsheets	Within one week of completion of generation of record
Tanknology	Site protocol checklist, site protocol data forms, sample chain of custody forms, training documentation	Scanned copy of documents emailed to PM within three days of generation of record
Analysis laboratories	LRBs, result raw data spreadsheets, QA and calibration data, chain of custody forms, training documentation	Copies of all records emailed to PM within two weeks of analysis.

SECTION B
DATA GENERATION AND ACQUISITION

B1 EXPERIMENTAL DESIGN

The following section will guide the pilot site inspections and all sampling and analyses that will be performed at each pilot site and on the samples collected at each site.

B1.1 Pilot Site Inspection

Tanknology will perform an inspection of up to six sites that have been selected by the CDFA. Appendix A includes some pertinent information about the selected pilot sites. The inspections will include visual documentation of the pilot site (photos and/or video) and completion a comprehensive inspection checklist that includes: acquiring copies of site records pertaining to equipment age and maintenance, fuel throughput and delivery, water bottom practices, known additives, and system treatments/responses. Appendix B includes the inspection checklist to be used by Tanknology technicians during this work and Appendix C includes a job safety analysis, which detail all critical actions performed once Tanknology technicians arrive at the pilot site and the possible hazards.

B1.2 Sampling

As part of the pilot site inspection, Tanknology staff will collect up to three fuel samples and as many as two water samples using a closed-core type sampling thief (TL-3573, Gammon, Manasquan, New Jersey), similar to the one shown in Figure 3. One fuel sample will be collected from the upper, middle, and lower fuel levels and up to two water sample(s) will be collected from the bottom of each tank in locations directly below different tank openings through

Figure 3. Closed-core sampling thief

which a sampler can be lowered. One vapor sample will be collected using two liter (L) Tedlar bags and another will be collected by pumping air through a sorbent cartridge. These samples will be collected from the ullage (tank headspace) vapor. In addition, corrosion substrate from the tank bottom, tank sides, ullage space, and tank equipment will be collected and analyzed for microbiological presence as well as a qualitative physical/chemical characterization at the Marathon Petroleum Company (Marathon) laboratory. Tank and dispenser fuel filtration media will also be sampled and sent for microbiological analysis.

Sampling and inspection will be coordinated around the site’s fuel delivery schedule. Inspection and sampling of sites will not be performed at sites that have received a fuel delivery within the previous 48 hours. Samples will be drawn prior to commencement of invasive measurements (water level, fuel temperature, etc.) that could potentially disturb the tank contents or contaminate the samples. Samples will be collected in the following order: headspace, upper fuel, middle fuel, bottom fuel/water, and corrosion substrate. Sampling will not take place through drop tubes or riser pipes that do not allow a representative sample to be collected or if the fuel level is below the applicable depth level (e.g., no upper fuel sample will be collected if the tank is only half full). Table 2 gives the location of the sample within the tank and the sample volume, container, and analysis laboratory.

Table 2. Sample Summary Information

Sample	Tank Location	Required Containers for Analysis
Fuel #1	Upper third	• 2 L amber glass bottle for chemical analyses at Marathon • 2 L sterile amber glass bottle then filtered for biological analysis at Battelle
Fuel #2	Middle third	
Fuel #3	Bottom third	
Water #1	Bottom	Sample split into three bottles: • 250 mL amber glass sterile bottle then filtered for biological analysis at Battelle • 2 L amber glass bottle for chemical analyses at Marathon • 250 mL amber glass bottle for chemical analysis at Chevron
Water #2 (optional)	Bottom	
Vapor #1	Headspace	• 2 L Tedlar bag for chemical analyses at Marathon
Vapor #2	Headspace	• 100 minute vapor sample on sorbent cartridge for chemical analysis at Columbia Analytical Services
Corrosive substrate	Bottom, tank walls, submerged equipment, and ullage space; tank or dispenser fuel filter media	Sample split into two bags: • Sterile plastic sample bags for analysis at Battelle and Marathon

B2 SAMPLING METHODS

B2.1 Fuel and Water Samples

The fuel and water samples undergoing chemical and microbiological analyses will be sampled following ASTM D7464-08[1]. This sampling method is specific to sampling for microbiological testing so the higher standard for cleanliness will be acceptable for the chemical analyses as well. Practically, asceptic sampling includes wearing sterile gloves, rinsing the sampling equipment with sterile deionized water and laboratory grade isopropyl alcohol before sampling and between sample locations. The step-by-step procedure for Core Thief Bottom Sampling is described in detail within Section 11.1.3 of the sampling method. Additionally, this method provides specific direction about the cleanliness of the sampling equipment in Sections 8-10. For the fuel samples, 4 L of fuel will be collected and homogenized by combining individual aliquots from the sampler and mixing in a sterile collection reservoir. For the water samples, a total volume of 1.5 L will be collected and homogenized in a similar fashion. A 2-L portion of each fuel sample and a 250-milliliter (mL) portion of each water sample will be filtered through separate cellulose filters (Analytical Filter Unit, #130, Nalgene, Rochester NY). The filters only will be shipped on ice overnight for analysis and the remaining liquid fuel (2 L to Marathon) and water samples (1 L to Marathon and 250 mL to Chevron) will be placed in amber glass bottles, wrapped in bubble packaging, and shipped to the analysis laboratories. Because of the potential for microbiological growth or a shift in the microbial population distribution, the filter samples need to be received at the microbiological laboratory within 24 hours following collection.

B2.2 Vapor Samples

Two types of vapor samples will be collected. One type of sample will be collected in a Tedlar bag following a procedure that includes the use of a vacuum box containing an empty Tedlar bag. This method is described in the EPA Emergency Response Team standard operating procedure #2149 for soil gas sampling[2]. To summarize, a vacuum pump is attached to a fitting on the vacuum box and evacuates the air in the vacuum box, creating a pressure differential causing the sample to be drawn into the bag. The sample drawn into the Tedlar bag never flows through the pump. The usual flow rate for bag sampling is three liters per minute (Lpm). Note that the bag should be filled only to 75-80% capacity.

The second type of vapor sample will be used to measure vapor phase carboxylic acids and will be collected by pumping headspace vapor through a sorbent cartridge (provided by Columbia Analytical Laboratories). Columbia Analytical Method 102 will be followed for this sampling approach. The sampling flow rate will be 1 Lpm for 100 minutes. Following sampling, the cartridge will be sealed and shipped to the analysis laboratory along with a field blank of an identical sorbent cartridge that was opened and then immediately resealed at the sample site.

B2.3 Corrosion Substrate Samples

If corrosion is identified during the inspection and sampling process at a site, an attempt will be made to collect a specimen of the corrosion substrate for characterization. Corrosion substrate is expected in three types: water bottom corrosion “sludge,” metallic corrosion on shafts and piping, and “nodule” substrate which is more brightly colored and composed of semi-spherical particulates. Water bottom corrosion will likely be sampled as part of the water sample and then will be transferred into a sterile bottle. Sterile scrapers and forceps will be used to loosen the metallic corrosion and nodule corrosion from metal shafts, piping, or other equipment and then it will be transferred to a sterile plastic bag and placed on ice for shipment. As the corrosion substrate does not lend itself to homogenization and the amount collected cannot be predicted, the sample obtained will be divided equally between the two receiving laboratories (Chevron and Battelle). Additionally, any tank or dispenser fuel filtration media that is available for sampling will be asceptically collected by cutting a dirty portion of the filter with a sterile scissor and placing in a sterile plastic bag and placed on ice for overnight shipment to the Battelle microbiological laboratory. Care should be taken during all sterile sampling efforts to prevent contamination with human cells by wearing sterile gloves and minimize any coughing or sneezing near the samples.

B3 SAMPLE HANDLING AND CUSTODY

Each sample will be handled according to ASTM D7464-08 Section 16. All sample bottles and sorbent cartridge packages will be labeled with the pilot site identification, the date and time of sampling, the type of sample (fuel, water, etc.), and name of the sampling technician. Each cooler containing the samples will have a chain-of-custody (COC) form that will be completed prior to shipment. The COC form will include the minimum requirements as stated in Battelle standard operating procedure (SOP) number ENV-ADM-009. These items include unique sample identification, date and time of sampling, sample description, storage condition, and the date, time, and by whom the samples were relinquished to the shipping company. A copy of the COC should be retained by the sampling technician. Upon receipt at the analysis laboratory, the integrity of the samples should be checked, documented, and receipt of the samples should be formally documented with a signature. Copies of all completed COCs will be provided to the Battelle PM.

B4 ANALYSIS METHODS

Table 3 gives the analysis methods that will be used for this project. The table includes the method title, standard method number (if applicable), and laboratory responsible for performing the analysis. The standard methods are very detailed and will not be reiterated in this document. There are two analyses requiring a non-standard method. In these two cases, a summary of the method will be provided in the results report.

Table 3. Analysis Methods and Responsible Laboratories

Method Title	Method Number	Matrix	Laboratory
Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy	Marathon method similar to ASTM D7371-07[3]	Fuel	Marathon
Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants	ASTM D5291-10[4]	Fuel and water	Marathon
Electrical Conductivity of Aviation and Distillate Fuels	ASTM D2624-09[5]	Fuel	Marathon
Density, Relative Density, and API Gravity of Liquids by Digital Density Meter	ASTM D4052-09[6]	Fuel and water	Marathon
Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection (hydrogen sulfide, sulfur content, sulfur speciation)	ASTM D5623-94[7]	Headspace vapor	Marathon
Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Ion Chromatography	Marathon method	Water	Marathon
Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines	NACE TM-0172[8]	Fuel	Marathon
Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection	ASTM D5762-10[9]	Fuel	Marathon
Carboxylic Acids in Petroleum Products	Marathon method	Fuel	Marathon

Method Title	Method Number	Matrix	Laboratory
Carboxylic Acids in Ambient Air Using Gas Chromatography/Mass Spectrometry	Columbia Method 102	Headspace vapor	Columbia Analytical Laboratories
Oxygen Concentration	Calculation	NA	NA
Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration	ASTM D6217-98[10]	Fuel and water	Marathon
Acid Number of Petroleum Products by Potentiometric Titration	ASTM D664-09a[11]	Fuel	Marathon
pH	EPA 150.1[12]	Water	Marathon
Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence	ASTM D5453-09[13]	Fuel	Marathon
Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration	ASTM D6304-07[14]	Fuel	Marathon
Water Content	Hygrometer	Headspace vapor	Onsite
Analysis of Solid Corrosive Substrate	Marathon method	Substrate	Marathon
Enumeration of Viable Bacteria and Fungi in Liquid Fuels-Filtration and Culture Procedures and Metagenomics Sequencing	ASTM D6974-09[15] and Metagenomics Sequencing[a]	Fuel, water, and corrosive substrate	Battelle

[a] Metagenomics sequencing is a method for identifying the repertoire of organisms in any environment/sample by analyzing the genetic information contained in the sample

B5 QUALITY CONTROL REQUIREMENTS

Each method listed in Table 3 has QC procedures/samples that are required for analysis along with the field samples to ensure the quality of the measurements. Those procedures/samples are listed in Table 4 as DQOs for acceptable method performance. In addition, method blanks will be included to verify no cross-contamination or carry-over between samples.

Table 4. Data Quality Objectives for Analysis Methods

Method Title	Method Number	QC Procedures	Recommended DQOs
Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Near Infrared Spectroscopy	Marathon method similar to ASTM D7371-07	QC check sample similar in composition to samples	Determination of QC limits in progress
Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants	ASTM D5291-10	QC check sample similar in composition to samples	EDTA check standard: C: 42.6 % ± 1.6 H: 5.56 % ± 0.55 N: 9.57 % ± 1.01 Precision: C: ± 0.15 H: ± 0.03 N: ± 0.1
Electrical Conductivity of Aviation and Distillate Fuels	ASTM D2624-09	Manufacturer calibration	Internal check of metal probe conductivity <1% error
Density, Relative Density, and API Gravity of Liquids by Digital Density Meter	ASTM D4052-09	QC check sample similar in composition to samples	Accuracy: 0.8433g/mL ± 0.0004 Precision: ± 0.0002
Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection (hydrogen sulfide, sulfur content, sulfur speciation)	Modified ASTM D5623-94	Calibration curve and QC check sample	Accuracy within 0.2 ppm
Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Ion Chromatography	Marathon method	Calibration curve and continuing QC check samples	Sulfate:4.09±0.14 ppm; chloride: 9.8 ±.2[1]
Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines	NACE TM-0172	Qualitative; visual scale of corrosion after set time	None required
Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection	ASTM D5762-10	Calibration curve and QC check sample of known nitrogen content	Accuracy and precision: 15 ppm ± 0.5
Carboxylic Acids in Petroleum Products	Marathon method	Semi-Quantative method only	None required
Carboxylic Acids in Ambient Air Using Gas Chromatography/Mass Spectrometry	Columbia Method 102	Calibration curve and continuing QC check samples	Within control limits of routine QC check sample analyses[1]

Method Title	Method Number	QC Procedures	Recommended DQOs
Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration	ASTM D6217-98	Duplicate samples	Duplicate less than 10% different
Acid Number of Petroleum Products by Potentiometric Titration	Will Likely be using D3242, which is meant for jet fuel, but should be in scope.	QC check sample similar in composition to samples	0.0039mg KOH/L ± 0.0005
pH	EPA 150.1	Calibration curve and continuing QC check samples	Second-source buffers that must be ± 0.05 pH units
Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence	ASTM D5453-09	Calibration curve and QC check sample similar in composition to samples	Accuracy: 8.75 ± 0.5 ppm. Precision: ± 0.2 ppm
Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration	ASTM D6304-07	QC check sample similar in composition to samples	Two QCs used. 163 ppm ± 46 and 337 ± 57. Precision: ± 30 at lower concentration and ± 14 at higher
Water Content	Hygrometer	Compare with equivalent instrument	Results within 20%
Organic Acids in Water	Chevron method	Qualitative analysis	None required
Analysis of Solid Corrosive Substrate	Marathon method	Semi-quantitative analyses	None required
Enumeration of Viable Bacteria and Fungi in Liquid Fuels-Filtration and Culture Procedures and Metagenomics Sequencing	ASTM D6974-09 and Metagenomics Sequencing	Qualitative analysis	None required

[1] ASTM D6299[16] "Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance" is used to determine acceptable performance

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The non-calibrated equipment needed for this project (samplers, sample containers, miscellaneous laboratory items, etc.) will be maintained and operated according to the quality requirements and documentation of any applicable standard method or of the laboratory responsible for its use. Only properly functioning equipment will be used; any observed malfunctioning will be documented and appropriate maintenance or replacement of malfunctioning equipment will be performed.

B7 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Some of the methods used during this project require calibration each day of analysis, but some require only a QC check sample to be analyzed to confirm the ongoing accuracy of calibration that is performed periodically (or possibly only by the manufacturer). Table 5 gives the calibration frequency required for each method.

Table 5. Frequency of Instrument Calibration

Method Title	Method Number	Instrument Make/Model	Frequency of Instrument Calibration
Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy	Marathon method similar to ASTM D7371-07	NIRSystems	Upon out of control QC check sample result
Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants	ASTM D5291-10	Leco TruSpec CHN	Upon out of control QC check sample result
Electrical Conductivity of Aviation and Distillate Fuels	ASTM D2624-09	Emcee Electronics Model 1152	Instrument-specific calibration involves daily zeroing
Density, Relative Density, and API Gravity of Liquids by Digital Density Meter	ASTM D4052-09	Anton Paar DMA4500M	Upon out of control QC check sample result
Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection (hydrogen sulfide, sulfur content, sulfur speciation)	Modified ASTM D5623-94	Agilent 7890 GC with Sievers 355 sulfur Chemilumines cence detector	Daily single point calibration to set response factors.
Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Ion	Marathon method	Metrohm 761 Compact IC / 762 Interface /	7 point calibration curve, performed as determined when QC check is outside

Method Title	Method Number	Instrument Make/Model	Frequency of Instrument Calibration
Chromatography		791 Detector / 837 Degasser	acceptable limits
Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines	NACE TM-0172	Kohler Instrument Corporation	Qualitative analysis; no calibration needed
Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection	ASTM D5762-10	Antek 9000HSN	Upon out of control QC check sample result
Carboxylic Acids in Petroleum Products	Marathon method	Agilent 6890GC/5973 MS	Semi-quanitiative, no calibration required
Carboxylic Acids in Ambient Air Using Gas Chromatography/Mass Spectrometry	Columbia Method 102	Agilent 6890GC/5973 MS	Daily 5 point calibration curve
Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration	ASTM D6217-98	Mettler-Toledo	Manufacturer balance calibration and daily accuracy check with mass standards
Acid Number of Petroleum Products by Potentiometric Titration	ASTM D3242,	None required	No calibration required for titration
pH	EPA 150.1	Orion 290A	Daily 3 point calibration curve
Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence	ASTM D5453-09	Antek 9000VLS	Upon out of control QC check sample result
Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration	ASTM D6304-07	Metrohm 831 KF coulometer	No Calibration – coulometric titration
Water Content	Hygrometer	RH-85 Handheld Hygrometer	Manufacturer calibration
Enumeration of Viable Bacteria and Fungi in Liquid Fuels-Filtration and Culture Procedures and Metagenomics Sequencing	ASTM D6974-09 and Metagenomics Sequencing	Ion Torrent, Illumina HiSeq2000	No calibration required, biological culture

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

All materials, supplies, and consumables to be used during this project will be ordered by the PM or designee. Unless specifically noted, all other supplies required for the evaluation are expected to be standard laboratory supplies (e.g. beakers, racks, etc.) that will not be required to meet a customized set of specifications. When possible, National Institute of Standards and Technology (NIST) traceable materials will be used for preparation of calibration standards and check standards.

B9 NON-DIRECT MEASUREMENTS

Any secondary data required for this project will be collected from the pilot site owners and operators and will be assumed to be accurate upon data gathering. Such information may include tank volume, throughput, additive information, etc.

B10 DATA MANAGEMENT

All project staff will acquire and record data electronically or manually as described in Section A10. All handwritten entries will be recorded in ink, and corrections to the entry will be made with a single line so as to not obliterate the original entry; the corrections will be initialed and dated. An explanation will accompany all non-obvious corrections. Records received by or generated by any of the project staff during the project will be reviewed by the PM or designee within two weeks of receipt or generation before the records are used to calculate, evaluate, or report results. The person performing the review will add his/her initials and date to the hard copy of the record being reviewed. In addition, all calculations, especially statistical calculations performed by project staff, will be spot-checked by the PM or designee to ensure that calculations are performed correctly. All spreadsheets and word processing documents applicable to this project will be stored on the Battelle network server, which is backed up daily.

SECTION C
ASSESSMENT AND OVERSIGHT

C1 ASSESSMENTS AND RESPONSE ACTIONS

Internal QC measures (e.g. QC check samples, regular review of raw data, spot-checking of calculations, etc.) described in this QAPP, implemented by the project staff and monitored by the PM, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the PM. Project staff have the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the PM, who will work to resolve any issues. Action will be taken to control the problem, identify a solution to the problem, and minimize losses and correct data, where possible. Battelle will be responsible for ensuring that the following audit is conducted as part of this project.

C1.1 Data Quality Audit

The Battelle QA Manager will audit at least 10% of the data acquired during the project. The Battelle QA Manager will trace the data from initial acquisition (reviewing at least 10% of raw data for each method), through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the audit will be checked. The Battelle QA Manager will prepare an audit report describing the results of the data quality audit.

C1.2 QA/QC Reporting

The data quality audit will be documented in assessment reports and will include:

- Identification of any adverse findings or potential problems;
- Response to adverse findings or potential problems;
- Recommendations for resolving problem;
- Cconfirmation that solutions have been implemented and are effective; and
- Citation of any noteworthy practices that may be of use to others.

SECTION D
DATA VALIDATION AND USABILITY

D1 DATA REVIEW, VALIDATION, AND VERIFICATION

Data validity and usability will be assessed through review of QC check samples to assess accuracy and precision. The acceptance criteria for the QC objectives generally rely on the generation of routine QC check sample performance data. Data verification is accomplished by ensuring the accuracy and completeness of data transcribed from raw data to the results report. A comparison of raw data sheets or LRB comments against final data will be conducted to flag any suspect data and resolve any questions about apparent outliers. The quality assessment, as described within Section C of this document, is designed to ensure the quality of these data.

D2 VALIDATION AND VERIFICATION METHODS

Data verification includes a visual inspection of hand written data to ensure that all entries were properly recorded and that any erroneous entries were properly noted, as described in Sections B10 and D1. Data validation efforts include the assessment of QC data and the performance of a quality audit (Section C) to determine if the data collection and measurement procedures met the quality objectives defined in the QAPP. The Battelle QA Manager will conduct an audit of data quality to verify that data review and validation procedures were completed, and to ensure the overall quality of the data.

D3 RECONCILIATION WITH USER REQUIREMENTS

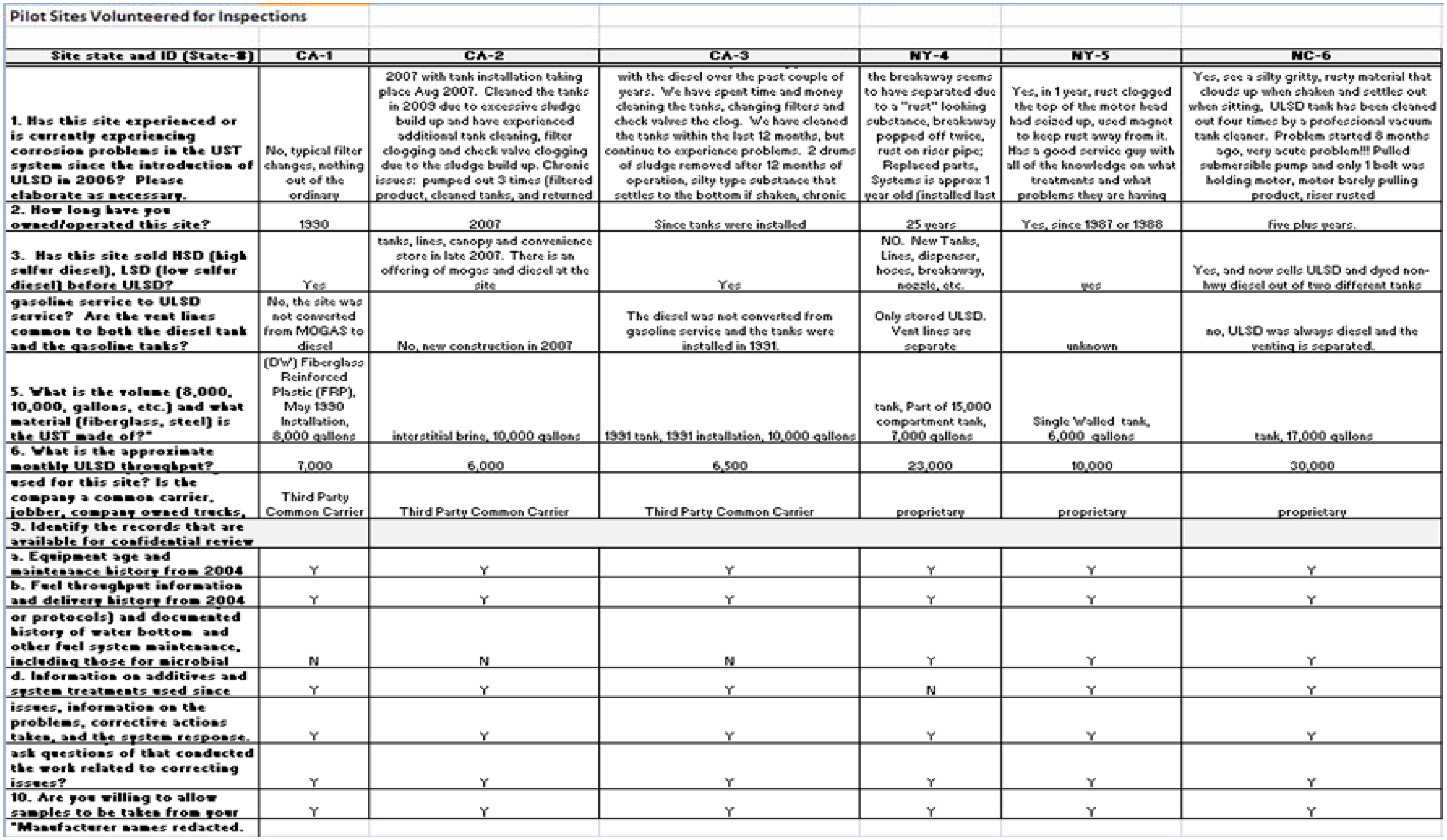
The data obtained during this project will provide thorough documentation of the required measurements. The data review and validation procedures described in the previous sections will verify that data meet the quality objectives and are accurately presented in the report generated from this project. The data generated throughout this project will be compiled into a results report. The results report will present tables of the measured data and resulting data describing the results of the site inspections and required measurements. Any limitations to the data will be addressed and discussed in the results report.

SECTION E
REFERENCES

1. U.S. EPA Soil Gas Sampling: SOP #2149, in Compendium of Emergency Response Team Groundwater Sampling Procedures, Office of Solid Waste and Emergency Response, Washington, D.C., January 1999.
2. ASTM Standard D7464-08, "Manual Sampling of Liquid Fuels, Associated Materials and Fuel System Components for Microbiological Testing, "ASTM International, West Conshohocken, PA, 2008.
3. ASTM Standard D7371-07, "Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy, "ASTM International, West Conshohocken, PA, 2007.
4. ASTM Standard D5291-10, "Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, "ASTM International, West Conshohocken, PA, 2010.
5. ASTM Standard D2624-09, "Electrical Conductivity of Aviation and Distillate Fuels," ASTM International, West Conshohocken, PA, 2009.
6. ASTM Standard D4052-09, "Density, Relative Density, and API Gravity of Liquids by Digital Density Meter, "ASTM International, West Conshohocken, PA, 2009.
7. ASTM Standard D5623-94, "Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection," ASTM International, West Conshohocken, PA, 1994.
8. NACE Standard TM-0172, "Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines, "NACE International, Houston, TX, 2001.
9. ASTM Standard D5762-10, "Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence," ASTM International, West Conshohocken, PA, 2010.
10. ASTM Standard D6217-98, "Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration," ASTM International, West Conshohocken, PA, 1998.

11. ASTM Standard D664-09a, "Acid Number of Petroleum Products by Potentiometric Titration, "ASTM International, West Conshohocken, PA, 2009.
12. EPA Method 150.1 "pH," U.S. Environmental Protection Agency, Washington, D.C., 1982.
13. ASTM Standard D5453-09, "Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence," ASTM International, West Conshohocken, PA, 2009.
14. ASTM Standard D6304-07, "Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration," ASTM International, West Conshohocken, PA, 2007.
15. ASTM Standard D6974-09, "Enumeration of Viable Bacteria and Fungi in Liquid Fuels-Filtration and Culture Procedures and Metagenomics Sequencing," ASTM International, West Conshohocken, PA, 2009.
16. ASTM Standard D6299-10, "Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance," ASTM International, West Conshohocken, PA, 2010.

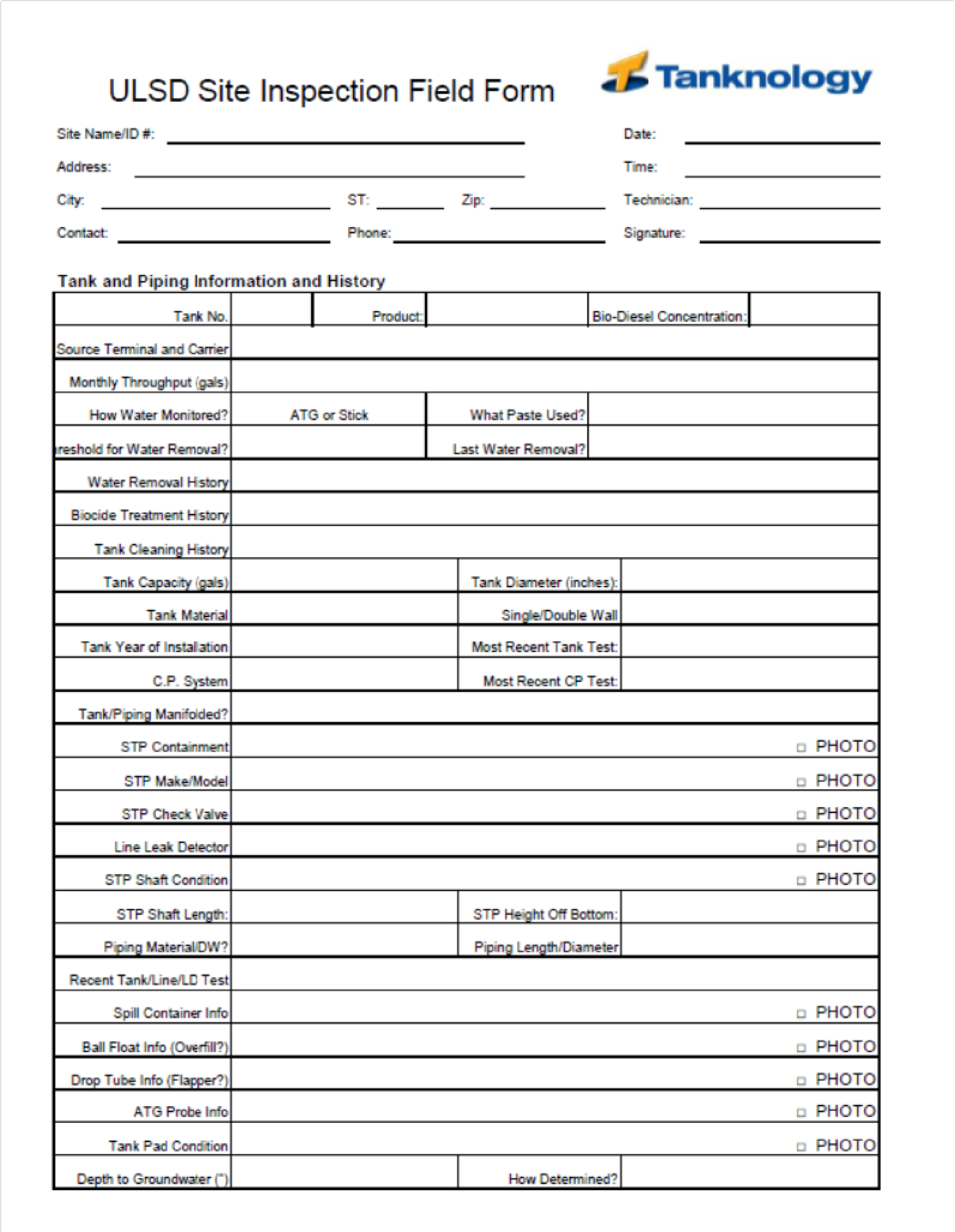
APPENDIX A Pilot Site Information Summaries



Pilot Sites Volunteered for Inspections

Site state and ID (State-#)	CA-1	CA-2	CA-3	NY-4	NY-5	NC-6
1. Has this site experienced or is currently experiencing corrosion problems in the UST system since the introduction of ULSD in 2006? Please elaborate as necessary.	No, typical filter changes, nothing out of the ordinary	2007 with tank installation taking place Aug 2007. Cleaned the tanks in 2009 due to excessive sludge build up and have experienced additional tank cleaning, filter clogging and check valve clogging due to the sludge build up. Chronic issues: pumped out 3 times (filtered product, cleaned tanks, and returned	with the diesel over the past couple of years. We have spent time and money cleaning the tanks, changing filters and check valves the clog. We have cleaned the tanks within the last 12 months, but continue to experience problems. 2 drums of sludge removed after 12 months of operation, silty type substance that settles to the bottom if shaken, chronic	the breakaway seems to have separated due to a "rust" looking substance, breakaway popped off twice, rust on riser pipe; Replaced parts, Systems is approx 1 year old (installed last	Yes, in 1 year, rust clogged the top of the motor head had seized up, used magnet to keep rust away from it. Has a good service guy with all of the knowledge on what treatments and what problems they are having	Yes, see a silty gritty, rusty material that clouds up when shaken and settles out when sitting. ULSD tank has been cleaned out four times by a professional vacuum tank cleaner. Problem started 8 months ago, very acute problem!!! Pulled submersible pump and only 1 bolt was holding motor, motor barely pulling product, riser rusted
2. How long have you owned/operated this site?	1990	2007	Since tanks were installed	25 years	Yes, since 1987 or 1988	five plus years.
3. Has this site sold HSD (high sulfur diesel), LSD (low sulfur diesel) before ULSD?	Yes	tanks, lines, canopy and convenience store in late 2007. There is an offering of mogas and diesel at the site	Yes	NO. New Tanks, Lines, dispenser, hoses, breakaway, nozzle, etc.	yes	Yes, and now sells ULSD and dyed non-hwy diesel out of two different tanks
gasoline service to ULSD service? Are the vent lines common to both the diesel tank and the gasoline tanks?	No, the site was not converted from MOGAS to diesel	No, new construction in 2007	The diesel was not converted from gasoline service and the tanks were installed in 1991.	Only stored ULSD. Vent lines are separate	unknown	no, ULSD was always diesel and the venting is separated.
5. What is the volume (8,000, 10,000, gallons, etc.) and what material (fiberglass, steel) is the UST made of?*	(DW) Fiberglass Reinforced Plastic (FRP), May 1990 Installation, 8,000 gallons	interstitial brine, 10,000 gallons	1991 tank, 1991 installation, 10,000 gallons	tank, Part of 15,000 compartment tank, 7,000 gallons	Single Walled tank, 6,000 gallons	tank, 17,000 gallons
6. What is the approximate monthly ULSD throughput?	7,000	6,000	6,500	23,000	10,000	30,000
used for this site? Is the company a common carrier, jobber, company owned trucks,	Third Party Common Carrier	Third Party Common Carrier	Third Party Common Carrier	proprietary	proprietary	proprietary
9. Identify the records that are available for confidential review						
a. Equipment age and maintenance history from 2004	Y	Y	Y	Y	Y	Y
b. Fuel throughput information and delivery history from 2004	Y	Y	Y	Y	Y	Y
or protocols) and documented history of water bottom and other fuel system maintenance, including those for microbial	N	N	N	Y	Y	Y
d. Information on additives and system treatments used since	Y	Y	Y	N	Y	Y
issues, information on the problems, corrective actions taken, and the system response.	Y	Y	Y	Y	Y	Y
ask questions of that conducted the work related to correcting issues?	Y	Y	Y	Y	Y	Y
10. Are you willing to allow samples to be taken from your	Y	Y	Y	Y	Y	Y
*Manufacturer names redacted.						

APPENDIX B Tanknology Inspection Checklist



ULSD Site Inspection Field Form

Tanknology

Site Name/ID #: ______________________ Date: ____________
Address: ______________________ Time: ____________
City: ____________ ST: ______ Zip: ________ Technician: ____________
Contact: ____________ Phone: ____________ Signature: ____________

Tank and Piping Information and History

Tank No.		Product:		Bio-Diesel Concentration:	
Source Terminal and Carrier					
Monthly Throughput (gals)					
How Water Monitored?	ATG or Stick	What Paste Used?			
reshold for Water Removal?		Last Water Removal?			
Water Removal History					
Biocide Treatment History					
Tank Cleaning History					
Tank Capacity (gals)		Tank Diameter (inches):			
Tank Material		Single/Double Wall			
Tank Year of Installation		Most Recent Tank Test:			
C.P. System		Most Recent CP Test:			
Tank/Piping Manifolded?					
STP Containment					☐ PHOTO
STP Make/Model					☐ PHOTO
STP Check Valve					☐ PHOTO
Line Leak Detector					☐ PHOTO
STP Shaft Condition					☐ PHOTO
STP Shaft Length:		STP Height Off Bottom:			
Piping Material/DW?		Piping Length/Diameter			
Recent Tank/Line/LD Test					
Spill Container Info					☐ PHOTO
Ball Float Info (Overfill?)					☐ PHOTO
Drop Tube Info (Flapper?)					☐ PHOTO
ATG Probe Info					☐ PHOTO
Tank Pad Condition					☐ PHOTO
Depth to Groundwater (")		How Determined?			

Observations	Fill Pipe	ATG	STP	Other ________
Tank Bottom to Grade (")				
Riser Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Cap/Adapter Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Visible Corrosion?				
Product Level				
Water Bottom Level				
Fuel Samples Taken?				
Vapor Samples Taken?				
Water Sample Taken?				
In-Tank Humidity				
In-Tank Temperature				

Dispenser Info	Dsp # ________	Dsp # ________	Dsp # ________	Dsp # ________
Dispenser Make/Model				
Dispenser Containment	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Filter Make/Model				
Filter Date Replaced				
Filter Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Meter Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Calibration Date				
Shear Valve Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Nozzle Make/Model				
Nozzle Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Swivels Condition	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Visible Leaks	☐ PHOTO	☐ PHOTO	☐ PHOTO	☐ PHOTO
Sample Taken				

Comments: ____

APPENDIX C Tanknology Job Hazard Analysis

MINIMUM REQUIRED PERSONAL PROTECTIVE EQUIPMENT (SEE CRITICAL ACTIONS FOR TASK-SPECIFIC REQUIREMENTS)			
☒ LIFE VEST ☐ HARD HAT ☐ LIFELINE / BODY HARNESS ☒ SAFETY GLASSES	☒ GOGGLES ☐ FACE SHIELD ☐ HEARING PROTECTION ☒ SAFETY SHOES	☐ AIR PURIFYING RESPIRATOR ☐ SUPPLIED RESPIRATOR ☒ PPE CLOTHING	☒ GLOVES ☒ Voltage Indicator ☐ OTHER

[1]JOB STEPS	[2]POTENTIAL HAZARDS	[3]CRITICAL ACTIONS
Arrival on site	Vehicle and Pedestrian Traffic. Forecourt Hazards Possible other contractors on site.	1- Wear PPE: Safety Vest, Steel toed boots, Safety Glasses, 100% cotton Tanknology uniform. 2- Contact MGR or site personal to explain job process and Safety Procedures. 3- Have Site Safety Checklist and CSE form filled out and ready to sign. 4- Conduct site safety meeting with any other contractors on site.
Position test vehicle	Vehicle and Pedestrian Traffic, Forecourt Hazards Unauthorized entry	1- Check all Forecourt and Pedestrian Traffic flow for test unit position 2- Deploy all Safety Equipment following Barricading procedures including Cones, Caution Tape, Flags and Fire Extinguishers
Open All Manhole Covers and Access Points at Tankfield	Vehicle and Pedestrian Traffic Unauthorized entry Tripping and Falling Lifting Exertion Hazardous Vapors	1- Maintain full barricade around tank pad. 2- Use proper lifting technique when opening turbine sump lids 3- Barricade open sumps or replace lids to avoid tripping or falling 4- Use LEL Meter and blower as necessary
Inspect Components at Tankfield	Vehicle and Pedestrian Traffic Unauthorized entry Sharp objects Insect Bites Possible product release	1- Maintain full barricade around tank pad. 2- Check for insects and spiders and other hazards after covers are removed 3- Use tools to remove any debris 4- Use proper tools to remove components 5- Use product-resistant gloves when handling wetted components
Remove STP and inspect internal components	Vehicle and Pedestrian Traffic Unauthorized entry Possible Hazardous Atmosphere Possible product release Electrical Hazard Over-Exertion	1- Maintain full barricade around tank pad. 2- Conduct Confined Space Entry procedures. 3- Check for stray voltage on/around STP 4- Perform Lock/out Tag/out & bag dispensers. 5- Verify product STP is disabled after Lockout/ Tagout completed. 6- Close product ball valve if present. Relieve excess pressure from line. Use absorbent cloth to collect any product release. 7- Spray STP bolts with WD-40 prior to removal. 8- Use tripod or lever to loosen STP prior to removal. 9- Use winch or two persons to assist in STP removal as necessary. 10- Replace O-rings, use proper lubrication, and reinstall STP after samples are taken.
Take Product/Vapor/Water Samples	Vehicle and Pedestrian Traffic Unauthorized entry Possible product release Possible hazardous atmosphere Possible electrical hazard	1- Maintain full barricade around tank pad. 2- Wear product resistant gloves 3- Use only hand pump, nitrogen-powered vacuum pump, or explosion-proof electric pump. 4- Connect any electric pump to GFCI. 5- Use absorbents to collect any product drips. 6- Secure all samples tightly to prevent product release. 7- Package samples per ASTM guidelines for safe shipment to laboratory

Inspect Dispensers and related equipment	Vehicle and Pedestrian Traffic Unauthorized entry Possible product release Sharp objects Insect Bites	1- Establish barricade around all dispensers 2- Perform Lockout/Tagout & bag dispensers 3- Wear leather gloves when removing covers. 4- Check for insects and spiders and other hazards. 5- Trip shear valves and close ball valve if present. 6- Remove filters to inspect internal elements 7- Use absorbents to collect any product release. 8- Replace filters when complete. 9- Remove Lockout/Tagout, open shear valves and ball valve. 10- Energize dispenser to check for leaks. 11- Install lead seals. 12- Conduct visual inspection with site manager.
Job Complete	Vehicle and Pedestrian Traffic Forecourt Hazards	1- Notify responsible person of any maintenance needs at location. 2- Complete Site Safety Checklist and all paperwork prior to leaving. 3- Place site back to original condition. 4- Remove all barricades. 5- Plan route and then exit site avoiding distractions.

[1] Each Job or Operation consists of a set of tasks / steps. Be sure to list all the steps in the sequence that they are performed. Specify the equipment or other details to set the basis for the associated hazards in Column 2

[2] A hazard is a potential danger. How can someone get hurt? Consider, but do not limit, the analysis to: **Contact** - victim is struck by or strikes an object; **Caught** - victim is caught on, caught in or caught between objects; **Fall** - victim falls to ground or lower level (includes slips and trips); **Exertion** - excessive strain or stress / ergonomics / lifting techniques; **Exposure** - inhalation/skin hazards. Specify the hazards and do not limit the description to a single word such as "Caught"

[3] Aligning with the first two columns, describe what actions or procedures are necessary to eliminate or minimize the risk. Be clear, concise and specific. Use objective, observable and quantified terms. Avoid subjective general statements such as, "be careful" or "use as appropriate".

Change History

Process Owner : VP Engineering	Approved By : VP Engineering

Rev	Date Effective	Page(s) Changed	Change Description	Process Owner	Approval
A	10/30/2011	All	New inspection procedure	Brad Hoffman	Brad Hoffman

Last Review:	Reviewed by:	Brad Hoffman	Review date:	10/30/2011

Appendix C

Sample Information and
Site Inspection Field Data

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Table C1 – Samples Collected During Site Inspections

Site ID	Date	Time	Sample ID	Type - Collection Device	Description
NC-1	8-Feb-12	838	8Feb12_01	filter wipe	Wiped outside drop tube with filter
NC-1	8-Feb-12	850	8Feb12_02	tedlar bag	Vapor collected
NC-1	8-Feb-12	915	8Feb12_03A	scrape	Cap of ball float riser
NC-1	8-Feb-12	915	8Feb12_03B	scrape	Cap of ball float riser
NC-1	8-Feb-12	930	8Feb12_04A	scrape	Inside ball float riser
NC-1	8-Feb-12	930	8Feb12_04B	scrape	Inside ball float riser
NC-1	8-Feb-12	945	8Feb12_06	filter wipe	Wiped ATG probe-water float with filter
NC-1	8-Feb-12	945	8Feb12_05	scrape	White crust top ATG probe
NC-1	8-Feb-12	1045	8Feb12_07A	fuel - bacon bomb	Consolidated fuel sample (1 of 2)
NC-1	8-Feb-12	1045	8Feb12_07B	fuel - bacon bomb	Consolidated fuel sample (2 of 2)
NC-1	8-Feb-12	1045	8Feb12_07C	filtered fuel	Filtered consolidated fuel sample
NC-1	8-Feb-12	1410	8Feb12_09	filtered water bottom	Filtered water bottom of 8Feb12-09 - < 25 mL
NC-1	8-Feb-12	1436	8Feb12_10	scrape	Functional element
NC-1	8-Feb-12	1448	8Feb12_11A	scrape	Inside STP riser and bowl
NC-1	8-Feb-12	1448	8Feb12_11B	scrape	Inside STP riser and bowl
NC-1	8-Feb-12	1457	8Feb12_12A	water bottom - bacon bomb	Consolidated water bottom from STP riser (very little from ATG and fill risers)
NC-1	8-Feb-12	1457	8Feb12_12B	water bottom - bacon bomb	Consolidated water bottom from STP riser (very little from ATG and fill risers)
NC-1	8-Feb-12	1457	8Feb12_12C	water bottom - bacon bomb	Consolidated water bottom from STP riser (2 jars) (very little from ATG and fill risers)
NC-1	8-Feb-12	1525	8Feb12_13	o-rings	O-rings from functional element
NC-1	8-Feb-12	1600	8Feb12_14	fuel - bacon bomb	fuel sample taken at the end of the day
NC-1	8-Feb-12	1229-1318	8Feb12_08A	skc tube	Vapor 1936.9 ml/min for 49 min
NC-1	8-Feb-12	1235-1321	8Feb12_08B	skc tube	Vapor 1980.8 mL/min for 46 min
NY-1	15-Feb-12	855	53609-06-03	scrape	Spare riser cap near fill/ATG
NY-1	15-Feb-12	915	53609-06-06	tedlar bag	Vapor collected from fill/ATG other riser
NY-1	15-Feb-12	945	53609-06-07	filter wipe	Wiped ATG probe-water float with filter
NY-1	15-Feb-12	1030	53609-06-08	fuel-bacon bomb	Consolidated fuel sample
NY-1	15-Feb-12	1030	53609-06-08A	fuel-bacon bomb	2 L of 53609-06-08 into 1-L amber glass jars
NY-1	15-Feb-12	1030	53609-06-08B	fuel-bacon bomb	1 L of 53609-06-08 into 1-L amber glass jar
NY-1	15-Feb-12	1030	53609-06-08C	filtered fuel	Filtered fuel of 53609-06-08 - 700 mL

Table C1 – Samples Collected During Site Inspections (continued)

Site ID	Date	Time	Sample ID	Type - Collection Device	Description
NY-1	15-Feb-12	1115	53609-06-09	water bottom - bacon bomb	Consolidated water bottom from fill riser (none from STP other riser)
NY-1	15-Feb-12	1115	53609-06-09A	water bottom - bacon bomb	~250-mL aliquot 53609-06-09
NY-1	15-Feb-12	1115	53609-06-09B	water bottom - bacon bomb	~250-mL aliquot 53609-06-09
NY-1	15-Feb-12	1115	53609-06-09C	water bottom - bacon bomb	~1-L aliquot 53609-06-09
NY-1	15-Feb-12	1115	53609-06-09D	filtered water bottom	Filtered water bottom of 53609-06-09 - 100 mL
NY-1	15-Feb-12	1355	53609-06-10A	Scrape	STP pump shaft scraping
NY-1	15-Feb-12	1355	53609-06-10B	Scrape	STP pump shaft scraping
NY-1	15-Feb-12	1400	53609-06-11	Scrape	Inside pump - wetted head
NY-1	15-Feb-12	1400	53609-06-12	Scrape	Inside STP riser - dry part
NY-1	15-Feb-12	838-1018	53609-06-05	skc tube	Vapor 983.59 mL/min for 100 min
NY-1	15-Feb-12	838-1018	53609-06-04	skc tube	Vapor 984.25 mL/min for 100 min
NY-2	16-Feb-12	751	53609-08-03a	scrape	Brass plug from ball float riser
NY-2	16-Feb-12	751	53609-08-03b	scrape	Brass plug from ball float riser
NY-2	16-Feb-12	801	53609-08-04a	scrape	Cast iron plug screwed into brass plug from ball float riser
NY-2	16-Feb-12	801	53609-08-04b	scrape	Cast iron plug screwed into brass plug from ball float riser
NY-2	16-Feb-12	805	53609-08-05a	scrape	Inside spare other riser
NY-2	16-Feb-12	805	53609-08-05b	scrape	Inside spare other riser
NY-2	16-Feb-12	900	53609-08-06a	scrape	Outside fill pipe
NY-2	16-Feb-12	900	53609-08-06b	scrape	Outside fill pipe
NY-2	16-Feb-12	905	53609-08-07	scrape	Inside riser pipe groove
NY-2	16-Feb-12	915	53609-08-08	fuel - bacon bomb	Consolidated fuel from fill and spare risers
NY-2	16-Feb-12	915	53609-08-08a	fuel - bacon bomb	1 L of 53609-08-08 glass jar
NY-2	16-Feb-12	915	53609-08-08b	fuel - bacon bomb	2 L into 2 1-L amber glass jars of 53609-08-08
NY-2	16-Feb-12	915	53609-08-08c	filtered fuel	Filtered fuel of 53609-08-08 - 800 mL
NY-2	16-Feb-12	950	53609-08-09	water bottom - bacon bomb	Consolidated water bottom from fill and spare risers
NY-2	16-Feb-12	950	53609-08-09a	water bottom - bacon bomb	~250-mL aliquot 53609-08-09
NY-2	16-Feb-12	950	53609-08-09b	water bottom - bacon bomb	~250-mL aliquot 53609-08-09
NY-2	16-Feb-12	950	53609-08-09c	water bottom - bacon bomb	~1-L aliquot 53609-08-09
NY-2	16-Feb-12	950	53609-08-09d	filtered water bottom	Filtered water bottom of 53609-08-09 - 50 mL

Table C1 – Samples Collected During Site Inspections (continued)

Site ID	Date	Time	Sample ID	Type - Collection Device	Description
NY-2	16-Feb-12	950	53609-08-09e	sediment - bacon bomb	Bottom sediment from 53609-08-09
NY-2	16-Feb-12	1030	53609-08-12	tedlar bag	Vapor collected from ball float riser
NY-2	16-Feb-12	1059	53609-08-13	o-rings	O-rings from functional element
NY-2	16-Feb-12	1150	53609-08-14	Scrape	Bottom of STP head
NY-2	16-Feb-12	1150	53609-08-15	Scrape	STP shaft
NY-2	16-Feb-12	1155	53609-08-16	Scrape	STP bowl
NY-2	16-Feb-12	1157	53609-08-17	o-rings	Packed discharge O-ring
NY-2	16-Feb-12	825-1005	53609-08-10	skc tube	Vapor 978.07 mL/min for 100 min
NY-2	16-Feb-12	825-1005	53609-08-11	skc tube	Vapor 979.16 mL/min for 100 min
CA-1	21-Feb-12	815	53609-11-03	filter wipe	Wiped ATG probe with filter
CA-1	21-Feb-12	834	53609-11-04	Scrape	Inside ATG riser
CA-1	21-Feb-12	838-1018	53609-11-05	skc tube	Vapor 1051.0 mL/min for 100 min
CA-1	21-Feb-12	838-1018	53609-11-06	skc tube	Vapor 1026.7 mL/min for 100 min
CA-1	21-Feb-12	1020	53609-11-07	tedlar bag	Vapor collected from ATG riser
CA-1	21-Feb-12	1143	53609-11-08	fuel - bacon bomb	Consolidated fuel from ATG and STP risers
CA-1	21-Feb-12	1143	53609-11-08a	fuel - bacon bomb	1 L of 53609-11-08 glass jar
CA-1	21-Feb-12	1143	53609-11-08b	fuel - bacon bomb	2 L of 53609-11-08 in 2 1-L glass jar
CA-1	21-Feb-12	1143	53609-11-08c	filtered fuel	Filtered fuel of 53609-11-08 - 800 mL
CA-1	21-Feb-12	1050	53609-11-09a	Scrape	STP shaft top
CA-1	21-Feb-12	1050	53609-11-09b	Scrape	STP shaft top
CA-1	21-Feb-12	1055	53609-11-09c	Scrape	STP shaft bottom
CA-1	21-Feb-12	1120	53609-11-10	o-rings	O-rings from STP
CA-1	21-Feb-12	1154	53609-11-11	water bottom - bacon bomb	Consolidated water bottom from STP riser (none from ATG or fill risers)
CA-1	21-Feb-12	1154	53609-11-11a	water bottom - bacon bomb	> 100 mL aliquot of 53609-11-11
CA-1	21-Feb-12	1154	53609-11-11b	water bottom - bacon bomb	> 100 mL aliquot of 53609-11-11
CA-1	21-Feb-12	1154	53609-11-11c	water bottom - bacon bomb	~600 mL aliquot of 53609-11-11
CA-1	21-Feb-12	1154	53609-11-11d	filtered water bottom	Filtered water bottom of 53609-11-11 - 75 mL
CA-1	21-Feb-12	1154	53609-11-11e	sediment - bacon bomb	Bottom sediment from 53609-11-11
CA-2	22-Feb-12	1032-1212	53609-14-03	skc tube	Vapor 1023.6 mL/min for 100 min
CA-2	22-Feb-12	1032-1212	53609-14-04	skc tube	Vapor 1034.0 mL/min for 100 min
CA-2	22-Feb-12	1110	53609-14-05	Scrape	STP shaft - dry portion

Table C1 – Samples Collected During Site Inspections (continued)

Site ID	Date	Time	Sample ID	Type - Collection Device	Description
CA-2	22-Feb-12	1112	53609-14-06a	scrape	STP bowl - wet portion
CA-2	22-Feb-12	1113	53609-14-06b	scrape	STP bowl - wet portion
CA-2	22-Feb-12	1125	53609-14-07	fuel - bacon bomb	Consolidated fuel from STP and other risers
CA-2	22-Feb-12	1125	53609-14-07a	fuel - bacon bomb	1 L of 53609-14-07
CA-2	22-Feb-12	1125	53609-14-07b	fuel - bacon bomb	2 L of 53609-14-07 in 2 1-L jars
CA-2	22-Feb-12	1125	53609-14-07c	filtered fuel	Filtered fuel of 53609-14-07 - 700 mL
CA-2	22-Feb-12	1136	53609-14-08	water bottom - bacon bomb	Consolidated water bottom from other risers (very little from STP riser)
CA-2	22-Feb-12	1136	53609-14-08a	water bottom - bacon bomb	< 200 mL aliquot 53609-14-08
CA-2	22-Feb-12	1136	53609-14-08b	water bottom - bacon bomb	< 200 mL aliquot 53609-14-08
CA-2	22-Feb-12	1136	53609-14-08c	water bottom - bacon bomb	~500 mL aliquot 53609-14-08
CA-2	22-Feb-12	1136	53609-14-08d	filtered water bottom	Filtered water bottom of 53609-14-08 - 50 mL
CA-2	22-Feb-12	1140	53609-14-09	sediment - bacon bomb	Bottom sediment from STP riser
CA-2	22-Feb-12	1230	53609-14-10	part	Corroded threading (part)
CA-2	22-Feb-12	1230	53609-14-11	part	STP check valve (part)
CA-2	22-Feb-12	1300	53609-14-12	tedlar bag	Vapor collected
CA-3	23-Feb-12	746	53609-17-03a	scrape	Inside ball float riser
CA-3	23-Feb-12	746	53609-17-03b	scrape	Inside ball float riser
CA-3	23-Feb-12	817-957	53609-17-04	skc tube	Vapor 1048.4 mL/min for 100 min
CA-3	23-Feb-12	817-957	53609-17-05	skc tube	Vapor 1012.3 mL/min for 100 min
CA-3	23-Feb-12	930	53609-17-06	scrape	STP shaft toward top
CA-3	23-Feb-12	940	53609-17-07a	scrape	STP shaft toward bottom
CA-3	23-Feb-12	940	53609-17-07b	scrape	STP shaft toward bottom
CA-3	23-Feb-12	1000	53609-17-08	tedlar bag	Vapor collected
CA-3	23-Feb-12	1002	53609-17-09	tedlar bag	Vapor collected duplicate
CA-3	23-Feb-12	1036	53609-17-10	fuel - bacon bomb	Consolidated fuel from fill and STP risers
CA-3	23-Feb-12	1036	53609-17-10a	fuel - bacon bomb	1 L of 53609-17-10
CA-3	23-Feb-12	1036	53609-17-10b	fuel - bacon bomb	2 L of 53609-17-10
CA-3	23-Feb-12	1036	53609-17-10c	filtered fuel	Filtered fuel of 53609-17-10 - 550 mL
CA-3	23-Feb-12	1048	53609-17-11	sediment - bacon bomb	Bottom sediment from STP riser
CA-3	23-Feb-12	1101	53609-17-12	water bottom - bacon bomb	Consolidated water bottom from ATG riser (none from STP riser)
CA-3	23-Feb-12	1101	53609-17-12a	water bottom - bacon bomb	~250-mL aliquot 53609-17-12

Table C1 – Samples Collected During Site Inspections (continued)

Site ID	Date	Time	Sample ID	Type - Collection Device	Description
CA-3	23-Feb-12	1101	53609-17-12b	water bottom - bacon bomb	~250-mL aliquot 53609-17-12
CA-3	23-Feb-12	1101	53609-17-12c	water bottom - bacon bomb	~1-L aliquot 53609-17-12
CA-3	23-Feb-12	1101	53609-17-12d	filtered water bottom	Filtered water bottom of 53609-17-12 - 100 mL (spotted and oily looking - will repeat)
CA-3	23-Feb-12	1101	53609-17-12e	filtered water bottom	Filtered water bottom of 53609-17-12 - 150 mL (repeat filter sample - looks uniform across filter as other filter samples did)

Table C2 – Site Inspection Data

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Inspection Date	2/8/2012	2/15/2012	2/16/2012	2/21/2012	2/22/2012	2/23/2012
Start Time	8:00 AM	7:00 AM	7:00 AM	7:30 AM	10:15 AM	7:00 AM
End Time	5:00 PM	4:30 PM	2:45 PM	3:30 PM	3:30 PM	2:00 PM
Tank No.	3	3	3	5	1	4
Source Terminal and Carrier*						
Most Recent Delivery	2/6/12 A.M.	2/9/2012	2/7/2012	2/12/2012	2/21/2012	2/23/2012
Monthly Throughput (gallons/month)	not recorded	18000	6500	26000	< 20000	25000
How Water Monitored?	ATG	ATG	ATG	ATG	ATG	ATG
Threshold for Water Removal?	3/4 - 1 inch	1-2 inches	2 inches	Any amount	ATG alarm	Any
Water Removal History	None	None	None	None	None	None
Biocide Treatment History	Yes, in November, 2011, January 2011, and December 2011	unknown	2 times in the last year	unknown	none	unknown
Tank Cleaning History	November 2010 and May 2011	No	No	~Dec 2011. Also cleaned ATG probe	About 6 months ago	unknown - signs of cleaning on tank bottom
Tank Capacity (gals)	17265	12000	6000	10000	12000	6000
Tank Material	FRP	FRP	FRP	DWF	DWF	FRP
Tank Year of Installation	Unknown	2008	1988	1990	1991	1991
Tank Diameter (inches):	120	120	92	92	120	92
Single/Double Wall	Double	Double	Single	Double	Double	Double
Most Recent Tank Test:	Unknown	NA	5/4/2010	11/22/2011	8/16/2011	2/10/2012
Most Recent CP Test:	NA	NA	NA	NA	NA	NA
Piping Manifolded?	No	No	No	No	No	No

*Information redacted.

Table C2 – Site Inspection Data (continued)

Site ID	**NC-1**	**NY-1**	**NY-2**	**CA-1**	**CA-2**	**CA-3**
Tank Manifolded?	No (but 3/4 compartmented)	No (compartment)	No	No	No	No
STP Containment*	Yes	Yes - FRP	None - buried in sand/dirt	Yes	Yes	Yes, FRP sumps
STP Make/Model*	(new motor ~ 6 months)					
STP Check Valve	plastic style - minor pitting	Not checked	OK condition. Some corrosion on clip on bottom	Good condition	OK condition. Maintenance crew replaced it	OK condition. Swift check used
Line Leak Detector*	Could not remove to inspect		no corrosion	Ok condition no corrosion	Corrosion inside swift-check valve housing	Transducer clean. Has swift check valve
STP Shaft Condition	Corrosion pits	Good condition. mild corrosion in wetted portion	Severely corroded above and below product	No corrosion on top 12 inches of shaft. Severe corrosion. Dirtier toward bottom	Corroded heavily. Missing by-pass tube	Very corroded
Piping Material/DW?*		DWF	buried - unknown	FRP/DW	DWF	FRP-DW
Piping Diameter	Unknown	2 inches	unknown	2 inches	Unknown	2 inches
Recent Tank/Line/LD Test	Unknown	NA	~1 month ago	Unknown	8/16/2011	Unknown
Spill Container Info*		Inside sump, cover	plastic liner collapsed		Inside sump	
Ball Float Info (Overfill?)	Not present, Riser with vent only	no ball float or extractor	none	Corroded - viewed from tank video	Could not remove. Brass cage covered with green deposits	Very corroded. Broke pin. Could not remove

*Vender information redacted.

Table C2 – Site Inspection Data (continued)

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Drop Tube Info (Flapper?)*	Yes - overfill protection	Some minor deposits white crystals	Internal overfill protection. Could not inspect. Heavy white deposits and orange drippings along drop tube	None		Overfill protection - Spotted stained. Float corroded
ATG Probe Info*	White crystal deposits	New style.	Good condition. No corrosion on head. Mild deposits on floats	Good condition. No corrosion on shaft. Some deposits on floats	White/brown spots down shaft.	Fairly clean.
Tank Pad Condition	Good - concrete	Excellent - concrete	Good - concrete, minor cracks	Excellent - concrete	Good - concrete	Good – concrete

*Vender information redacted.

Table C3 – Riser Pipe Inspection Data

NC-1					
Riser ID	**Fill Pipe**	**ATG**	**STP**	**Ball Float**	
Riser Condition	OK	Minor corrosion	OK	Severe corrosion	
Cap/Adapter Condition	OK	OK	--	Severe corrosion	
Visible Corrosion?	Minor/inside	Minor	Corroded	Severe - only 1 thread	
Product Level (inches)	NA	27.5	NA	NA	
Water Bottom Level	None	None	Trace	None	
Fuel Samples Taken?	Yes	Yes	No	No	
Vapor Samples Taken?	Yes	No	No	No	
Water Sample Taken?	No	No	Yes	No	**Averages**
In-Tank Humidity (%)	98.4%	78.0%	--	96.3%	90.9%
In-Tank Temperature (°F)	53.2	61.9	--	56.2	57.1

NY-1 ("clean" site)					
Riser ID	**Fill Pipe**	**ATG**	**STP**	**By Fill**	
Riser Condition	OK	OK	OK	Good	
Cap/Adapter Condition	Good	OK	OK	Good	
Visible Corrosion?	No	No	Minor	Minor	
Product Level (inches)	NA	48	NA	NA	
Water Bottom Level	Yes	None	None	None	
Fuel Samples Taken?	Yes	No	No	Yes	
Vapor Samples Taken?	No	No	No	Yes	
Water Sample Taken?	Yes	No	No	No	**Averages**
In-Tank Humidity	79.5%	83.9%	--	86.6%	83.3%
In-Tank Temperature (°F)	48.1	47.5	--	44.8	46.8

-- = not measured

Table C3 – Riser Pipe Inspection Data (continued)

NY-2						
Riser ID	**Fill Pipe**	**ATG**	**STP**	**Ball Float**	**Other**	
Riser Condition	OK	OK	Bad	Good	Corroded	
Cap/Adapter Condition	OK	OK	--	Good	OK	
Visible Corrosion?	Yes - on drop tube	Minor	Yes	Yes - on plug	Yes - on riser	
Product Level (inches)	NA	35	NA	NA	NA	
Water Bottom Level	No	No	No	No	Yes	
Fuel Samples Taken?	Yes	No	No	Yes	No	
Vapor Samples Taken?	No	No	No	Yes	No	
Water Sample Taken?	No	No	No	No	Yes	**Averages**
In-Tank Humidity	93.9%	93.6%	--	96.2%	98.3%	95.5%
In-Tank Temperature (°F)	45.1	44.7	--	43.7	45.2	44.7

CA-1					
Riser ID	**Fill Pipe**	**ATG**	**STP**	**Ball Float**	
Riser Condition	NA	OK	Good	--	
Cap/Adapter Condition	Good	Good	--	OK	
Visible Corrosion?	NA	Minor	Yes	NA	
Product Level (inches)	NA	15	NA	NA	
Water Bottom Level	No	No	Trace	No	
Fuel Samples Taken?	No	Yes	Yes	No	
Vapor Samples Taken?	No	Yes	No	No	
Water Sample Taken?	No	No	Yes	No	**Averages**
In-Tank Humidity	--	93.4%	54.0%	--	73.7%
In-Tank Temperature (°F)	--	54.5	69	--	61.8

-- = not measured

Table C3 – Riser Pipe Inspection Data (continued)

CA-2					
Riser ID	**Fill Pipe**	**ATG**	**STP**	**Other**	
Riser Condition	Good	OK	Bad	--	
Cap/Adapter Condition	OK	OK	--	--	
Visible Corrosion?	No	Minor	Yes	--	
Product Level (inches)	NA	49	NA	NA	
Water Bottom Level	--	--	--	--	
Fuel Samples Taken?	Yes	No	Yes	No	
Vapor Samples Taken?	No	Yes	No	No	
Water Sample Taken?	Yes	No	No	No	**Averages**
In-Tank Humidity	--	78.3%	65.3%	--	71.8%
In-Tank Temperature (°F)	--	63.8	69	--	66.4

CA-3					
Riser ID	**Fill Pipe**	**ATG**	**STP**	**Ball Float**	
Riser Condition	OK	Corroded	Bad	Bad	
Cap/Adapter Condition	OK	OK	--	OK	
Visible Corrosion?	Slight	Yes	Heavy	Severe	
Product Level (inches)	NA	28	NA	NA	
Water Bottom Level	No	Yes	No	No	
Fuel Samples Taken?	No	Yes	Yes	No	
Vapor Samples Taken?	No	Yes	No	No	
Water Sample Taken?	Yes	Yes	No	No	**Averages**
In-Tank Humidity	--	97.3%	91.1%	97.3%	95.2%
In-Tank Temperature (°F)	--	55.8	65.6	53.1	58.2

-- = not measured

Table C4 – Dispenser Inspection Data

NC-1			
Dispenser #	**17**	**15**	**16**
Dispenser Make/Model*			
Dispenser Containment	Yes	Yes	Yes
Filter Make/Model*			
Filter Date Replaced	5/17/2011	1/24/2012	1/24/2012
Filter Condition (internal)	Good	Good	Good
Meter Condition	OK	OK	OK
Calibration Date	2011 Jan	2011 Jan	2011 Jan
Shear Valve Condition	OK	OK	OK
Nozzle Make/Model*			
Nozzle Condition	OK	OK	OK
Swivels Condition	OK	OK	OK
Visible Leaks	No	No	No

NY-1	
Dispenser #	**5/6**
Dispenser Make/Model*	
Dispenser Containment	Yes
Filter Make/Model*	
Filter Date Replaced	No Date
Filter Condition	Good
Meter Condition	OK
Calibration Date	Unknown
Shear Valve Condition	Good
Nozzle Make/Model*	
Nozzle Condition	Good
Swivels Condition	Good
Visible Leaks	No

*Information redacted.

Table C4 – Dispenser Inspection Data (continued)

NY-2	
Dispenser #	**3/4**
Dispenser Make/Model*	
Dispenser Containment	None
Filter Make/Model	None
Filter Date Replaced	NA
Filter Condition	NA
Meter Condition	OK
Calibration Date	Unknown
Shear Valve Condition	OK
Nozzle Make/Model*	
Nozzle Condition	OK
Swivels Condition	OK
Visible Leaks	No

CA-1			
Dispenser #	**3/4**	**5/6**	**11/12**
Dispenser Make/Model*			
Dispenser Containment	Yes	Yes	Yes
Filter Make/Model*			
Filter Date Replaced	2/2/2012	2/2/2012	2/2/2012
Filter Condition	Good	Good	Good
Meter Condition	OK	OK	OK
Calibration Date	2011	2011	2011
Shear Valve Condition	Good	Good	OK
Nozzle Make/Model*			
Nozzle Condition	Good	OK	OK
Swivels Condition	Good	OK	OK
Visible Leaks	No	No	No

*Information redacted.

Table C4 – Dispenser Inspection Data (continued)

CA-2		
Dispenser #	**1/2**	**7/8**
Dispenser Make/Model*		
Dispenser Containment	Yes	Yes
Filter Make/Model*		
Filter Date Replaced	1/13/2012	1/13/2012
Filter Condition	Good	Good
Meter Condition	OK	OK
Calibration Date	2011 May 21	2011 May 21
Shear Valve Condition	OK	OK
Nozzle Make/Model*		
Nozzle Condition	OK	OK
Swivels Condition	OK	OK
Visible Leaks	No	No

CA-3				
Dispenser #	**3/4**	**7/8**	**9/10**	**13/14**
Dispenser Make/Model*				
Dispenser Containment	Yes	Yes	Yes	Yes
Filter Make/Model*				
Filter Date Replaced	1/9/2012	1/9/2012	1/9/2012	1/9/2012
Filter Condition	Good	Good	Good	Good
Meter Condition	OK	OK	OK	OK
Calibration Date	Unknown	Unknown	Unknown	Unknown
Shear Valve Condition	OK	OK	OK	OK
Nozzle Make/Model*				
Nozzle Condition	OK	OK	OK	OK
Swivels Condition	OK	OK	OK	OK
Visible Leaks	No	No	No	No

*Information redacted.

Appendix D

Sequencing Supplementary Data

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Table D1 – Raw Sequencing Data Statistics

Sample	Total # of reads per sample	Total # reads discarded <Q17	Total # of reads per sample after filtering	Percentage of reads discarded (%)	Filtered BLAST hits	Total Number of assigned reads (KRONA)	Percentage (Assigned KRONA reads / Filtered Sequencing reads)	Percentage (Assigned KRONA Reads / Filtered BLAST hits)
53609_06_09D	6.10E+07	7.53E+06	5.35E+07	12.3%	1.13E+05	1.10E+05	0.21%	97%
53609_08_09D	8.97E+07	1.05E+07	7.93E+07	11.7%	2.66E+05	2.42E+05	0.31%	91%
53609_14_08D	6.96E+07	9.09E+06	6.05E+07	13.1%	1.31E+05	1.29E+05	0.21%	99%
53609_14_09	9.57E+07	1.15E+07	8.42E+07	12.0%	2.65E+05	2.46E+05	0.29%	93%
Average	8.02E+07	1.07E+07	6.95E+07	13.3%	164036.00	1.54E+05	0.22%	96%

Table D2 – Positive genetics hits for each taxa in sample 53609-06-09D-Filtered Water Bottom (NY-1)

Count	TaxaID	Organism Name	Percent
33210	634452	Acetobacter pasteurianus IFO 3283-01	30.22%
22195	634177	Gluconacetobacter xylinus IFO 3288	20.20%
9566	714995	Acetobacter sp. LMG 1524	8.70%
7046	272568	Gluconacetobacter diazotrophicus 'Dobereiner PA1 5'	6.41%
6980	632112	Lactobacillus phage Lb338-1	6.35%
4547	290633	Gluconobacter oxydans 621H	4.14%
2662	381046	Kluyveromyces thermotolerans	2.42%
1645	525371	Roseomonas cervicalis ATCC 49957	1.50%
1517	391165	Granulibacter bethesdensis CGDNIH1	1.38%
1327	284593	Candida glabrata ATCC 2001	1.21%
937	559292	Saccharomyces cerevisiae S288c	0.85%
914	374840	Enterobacteria phage phiX174 sensu lato	0.83%
791	28985	Candida sphaerica	0.72%
788	559307	Zygosaccharomyces rouxii CBS 732	0.72%
606	399741	Serratia proteamaculans 568	0.55%
556	572480	Arcobacter nitrofigilis DSM 7299	0.51%
497	4954	Zygosaccharomyces bailii	0.45%
466	391600	Brevundimonas sp. BAL3	0.42%
460	583346	Clostridium kluyveri NBRC 12016	0.42%
446	469595	Citrobacter sp. 30_2	0.41%
401	536227	Clostridium carboxidivorans P7	0.36%
372	284591	Yarrowia lipolytica CLIB122	0.34%
368	460265	Methylobacterium nodulans ORS 2060	0.33%
354	525338	Lactobacillus plantarum subsp. plantarum ATCC 14917	0.32%
307	575586	Acinetobacter johnsonii SH046	0.28%
300	926570	Acidiphilium multivorum AIU301	0.27%
297	520522	Saccharomyces pastorianus Weihenstephan 34/70	0.27%
290	436907	Vanderwaltozyma polyspora DSM 70294	0.26%
258	208963	Pseudomonas aeruginosa UCBPP-PA14	0.23%
210	4952	Candida lipolytica	0.19%
196	6945	Ixodes dammini	0.18%
192	51657	Kluyveromyces delphensis	0.17%
178	184778	Candida deformans	0.16%
173	880591	Ketogulonicigenium vulgare Y25	0.16%
171	294746	Meyerozyma guilliermondii ATCC 6260	0.16%
165	96563	Pseudomonas stutzeri ATCC 17588	0.15%
154	768492	Serratia sp. AS9	0.14%

Count	TaxaID	Organism Name	Percent
153	366394	Sinorhizobium medicae WSM419	0.14%
147	746360	Pseudomonas fluorescens WH6	0.13%
144	450748	Propionibacterium sp. 5_U_42AFAA	0.13%
142	51914	Candida castellii	0.13%
138	303	Bacillus fluorescens putidus Flugge 1886	0.13%
137	525337	Lactobacillus paracasei subsp. paracasei ATCC 25302	0.12%
129	370354	Entamoeba dispar SAW760	0.12%
128	575588	Acinetobacter lwoffii SH145	0.12%
128	658080	Lachnospiraceae bacterium 5-2-56FAA	0.12%
127	27293	Kazachstania servazzii	0.12%
127	314266	Sphingomonas sp. SKA58	0.12%
123	216595	Pseudomonas fluorescens SBW25	0.11%
121	266265	Burkholderia cepacia LB400	0.11%
118	500640	Citrobacter sp. ATCC 29220	0.11%
117	537973	Lactobacillus paracasei subsp. paracasei 8700:2	0.11%
116	520461	Brucella pinnipedialis B2/94	0.11%
106	197054	Candida galli	0.10%

Table D3 - Positive genetics hits for each taxa in sample 53609-08-09D Filtered Water Bottom (NY-2)

Count	TaxaID	Organism Name	Percent
49891	634452	Acetobacter pasteurianus IFO 3283-01	23.03%
32506	525337	Lactobacillus paracasei subsp. paracasei ATCC 25302	15.01%
27741	634177	Gluconacetobacter xylinus IFO 3288	12.81%
13589	714995	Acetobacter sp. LMG 1524	6.27%
12944	537973	Lactobacillus paracasei subsp. paracasei 8700:2	5.98%
10101	868131	Methanobacterium paludis SWAN-1	4.66%
9629	272568	Gluconacetobacter diazotrophicus 'Dobereiner PA1 5'	4.45%
8183	543734	Lactobacillus casei BL23	3.78%
7942	290633	Gluconobacter oxydans 621H	3.67%
5834	96563	Pseudomonas stutzeri ATCC 17588	2.69%
4309	321967	Lactobacillus casei ATCC 334	1.99%
3957	525361	Lactobacillus rhamnosus BCM-HMP0056	1.83%
3655	498216	Lactobacillus casei str. Zhang	1.69%
2422	379731	Pseudomonas stutzeri A1501	1.12%
2094	47714	Lactobacillus casei subsp. alactosus	0.97%
1656	568704	Lactobacillus rhamnosus LC705	0.76%
1372	391165	Granulibacter bethesdensis CGDNIH1	0.63%
1321	374840	Enterobacteria phage phiX174 sensu lato	0.61%
1114	525371	Roseomonas cervicalis ATCC 49957	0.51%
1027	51369	Lactobacillus casei bacteriophage A2	0.47%
831	742766	Dysgonomonas gadei 1145589	0.38%
712	535289	Acidovorax ebreus TPSY	0.33%
710	568703	Lactobacillus rhamnosus ATCC 53103	0.33%
684	232721	Acidovorax sp. JS42	0.32%
593	496874	Lactobacillus phage Lrm1	0.27%
499	575599	Lactobacillus fermentum 28-3-CH	0.23%
462	632112	Lactobacillus phage Lb338-1	0.21%
436	596154	Alicycliphilus denitrificans DSM 14773	0.20%
366	460265	Methylobacterium nodulans ORS 2060	0.17%
357	913848	Lactobacillus coryniformis subsp. coryniformis ATCC 25602	0.16%
331	279281	Bacteriophage phi AT3	0.15%
246	486408	Lactobacillus rhamnosus HN001	0.11%
243	511437	Lactobacillus buchneri NRRL B-30929	0.11%
225	146269	Bacteriophage Lc-Nu	0.10%
208	1597	Lactobacillus paracasei	0.10%

Table D4 – Positive genetics hits for each taxa in sample 53609-14-08d Filtered Water Bottom (CA-2)

Count	TaxaID	Organism Name	Percent
51319	634177	Gluconacetobacter xylinus IFO 3288	39.80%
30707	634452	Acetobacter pasteurianus IFO 3283-01	23.81%
25713	290633	Gluconobacter oxydans 621H	19.94%
12783	272568	Gluconacetobacter diazotrophicus 'Dobereiner PA1 5'	9.91%
4775	714995	Acetobacter sp. LMG 1524	3.70%
1065	374840	Enterobacteria phage phiX174 sensu lato	0.83%
428	622759	Zymomonas mobilis NCIMB 11163	0.33%
341	555778	Halothiobacillus neapolitanus ATCC 23641	0.26%
323	391165	Granulibacter bethesdensis CGDNIH1	0.25%
229	314266	Sphingomonas sp. SKA58	0.18%
211	244592	Ahrensia sp. DFL-11	0.16%
153	926570	Acidiphilium multivorum AIU301	0.12%
146	370354	Entamoeba dispar SAW760	0.11%

Table D5 – Positive genetics hits for each taxa in sample 53609-14-09 Sediment Bacon Bomb (CA-2)

Count	TaxaID	Organism Name	Percent
106031	634177	Gluconacetobacter xylinus IFO 3288	43.14%
46856	290633	Gluconobacter oxydans 621H	19.06%
46577	634452	Acetobacter pasteurianus IFO 3283-01	18.95%
21169	272568	Gluconacetobacter diazotrophicus 'Dobereiner PA1 5'	8.61%
8294	714995	Acetobacter sp. LMG 1524	3.37%
3768	525337	Lactobacillus paracasei subsp. paracasei ATCC 25302	1.53%
2198	537973	Lactobacillus paracasei subsp. paracasei 8700:2	0.89%
1510	374840	Enterobacteria phage phiX174 sensu lato	0.61%
1332	543734	Lactobacillus casei BL23	0.54%
805	321967	Lactobacillus casei ATCC 334	0.33%
530	391165	Granulibacter bethesdensis CGDNIH1	0.22%
501	622759	Zymomonas mobilis NCIMB 11163	0.20%
475	525361	Lactobacillus rhamnosus BCM-HMP0056	0.19%
445	555778	Halothiobacillus neapolitanus ATCC 23641	0.18%
429	926570	Acidiphilium multivorum AIU301	0.17%
428	498216	Lactobacillus casei str. Zhang	0.17%
337	244592	Ahrensia sp. DFL-11	0.14%
315	525338	Lactobacillus plantarum subsp. plantarum ATCC 14917	0.13%
299	568703	Lactobacillus rhamnosus ATCC 53103	0.12%
268	913848	Lactobacillus coryniformis subsp. coryniformis ATCC 25602	0.11%

Figure D1 - 53609-06-09d Filtered Water Bottom (NY-1) Microbial Profile

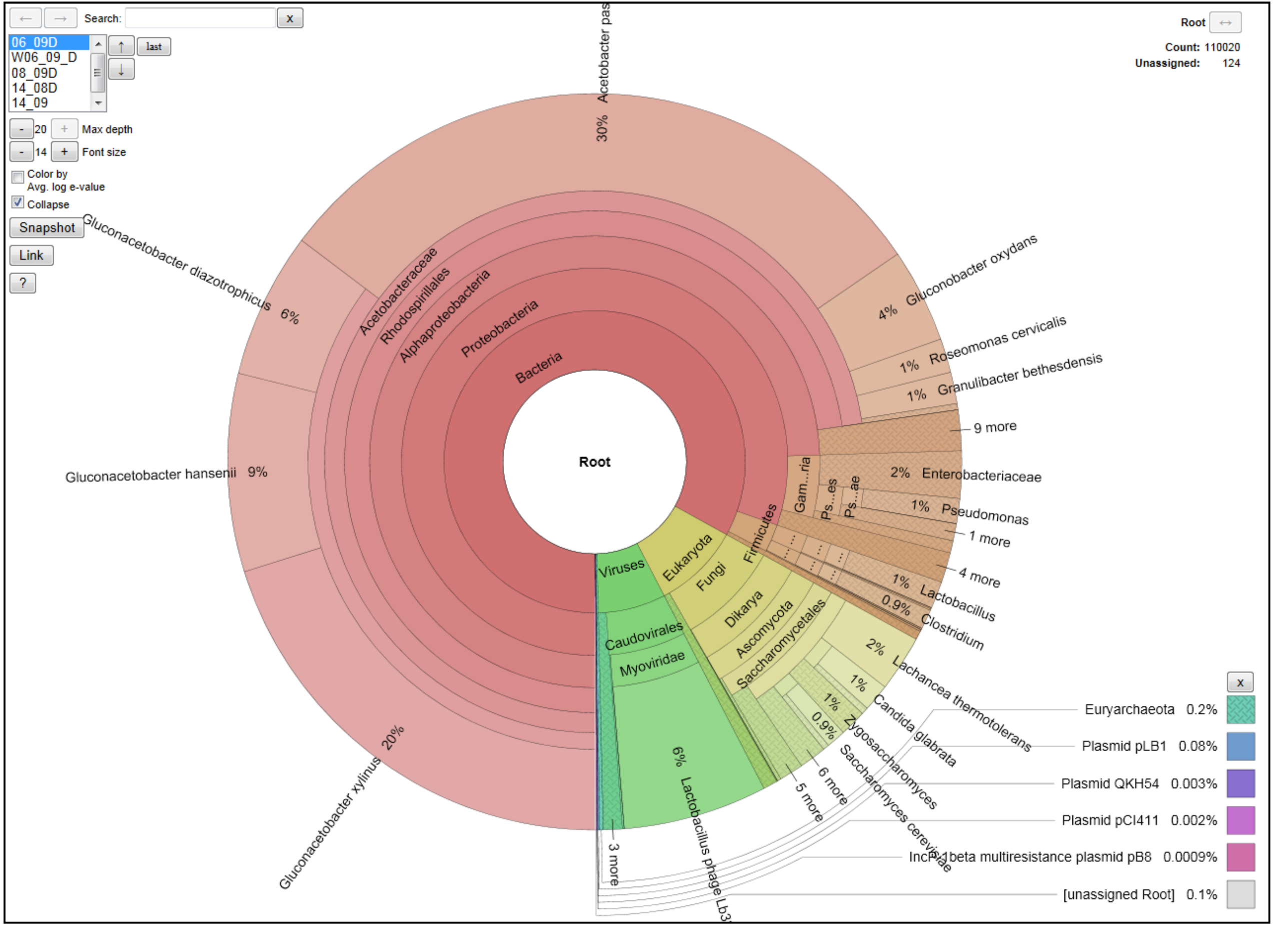


Figure D2 - 53609-08-09d Filtered Water Bottom (NY-2) Microbial Profile

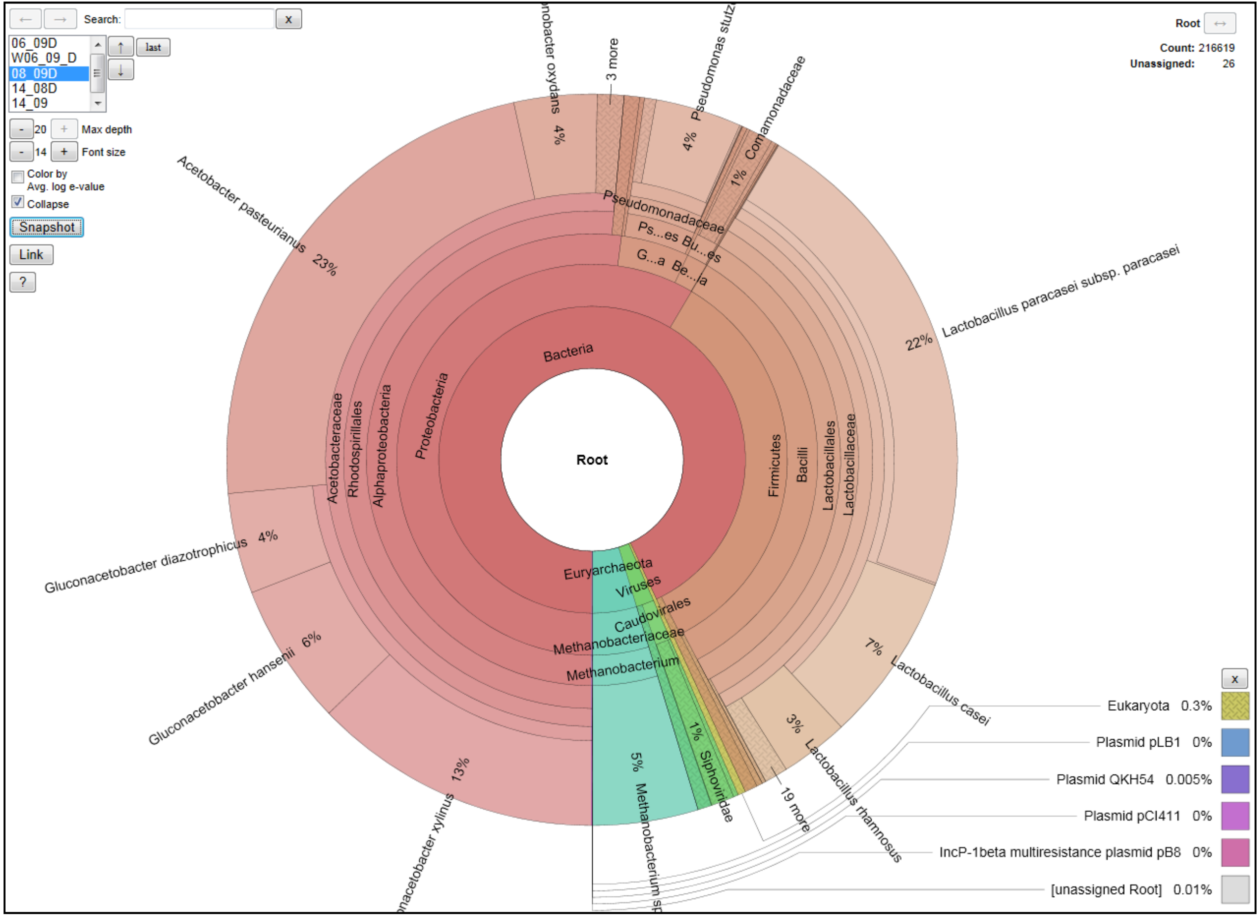


Figure D3 - 53609-14-08d Filtered Water bottom (CA-2) Microbial Profile

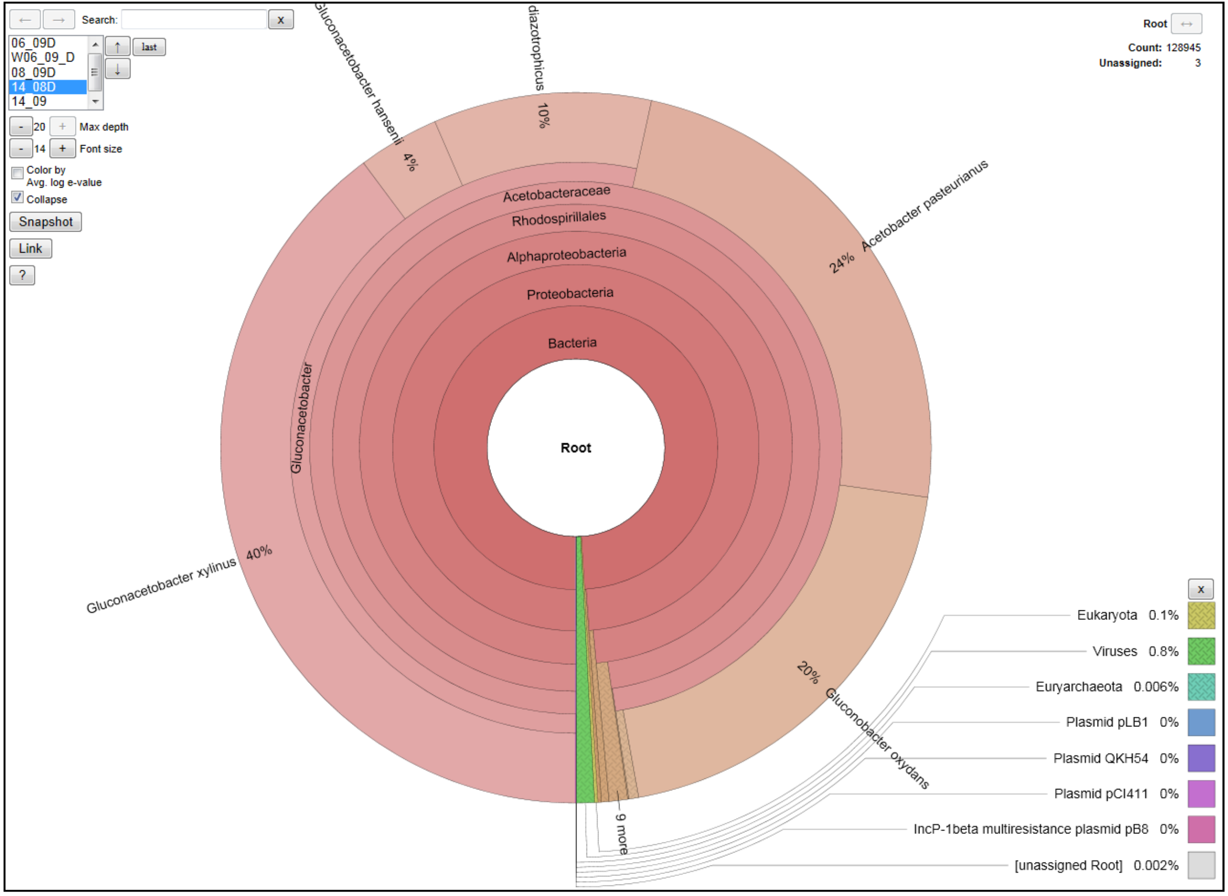


Figure D4 - 53609-14-09 Sediment bacon-bomb (CA-2) Microbial Profile

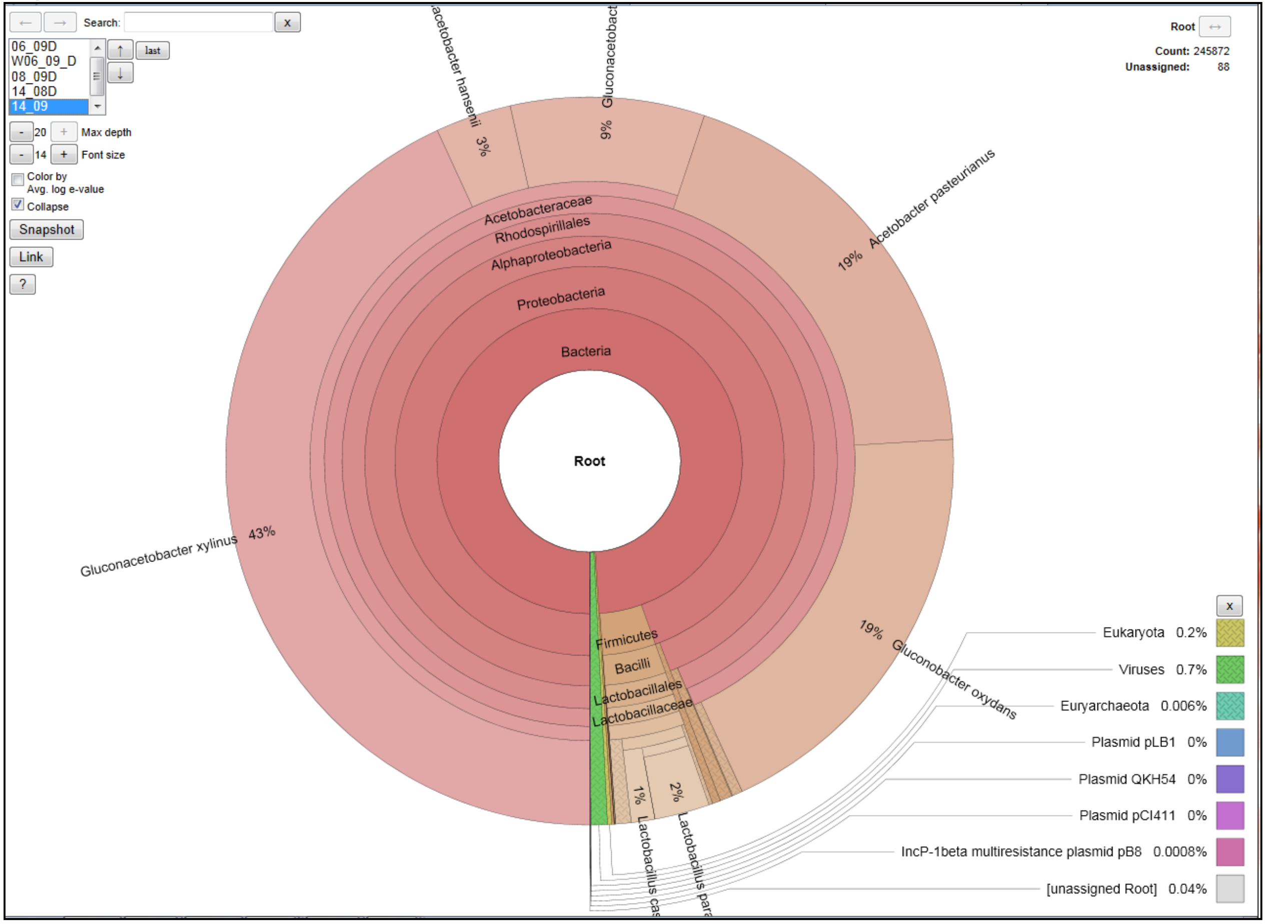


Figure D5 – 16s rRNA Amplification

Lane assignment

Gel 1

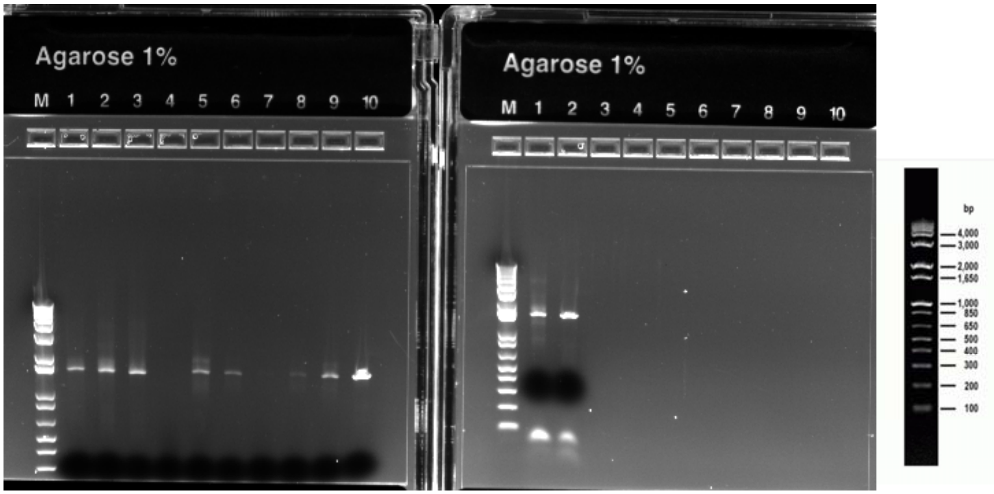
8Feb12_07C

1. 8Feb12_09
2. 53609-06-08C
3. 53609-08-09e
4. 53609-08-08c
5. 53609-11-11e
6. 53609-11-08c
7. 53609-11-11d
8. 53609-14-07c
9. 53609-17-11

Gel 2

1. 53609-17-10c

53609-17-12d



Appendix E

Characteristics of Dominant Identified Organisms

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Appendix E- Characteristics of dominants organisms identified in samples

Bold characteristics directly relate to this research project.

- *Acetobacter sp.*
    - Gram negative
    - Some motile
    - No spores
    - Obligate aerobe (requires oxygen)
    - Optimal temperature 25-30°C, pH 5.4-6.3
    - **Oxidize Ethanol to Acetic Acid**
    - Oxidize acetate or lactate to CO_2 or H_2O
    - Acid is formed from n-propanol, n-butanol and D-glucose
    - **Prefer alcohol enriched environments**
    - Environmental bacterium

- *Gluconacetobacter sp.*
    - **N_2-fixing**
    - Gram negative
    - Some motile
    - No spores
    - Obligate aerobe (requires oxygen)
    - Optimal temperature 25-30°C, pH 5.4-6.3
    - **Oxidize Ethanol to Acetic Acid**
    - Oxidize acetate or lactate to CO_2 or H_2O
    - Acid is formed from n-propanol, n-butanol and D-glucose
    - **Prefer alcohol enriched environments**
    - **Produces cellulose (Biofilm); *G. xylinus***
    - Environmental bacterium

- *Gluconabacter oxydans*
    - Gram negative
    - Some motile
    - No spores
    - Obligate aerobe (requires oxygen)
    - Some species can use thiosulfate and produce H_2S
    - Optimal temperature 25-30°C, no growth at 37°C
    - Optimal pH 5.5-6.0. Can grow in ph 3.6.
    - **Oxidize Ethanol to Acetic Acid**
    - Do not oxidize acetate or lactate to CO_2 or H_2O
    - Produce ketogluconic acid from glucose
    - **Prefer sugar-enriched environments**
    - Environmental bacterium

- *Lactobacillus sp.*
    - Gram positive
    - No spores
    - Non-motile
    - **Facultative anaerobe – grow best under reduced oxygen tension (limited oxygen)**
    - **Fermentative and saccharoclastic**
    - **Produce lactic acid**
    - Optimum growth temperature 30-40°C
    - Environmental bacteria associated with animals and vegetables

- *Zygosaccharomyces sp.*
    - High tolerance to sugar (50-60%), ethanol (up to 18%), acetic acid (2.0-2.5%), low pH tolerance
    - Can utilize acetic acid, ethanol, glucose, proprionic acid, formic acid, but not lactic acid as energy source
    - **May produce ethanol under fermentative conditions**

Appendix F

Chemical Analysis Results of Water Bottoms, Fuels, and Vapor Samples

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Table F1 – Water Bottom Chemical Analysis Results

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Fluoride, ppmw	1074	1205	1796	4653	4372	3595
Chloride, ppmw	6974	3871	1933	1166	805	162
Chloride, ppmw	6400	3800	2000	190	1200	820
Chloride, ppmw	7000	4000	2000	1000	660	200
Chloride, average, ppmw (n = 3)	**6791**	**3890**	**1978**	**785**	**888**	**394**
Nitrite, ppmw	<1	<1	<1	<1	<1	<1
Bromide, ppmw	<1	<1	<1	<1	<1	<1
Nitrate, ppmw	7.7	507	96	<1	345	<1
Nitrate, ppmw	70	520	23	26	270	27
Nitrate, average, ppmw (n = 2)	**39**	**514**	**60**	**26**	**308**	**27**
Phosphate, ppmw	25	<1	<1	<1	<1	<1
Sulfate, ppmw	519	509	364	795	445	502
Sulfate, ppmw	360	430	260	400	100	250
Sulfate, average, ppmw (n = 2)	**440**	**470**	**312**	**598**	**273**	**376**
Sodium, ppmw	6124	2291	1886	581	158	182
Ammonium, ppmw	871	<1	452	30	37	5.2
MEA, ppmw	<1	<1	<1	<1	<1	<1
DEA, ppmw	<1	<1	<1	<1	<1	<1
Potassium, ppmw	370	639	278	<1	45	51
TEA, ppmw	<1	<1	<1	<1	<1	<1
MDEA, ppmw	<1	<1	<1	<1	<1	<1
Magnesium, ppmw	<1	<1	112	63	614	25
Calcium, ppmw	<1	<1	<1	732	586	242
pH	5.2	4.6	4.2	3.7	3.9	3.6
pH	5.3	4.6	4.1	3.5	3.7	3.8
pH	5.25	4.62	4.10	3.69	3.83	3.54
pH, average (n = 3)	**5.3**	**4.6**	**4.1**	**3.6**	**3.8**	**3.6**
Formate, ppmw	78	1400	69	350	300	280
Acetate, ppmw	17000	9000	18000	20000	22000	15000
Acetate, ppmw	16000	9000	24000	25000	13000	25000
Acetate, average, ppmw (n = 2)	**16500**	**9000**	**21000**	**22500**	**17500**	**20000**
Conductivity, µS/cm	21000	17000	12000	4000	7500	8000

Table F1 – Water Bottom Chemical Analysis Results (continued)

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Glycolate, ppmw	<100	4000	<100	11000	11000	5000
Carbonate, ppmw	12	57	19	65	72	41
Fouling GC-MS Scan	methyl vinyl ketone, acetic acid, ethanol, 1,2-ethane diol, propylene glycol, N-butyl-1-butanamine, N-ethyl-cyclohexylamine	methanol, ethanol, acetic acid, 1,2-ethane diol, propylene glycol, N,N-dimethyl formamide, significant N,N-dimethylbenzenemethanamine, unidentified phthalate	ethanol, acetic acid, 2-hexanone	acetic acid, glycol, ethanol	acetic acid, 1,1'-oxybis-2-propanol, traces of glycol and dioxane	acetic acid, traces of dioxane, glycol, and 2,5-dimethyl-1,4-dioxane, very faint trace of ethanol

Table F1 – Water Bottom Chemical Analysis Results (continued)

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Al, ppmv	105.1	125.1	247.1	400.0	459.4	112.2
As, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
B, ppmv	4.7	5.6	4.0	150.4	5.4	12.3
Ba, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	1.7	< 1.9
Bi, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
Ca, ppmv	171.6	343.0	280.1	812.8	529.1	252.4
Cd, ppmv	< 0.9	< 1.0	< 1.0	5.2	5.6	2.6
Co, ppmv	< 0.9	2.1	< 1.0	< 1.0	1.0	< 0.9
Cr, ppmv	< 0.9	< 1.2	< 1.0	3.6	2.9	1.7
Cu, ppmv	2.7	1.1	16.3	3.0	2.4	38.1
Fe, ppmv	420.6	2217	912.2	4962	4069	2746
K, ppmv	55.9	59.9	65.9	31.0	20.0	11.5
Li, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
Mg, ppmv	36.8	1231	113.5	74.6	523.4	36
Mn, ppmv	37.7	73.3	19.8	219.8	46.9	74.2
Mo, ppmv	< 0.9	< 1.0	< 1.0	< 1.0	< 1.0	< 0.9
Na, ppmv	5355	2183	1695	549.4	158.6	192
Ni, ppmv	7.1	3.2	3.5	7.6	8.9	5.6
P, ppmv	3.3	< 2.3	14.2	3.1	< 1.9	< 1.9
Pb, ppmv	3.3	< 2.0	39.4	4.4	7.4	12.0
Pd, ppmv	< 9.4	< 9.5	< 9.5	< 9.6	< 9.5	< 9.3
Pt, ppmv	< 5.6	< 12.3	< 5.7	< 29.1	< 23.6	< 15.8
S, ppmv	352.7	689.1	235.9	239.5	84.5	114
Si, ppmv	24.0	30.0	29.9	52.8	50.5	33.1
Sn, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	2.2	< 1.9
Sr, ppmv	< 1.9	< 1.9	< 1.9	4.7	2.5	3.5
Ti, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
V, ppmv	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
Zn, ppmv	22.6	1494	926.8	596.1	413.8	83.2

Table F2 – Fuel Chemical Analysis Results

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
API Gravity @ 60°F	36.00	35.24	35.18	39.25	38.70	38.95
Biodiesel, volume%	<0.3	3.55	0.40	<0.3	<0.3	<0.3
Nitrogen, ppmw	3	15	12	<2	<2	<2
Fouling GC-MS Scan	trace EtOH	trace EtOH, C-18 FAME, lesser C16, C20, trace C22 and C24	trace EtOH	trace EtOH	NTR	NTR
Cond. ps/m @ Ambient	125	1200	183	30	70	64
NACE TM01-72 Rating	A	A	A	D*	C*	C*
Sulfur, ppmw	7.2	7.7	7.3	5.9	6.4	6.2
H_2O, ppmw	39	65	46	44	41	29
Total Acid Number, mg KOH/L	0.01	0.04	0.02	0.002	0.005	0.006
Carbon, wt%	85.8	84.5	86	85	85.5	85.8
Hydrogen, wt%	13.2	13	13.1	13.7	13.7	13.8
Particulate, mg/L	54.5	87.4	91.4	114.8	69	122.2
Formate, ppmw	<LOQ	5.6	<LOQ	<LOQ	<LOQ	<LOQ
Acetate, ppmw	<LOQ	7.7	2.8	2.7	<LOQ	5.9

* = indicates a failing result

NTR = nothing to report outside of normal expected hydrocarbons

Table F3 – Vapor Chemical Analysis Results – SKC Tube

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Formic Acid, ppbv	18	48	110	190	88	72
Acetic Acid, ppbv	570	1,800	3,600	7,800	9,500	16,000
Propionic Acid (Propanoic), ppbv	1.6	15	2.3	1.8	1.7	2.0
2-Methylpropanoic Acid (Isobutyric), ppbv	< 0.77	0.79	< 0.74	< 0.69	< 0.71	< 0.69
Butanoic Acid (Butyric), ppbv	< 0.77	0.85	< 0.74	< 0.69	< 0.71	< 0.69
2-Methylbutanoic Acid, ppbv	< 0.66	< 0.63	< 0.64	< 0.59	< 0.61	< 0.60
3-Methylbutanoic Acid (Isovaleric), ppbv	< 0.66	< 0.63	< 0.64	< 0.59	< 0.61	< 0.59
Pentanoic Acid (Valeric), ppbv	< 0.66	< 0.63	< 0.64	< 0.59	< 0.61	< 0.59
2-Methylpentanoic Acid, ppbv	< 0.57	< 0.55	< 0.56	< 0.52	< 0.53	< 0.52
3-Methylpentanoic Acid, ppbv	< 0.57	< 0.55	< 0.56	< 0.52	< 0.53	< 0.52
4-Methylpentanoic Acid (Isocaproic), ppbv	< 0.58	< 0.55	< 0.56	< 0.52	< 0.53	< 0.52
Hexanoic Acid (Caproic), ppbv	< 0.57	< 0.55	< 0.55	< 0.52	< 0.53	< 0.52
Heptanoic Acid (Enanthoic), ppbv	< 0.50	< 0.48	< 0.49	< 0.45	< 0.46	< 0.45
2-Ethylhexanoic Acid, ppbv	< 0.46	< 0.44	< 0.45	< 0.42	< 0.43	< 0.42
Cyclohexanecarboxylic Acid, ppbv	< 0.52	< 0.50	< 0.50	< 0.47	< 0.48	< 0.47
Octanoic Acid (Caprylic), ppbv	< 0.46	< 0.44	< 0.45	< 0.41	< 0.43	< 0.42
Benzoic Acid, ppbv	< 0.59	< 0.57	< 0.57	< 0.53	< 0.55	< 0.53
Nonanoic Acid (Pelargonic), ppbv	< 0.41	< 0.40	< 0.40	< 0.37	< 0.38	< 0.37

Table F4 – Vapor Chemical Analysis Results – Tedlar Bag

Site ID	NC-1	NY-1	NY-2	CA-1	CA-2	CA-3
Carbonyl Sulfide (COS), ppmw	0.14	bag ruptured	0.29	not received	0.12	0.22 0.14 (duplicate)

Appendix G

Corrosion Discussion and Chemical Analysis Results of Bottom Sediments and Scrapings

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XRD

Scrape samples-XRD analysis of samples scraped from the riser pipes and UST equipment, as well as, solids obtained from a wipe sample was performed. The XRD patterns for the analyzed samples are shown in Table G2. In all cases the mineralogy of the samples was nearly identical indicating the only phase present is goethite (α-FeOOH). Goethite forms in aqueous media by direct precipitation of soluble Iron [Fe(III)] species, supplied by the hydrolysis of Fe(III) solutions, by dissolution of a solid precursor, or by oxidation/hydrolysis of Fe(II) slat solution. The presence of steel would provide a suitable source of iron in the system for the formation of iron oxides via oxidation of Fe(0) to Fe (II) to Fe(III). This result is consistent with the corrosion that was empirically observed across different sites. Weak patterns from other sites generally found various combinations of goethite, magnetite (Fe_3O_4), and lepidocrocite (FeOOH), which is a polymorph of goethite. There were a limited number of samples that contained various copper (Cu), zinc (Zn), and aluminum (Al) compounds which might be expected given that depending on manufacturer brass, galvanized steel, and aluminum alloys are all used in these systems.

XRF

Particulates in Fuel and Water samples-XRF was conducted on particulate filtered from fuel and water samples taken from all sample sites. For ease of comparison concentrations were generalized as Major (greater than 1%), Minor (from 0.1% to 0.9%), or Trace (less than 0.1%) and the results are summarized in Table G6. In a rough comparison between the fuel and water samples the water appears to, in general, contain higher concentrations of the measured elements. This would be consistent with the majority of corrosion processes occurring in the aqueous phase. Most of the elements detected would be consistent with being produced from the dissolution of steel as many of the elements are common alloying additions. In particular, high levels of Fe are detected and expected based on the actual observation. The relatively small quantities of Nickel (Ni) and Chromium (Cr) could be interpreted as circumstantial evidence that any stainless steel used in the system is corroding at lower rates than the steel components – although it should be noted that a relatively smaller proportion of stainless steel is used in these systems relative to plain carbon steels. Elevated concentrations of Cu and Zn were detected in the aqueous phase of some sites and could be attributed to corrosion of brass or the dissolution of galvanized zinc coatings used on some steel components. Both brass and galvanized steel can be present in UST assemblies. Similarly, Al components are often used in these systems and their corrosion may be associated with the higher amounts of detected aluminum in the water phase. The presence of high concentration of chloride (Cl) is a concern from a corrosion perspective as chlorides lead to the breakdown of passivity and can enhance pitting.

Scrape samples-XRF was also conducted on scale samples collected from different retail sites with results summarized in Table G4. As with the XRD data the results are consistent with what would be expected from corrosion of Fe-rich alloys and steels. By proportion large concentrations of Fe (~50-65%) and Oxygen (~30-40%) were detected. Many of the other elements detected in smaller quantities, Manganese (Mn) for example, are common alloying additions used in steels and conceivable would be present in the corrosion product. It should be noted that although Fe and O were generally present in the highest concentration there were also instances in which Zn or Cu and Zn were detected in large concentrations. These could be attributed to degradation of galvanized steels and brass components which are both reported to be used in diesel USTs.

GC-MS

Gas chromatography was used to determine the presence of vaporizable compounds in samples taken from a number of different locations at each site. As an example, samples were obtained from the STP pump shaft, inside the STP riser, the brass plug and cast iron plugs on the ball float riser, the STP bowl, and from sediment at the bottom of the UST among other locations. It is believed that this selection of samples provided a representative overview of the system across different geographic locations as a whole and was used to look for patterns at different sites. Water and an assortment of boiling range hydrocarbons were common to all samples and locations sampled. This would be expected given diesel and the introduction of water into the system as described in the report. Of particular relevance, acetic acid was detected, sometimes in large amounts, in at least one sample from every location and was present in approximately 75 percent of the samples overall. Additionally, acetaldehyde was found in at least one sample collected from every site with the exception of NC-1. Acetaldehyde is an intermediary compound that forms when ethanol is oxidized and can be converted into acetic acid. The presence of both acetic acid and acetaldehyde would have an effect on total acidity with possible consequences for the materials ULSD USTs. The NY-1 site was the only site found to contain methanol.

ICP-MS

ICP-MS analysis was also used for a determination of elemental components in the aqueous portion of fuel samples and samples taken from scrapings and deposits obtained from each site. Summary ICP results can be found in Table G1. Generally, as with other analysis performed for this study, the species detected are consistent with either corrosion of component materials or species that might promote corrosion. Appreciable quantities of Fe, Al, Mg, Mn, S, Zn, Si, Na, and Ca (the Na and Ca were likely from mineral components in the water samples) were found in the aqueous portions of fuel at most sites with Cu found in noticeable amounts at 2 sites. Although the exact compositions of a scrape sample is dictated by the surface material they are obtained from, Fe was generally found to exist in large amounts in nearly every scrape sample analyzed. This is consistent with the XRD and XRF results discussed above and expected given the amount of steel used in the systems. Other elements detected across most samples in appreciable but significantly lower concentrations as compared to Fe include: Al, Cr, Cu, Ni, Pb, S, Si, and Zn, while Ca, Cd, Sn, and Ti were also found in a small number of samples. Given the large amount of observed corrosion and an understanding that these systems can contain a combination of steel, stainless steel, brass, aluminum and galvanized steel components it is not surprising that most of the elements above were detected. Additionally, as would be expected there appears to be a correlation between the material where the sample was obtained from and the ICP-MS analysis.

For example, a sample taken from a brass plug from a ball float riser (NY-2) was found to contain elevated concentrations of Cu, Zn, and Sn as might be expected from a corroding brass surface. Similarly, samples obtained from the outside of the fill pipe and inside of the riser pipe groove (both NY-2) both contained elevated concentrations of Al with appreciable amounts of Cu, Fe, Mg, Si and Zn, which all are common alloying elements found in aluminum alloys. Samples obtained from both the top and bottom of the STP shaft of the CA-3 site were found to predominately contain Fe but also contained quantities of Cr, Ni, and Mo which might be associated with a stainless steel. The above serves as circumstantial evidence that not only are the carbon steel components of this system susceptible to corrosion but the brass, aluminum, and stainless components may also undergo some level of attack in the environments encountered with diesel USTs.

Table G1 – ICP Analysis Results of Bottom Sediment and Scraping

Site ID	NC-1	NC-1	NC-1	NY-1	NY-2	NY-2
Sample Description	**scraping cap of ball float riser**	**scraping inside of ball float riser**	**scraping STP riser & bowl**	**scraping inside STP riser**	**scraping brass plug on ball float riser**	**scraping cast iron plug from brass plug on ball float riser**
Sample ID	**8Feb12_03A**	**8Feb12_04A**	**8Feb12_11A**	**53609-06-12 split**	**53609-08-03a**	**53609-08-04a**
Al (ppmw)	581.8	823.5	999.9	<54.5	< 62.1	682.2
As (ppmw)	< 24.3	< 30.7	< 25.7	< 21.8	< 24.8	< 28.4
B (ppmw)	< 24.3	< 30.7	< 25.7	<120.7	< 24.8	< 28.4
Ba (ppmw)	< 24.3	< 30.7	< 25.7	< 21.8	< 24.8	< 28.4
Be (ppmw)	< 12.2	< 15.4	< 12.9	< 10.9	< 12.4	< 14.2
Bi (ppmw)	55.8	93.4	51.9	<117	< 24.8	56.6
Ca (ppmw)	37.8	45.2	105.6	<104.1	202.3	92.4
Cd (ppmw)	51.4	81.7	51.1	<141.30	< 12.4	53.2
Co (ppmw)	14.9	20.4	< 12.9	<19.4	< 12.4	< 14.2
Cr (ppmw)	< 12.2	32.4	108.4	<178.9	< 12.4	90.3
Cu (ppmw)	< 12.2	< 15.4	108.3	<16.98	150300.0	1142.0
Fe (ppmw)	359400	539100.0	353800.0	421500.0	2381.0	407300.0
K (ppmw)	< 73.0	< 92.1	< 77.2	< 65.4	< 74.5	< 85.2
Li (ppmw)	< 24.3	< 30.7	< 25.7	< 21.8	< 24.8	< 28.4
Mg (ppmw)	< 12.2	25.9	17.8	59.1	93.7	53.2
Mn (ppmw)	355.7	4453.0	1826.0	3105.0	67.4	571.3
Mo (ppmw)	< 12.2	< 15.4	< 12.9	< 10.9	< 12.4	15.7
Na (ppmw)	< 36.5	< 46.1	67.1	68.8	< 37.2	< 42.6
Ni (ppmw)	30.7	139.0	231.3	<128.30	730.0	36.3
P (ppmw)	58.5	68.9	141.2	220.5	< 24.8	88.0
Pb (ppmw)	<33.8	<47.0	<39.51	<93.4	6017.0	102.3
S (ppmw)	126.8	335.8	208.6	261.9	1124.0	1090.0
Sb (ppmw)	< 60.8	< 76.8	< 64.3	< 54.5	< 62.1	< 71.0
Se (ppmw)	< 12.2	< 15.4	< 12.9	< 10.9	< 12.4	< 14.2
Si (ppmw)	1529.0	1132.0	1193.0	240.7	< 24.8	3925.0
Sn (ppmw)	< 24.3	< 30.7	< 25.7	<36.1	2013.0	98.1
Ti (ppmw)	< 24.3	< 30.7	< 25.7	< 21.8	< 24.8	< 28.4
V (ppmw)	< 24.3	< 30.7	< 25.7	< 21.8	< 24.8	< 28.4
Zn (ppmw)	< 12.2	53.2	48.9	<83.2	8159.0	79.9

Table G1 – ICP Analysis Results of Bottom Sediment and Scraping (continued)

Site ID	NY-2	NY-2	NY-2	NY-2	NY-2	NY-2
Sample Description	**scraping inside spare other riser**	**scraping outside of fill pipe**	**scraping inside riser pipe groove**	**sediment water bottom**	**scraping bottom of pump head**	**scraping STP shaft**
Sample ID	**53609-08-05a**	**53609-08-06a**	**53609-08-07 split**	**53609-08-09e split a**	**53609-08-14 split**	**53609-08-15 split**
Al (ppmw)	1289.0	89260	65630	367.6	927.2	878.0
As (ppmw)	< 23.3	<25.9	< 13.0	< 24.2	< 25.2	< 29.3
B (ppmw)	< 23.3	<25.9	< 25.9	< 24.2	< 25.2	< 29.3
Ba (ppmw)	< 23.3	<25.9	<25.9	< 24.2	< 25.2	< 29.3
Be (ppmw)	< 11.7	<13.0	< 2.6	< 12.1	< 12.6	< 14.7
Bi (ppmw)	42.1	<25.9	< 25.9	< 24.2	100.1	63.2
Ca (ppmw)	23.5	88.45	105.0	269.1	78.8	83.8
Cd (ppmw)	44.3	<13.0	< 2.6	< 12.1	59.5	57.3
Co (ppmw)	< 11.7	<13.0	< 2.6	< 12.1	15.9	< 14.7
Cr (ppmw)	66.1	39.97	42.2	< 12.1	192.0	187.5
Cu (ppmw)	879.4	52.56	862.1	231.5	42.9	38.5
Fe (ppmw)	294400.0	1768	972.3	2454.0	410400.0	396600.0
K (ppmw)	< 69.9	<151	298.6	< 72.7	< 75.5	< 88.0
Li (ppmw)	< 23.3	<25.9	< 2.6	< 24.2	< 25.2	< 29.3
Mg (ppmw)	18.8	386.10	204.9	107.8	18.0	24.7
Mn (ppmw)	1037.0	128.10	79.1	27.1	2557.0	2519.0
Mo (ppmw)	< 11.7	<13.0	< 2.6	< 12.1	17.3	16.0
Na (ppmw)	< 35.0	824.40	25810.0	1612.0	80.5	450.4
Ni (ppmw)	71.5	4.82	13.2	< 12.1	67.6	74.3
P (ppmw)	< 23.3	<45.8	45.3	67.6	103.3	117.1
Pb (ppmw)	836.7	82.10	<84.8	58.9	<71.26	<35.35
S (ppmw)	439.9	494.7	102.4	268.4	1071.0	646.8
Sb (ppmw)	< 58.3	<64.8	< 13.0	< 60.6	< 62.9	< 73.4
Se (ppmw)	< 11.7	<13.0	< 13.0	< 12.1	< 12.6	< 14.7
Si (ppmw)	127.8	743.20	870.4	< 24.2	183.1	151.7
Sn (ppmw)	74.9	<2.59	<25.9	< 24.2	< 25.2	< 29.3
Ti (ppmw)	< 23.3	47.09	79.6	< 24.2	< 25.2	< 29.3
V (ppmw)	< 23.3	<25.9	<25.4	< 24.2	< 25.2	< 29.3
Zn (ppmw)	54360.0	10960	3451.0	1511.0	74.3	52.4

Table G1 – ICP Analysis Results of Bottom Sediment and Scraping (continued)

Site ID	NY-2	NY-2	CA-1	CA-1	CA-1	CA-1	CA-2
Sample Description	**scraping STP shaft**	**scraping STP bowl**	**scraping ATG riser**	**scraping top of STP shaft**	**scraping bottom of STP shaft**	**sediment water bottom**	**scraping STP bowl**
Sample ID	**53609-08-15 split**	**53609-08-16 split**	**53609-11-04 split**	**53609-11-09a**	**53609-11-09c split**	**53609-11-11e split a**	**53609-14-06a**
Al (ppmw)	878.0	725.1	<58.8	587.2	761.9	886	805.4
As (ppmw)	< 29.3	< 20.9	< 23.5	< 25.1	< 27.0	<26.9	< 29.1
B (ppmw)	< 29.3	< 20.9	<110.30	< 25.1	<54.11	<26.9	< 29.1
Ba (ppmw)	< 29.3	< 20.9	< 23.5	< 25.1	< 27.0	<26.9	< 29.1
Be (ppmw)	< 14.7	< 10.4	< 11.8	< 12.6	< 13.5	<13.5	< 14.5
Bi (ppmw)	63.2	57.3	<163.8	49.3	<54.8	56.8	52.3
Ca (ppmw)	83.8	45.5	<141	15.8	33.9	236	516.8
Cd (ppmw)	57.3	64.2	<182.8	47.9	57.3	<13.5	53.3
Co (ppmw)	< 14.7	17.8	<67.73	19.8	< 13.5	15.0	< 14.5
Cr (ppmw)	187.5	76.0	<34.9	135.5	195.1	223.8	97.8
Cu (ppmw)	38.5	11.0	<46.48	< 12.6	< 13.5	130.9	25.8
Fe (ppmw)	396600.0	375700.0	517600.0	394700	279300.0	478100	395500.0
K (ppmw)	< 88.0	< 62.7	< 70.6	< 75.4	< 81.1	<129.5	< 87.2
Li (ppmw)	< 29.3	< 20.9	< 23.5	< 25.1	< 27.0	<26.9	< 29.1
Mg (ppmw)	24.7	19.6	32.6	< 12.6	< 13.5	17.1	237.9
Mn (ppmw)	2519.0	1524.0	2428.0	1401.0	734.3	1702	1061.0
Mo (ppmw)	16.0	< 10.4	< 11.8	< 12.6	< 13.5	35.1	< 14.5
Na (ppmw)	450.4	63.2	< 35.3	< 37.7	< 40.5	83.2	< 43.6
Ni (ppmw)	74.3	57.3	<190.4	129.3	42.7	102	51.4
P (ppmw)	117.1	112.0	192.2	56.0	111.5	126	138.9
Pb (ppmw)	<35.35	<48.0	<175.5	<41.09	<38.85	<39.4	<40.7
S (ppmw)	646.8	306.3	294.1	< 62.8	< 67.6	191.5	211.4
Sb (ppmw)	< 73.4	< 52.2	< 58.8	< 62.8	< 67.6	<67.4	< 72.7
Se (ppmw)	< 14.7	< 10.4	< 11.8	< 12.6	< 13.5	<13.5	< 14.5
Si (ppmw)	151.7	1640.0	125.7	< 25.1	< 27.0	522.7	1887.0
Sn (ppmw)	< 29.3	< 20.9	<39.3	< 25.1	< 27.0	<26.9	< 29.1
Ti (ppmw)	< 29.3	< 20.9	< 23.5	< 25.1	< 27.0	<26.9	58.0
V (ppmw)	< 29.3	< 20.9	< 23.5	< 25.1	< 27.0	<26.9	< 29.1
Zn (ppmw)	52.4	24.9	2644.0	16.7	<52.6	235	172.2

Table G1 – ICP Analysis Results of Bottom Sediment and Scraping (continued)

Site ID	CA-2	CA-2	CA-3	CA-3	CA-3	CA-3
Sample Description	**scraping STP bowl**	**sediment STP riser, no water**	**scraping ball float riser**	**scraping top of STP shaft**	**scraping bottom of STP shaft**	**sediment STP riser, no water**
Sample ID	**53609-14-06a**	**53609-14-09 split a**	**53609-17-03a**	**53609-17-06 split**	**53609-17-07a**	**53609-17-11 split a**
Al (ppmw)	805.4	648.8	687.6	706.4	551.3	714.0
As (ppmw)	< 29.1	< 24.1	< 28.0	< 25.7	< 30.0	< 25.0
B (ppmw)	< 29.1	< 24.1	< 28.0	< 25.7	< 30.0	< 25.0
Ba (ppmw)	< 29.1	< 24.1	< 28.0	< 25.7	< 30.0	< 25.0
Be (ppmw)	< 14.5	< 12.0	< 14.0	< 12.8	< 15.0	< 12.5
Bi (ppmw)	52.3	< 24.1	67.1	61.3	49.0	56.5
Ca (ppmw)	516.8	530.4	15.6	26.2	37.1	668.6
Cd (ppmw)	53.3	16.4	64.3	55.2	43.5	51.5
Co (ppmw)	< 14.5	< 12.0	21.5	33	26.8	14.2
Cr (ppmw)	97.8	34.5	< 14.0	278.5	263.6	185.5
Cu (ppmw)	25.8	66.3	274.8	475.1	268.7	256.9
Fe (ppmw)	395500.0	107600.0	448500.0	451500	360500.0	360400.0
K (ppmw)	< 87.2	< 72.2	< 83.9	< 77.0	< 89.9	< 75.0
Li (ppmw)	< 29.1	< 24.1	< 28.0	< 25.7	< 30.0	< 25.0
Mg (ppmw)	237.9	460.5	< 14.0	< 12.8	< 15.0	26.7
Mn (ppmw)	1061.0	667.8	2573.0	1977	1698.0	2532.0
Mo (ppmw)	< 14.5	< 12.0	< 14.0	48.7	40.4	38.4
Na (ppmw)	< 43.6	161.7	< 41.9	< 38.5	< 45.0	< 37.5
Ni (ppmw)	51.4	31.5	131.9	314.9	196.8	141.5
P (ppmw)	138.9	99.7	39.4	40.2	46.0	857.7
Pb (ppmw)	<40.7	< 24.1	680.6	<43.4	<33.1	<37.73
S (ppmw)	211.4	269.5	82.1	233.3	124.1	169.4
Sb (ppmw)	< 72.7	< 60.2	< 69.9	< 64.2	< 75.0	< 62.5
Se (ppmw)	< 14.5	< 12.0	< 14.0	< 12.8	< 15.0	< 12.5
Si (ppmw)	1887.0	270.1	200.6	77.8	36.6	624.4
Sn (ppmw)	< 29.1	< 24.1	< 28.0	35.5	< 30.0	30.6
Ti (ppmw)	58.0	< 24.1	< 28.0	< 25.7	< 30.0	< 25.0
V (ppmw)	< 29.1	< 24.1	< 28.0	< 25.7	< 30.0	< 25.0
Zn (ppmw)	172.2	333.3	302.3	16.6	< 15.0	21.5

Table G2 –X-Ray Diffraction Patterns for Scale Samples

Site ID	Sample ID	Results
NC-1	08Feb12-03B	weak pattern: Goethite; Lepidocrocite
NC-1	08Feb12-03B	Duplicate analysis-moderate pattern: Goethite; Lepidocrocite
NC-1	08Feb12-04B	weak pattern: Goethite; Lepidocrocite
NC-1	08Feb12-04B	Duplicate analysis-moderate pattern: Goethite; Lepidocrocite
NC-1	08Feb12-05	moderate pattern: Quartz; Goethite; Zinc Oxide
NC-1	08Feb12-11B	weak pattern: Goethite; Lepidocrocite
NC-1	08Feb12-11B	Duplicate analysis-moderate pattern: Goethite; Lepidocrocite
NY-1	53609-06-03	weak pattern: Alumina
NY-1	53609-06-10A	weak pattern: Goethite
NY-1	53609-06-10B	weak pattern: Goethite; Lepidocrocite
NY-1	53609-06-10B	weak pattern: Goethite; Lepidocrocite
NY-1	53609-06-11	weak pattern: Goethite
NY-1	53609-06-12	moderate pattern: Goethite; Lepidocrocite
NY-2	53609-08-03B	moderate pattern: Copper Acetate Hydroxide Hydrate
NY-2	53609-08-04B	weak pattern: Goethite
NY-2	53609-08-05B	moderate pattern: Goethite; Lepidocrocite
NY-2	53609-08-06B	moderate pattern: Aluminum Acetate Hydroxide Hydrate; Aluminum Acetate Hydroxide
NY-2	53609-08-07	moderate pattern: Dawsonite
NY-2	53609-08-09E-Split	no XRD: sample ruptured inside XRF, not enough material reclaimed
NY-2	53609-08-14	moderate pattern: Goethite; Lepidocrocite
NY-2	53609-08-15	weak pattern: Goethite; Magnetite
NY-2	53609-08-16	moderate pattern: Goethite; Lepidocrocite
CA-1	53609-11-04	moderate pattern: Goethite; Lepidocrocite
CA-1	53609-11-09B	moderate pattern: Goethite; organics
CA-1	53609-11-09C	moderate pattern: Goethite; organics
CA-1	53609-11-11E-Split	weak pattern: Goethite; Magnetite
CA-2	53609-14-05	moderate pattern: Goethite; organics
CA-2	53609-14-06B	weak pattern: Goethite
CA-2	53609-14-09-SB	weak pattern: Goethite; Magnetite
CA-3	53609-17-06	weak pattern: Goethite; Magnetite
CA-3	53609-17-07B	weak pattern: Goethite; Magnetite
CA-3	53609-17-11-Split	weak pattern: Goethite; Magnetite

Table G3 –X-Ray Fluorescence for Scale Samples from Retail Sites (Weight %)

Site ID	**NC-1**	**NC-1**	**NC-1**	**NC-1**	**NY-1**	**NY-1**
Sample ID	**8Feb12-03B**	**8Feb12-04B**	**8Feb12-05**	**8Feb12-11B**	**53609-06-03**	**53609-06-10A**
Sodium						
Magnesium			0.14		0.24	0.14
Aluminum	0.03		0.91	0.38	49.8	0.06
Silicon	0.47	0.08	5.91	0.07	0.85	0.32
Phosphorus			0.04	0.02		0.01
Sulfur	0.02	0.03	0.19	0.04	0.19	0.09
Chlorine			0.03	0.02	0.03	0.21
Potassium			0.17			0.007
Calcium	0.007		0.12	0.007	0.04	0.11
Scandium						
Titanium			0.04	0.006	0.07	0.14
Vanadium					0.01	
Chromium			0.005	0.02	0.02	0.01
Manganese	0.10	0.50	0.32	0.48	0.03	0.37
Iron	68.8	69.2	30.2	67.9	1.2	67.9
Cobalt	0.03			0.05		0.02
Nickel		0.01	0.02	0.13	0.02	
Copper			0.15	0.05	0.21	
Zinc			32.2	0.009	0.31	0.23
Gallium					0.01	
Germanium						
Arsenic						
Zirconium			0.02			
Molybdenum	0.01		0.03	0.007	0.03	0.009
Silver						
Cadmium			0.01			
Indium						
Tin						
Antimony						
Iodine						
Cesium	0.05		0.08		0.17	
Barium	0.08		0.11		0.22	
Platinum			0.05			
Mercury				0.02		
Lead					0.04	
Bismuth						
Lanthanum	0.01		0.01	0.02		0.02
Oxygen (calc.)	30.4	30.2	29.2	30.8	46.5	30.4

Table G3 –X-Ray Fluorescence for Scale Samples from Retail Sites (Weight %) (continued)

Site ID	NY-1	NY-1	NY-1	NY-1	NY-2	NY-2	NY-2
Sample ID	53609-06-10A	53609-06-10B	53609-06-11	53609-06-12	53609-08-03B	53609-08-04B	53609-08-05B
Sodium							
Magnesium	0.14	0.09		0.06	0.05	0.17	
Aluminum	0.06	0.03	0.20	0.03	0.03	0.007	0.48
Silicon	0.32	0.13	0.40	0.08	0.03	0.38	0.15
Phosphorus	0.01	0.006	0.007	0.006			0.005
Sulfur	0.09	0.05	0.05	0.05	0.33	0.18	0.13
Chlorine	0.21	0.05	0.06	0.008			
Potassium	0.007						
Calcium	0.11	0.08	0.007	0.03	0.09	0.07	0.007
Scandium							
Titanium	0.14	0.01	0.008	0.01		0.05	0.009
Vanadium							
Chromium	0.01	0.01	0.02	0.005		0.006	
Manganese	0.37	0.49	0.17	0.51	0.03	0.13	0.16
Iron	67.9	68.6	68.6	68.9	0.75	67.8	44.5
Cobalt	0.02			0.01		0.02	0.02
Nickel			0.02	0.008	0.41		0.01
Copper			0.03		67.3	0.70	0.55
Zinc	0.23	0.05	0.05	0.07	4.39	0.03	26.6
Gallium							
Germanium			0.008				
Arsenic							
Zirconium							
Molybdenum	0.009		0.009	0.006	0.01	0.01	0.005
Silver		0.07			0.008		
Cadmium							0.005
Indium							0.007
Tin					2.2	0.03	0.03
Antimony					0.04		
Iodine		0.01					
Cesium		0.007					
Barium		0.05					
Platinum							
Mercury							
Lead					4.09	0.04	0.40
Bismuth							
Lanthanum	0.02	0.02	0.02	0.01	0.01	0.02	0.02
Oxygen (calc.)	30.4	30.2	30.4	30.2	20.2	30.4	27.0

Table G3 –X-Ray Fluorescence for Scale Samples from Retail Sites (Weight %) (continued)

Site ID	**NY-2**	**NY-2**	**NY-2**	**NY-2**	**NY-2**	**NY-2**	**NY-2**	**CA-1**
Sample ID	**53609-08-05B**	**53609-08-06B**	**53609-08-07**	**53609-08-09E-Split**	**53609-08-14**	**53609-08-15**	**53609-08-16**	**53609-11-09C**
Sodium			14.4	2.2				
Magnesium		0.31	0.23	0.33				
Aluminum	0.48	41.5	35.25	1.6	0.02	0.03	0.03	0.01
Silicon	0.15	0.61	1.5	1.8	0.05	0.03	0.32	0.005
Phosphorus	0.005		0.008	0.36	0.005		0.02	
Sulfur	0.13	0.79	0.06	0.72	0.11	0.15	0.07	
Chlorine		2.1	2.2	1.9	0.01	0.08	0.008	
Potassium		0.01	0.2	0.08		0.008		
Calcium	0.007	0.07	0.05	0.33	0.008	0.03	0.02	
Scandium								
Titanium	0.009	0.05	0.06	0.09	0.006	0.005	0.006	
Vanadium		0.005	0.01					
Chromium		0.02	0.02	0.02	0.01	0.03		0.02
Manganese	0.16	0.14	0.06	0.24	0.39	0.48	0.26	0.17
Iron	44.5	3.3	0.69	53.9	68.7	68.8	68.9	69.6
Cobalt	0.02			0.01	0.04	0.02		
Nickel	0.01		0.008	0.02	0.02		0.008	
Copper	0.55	0.15	0.76	0.81	0.006			
Zinc	26.6	8.2	4.4	4.2	0.06	0.03	0.006	0.01
Gallium			0.01					
Germanium								
Arsenic						0.03		
Zirconium		0.009						
Molybdenum	0.005	0.008		0.009	0.01	0.008	0.007	0.005
Silver								
Cadmium	0.005							
Indium	0.007							
Tin	0.03							
Antimony								
Iodine								
Cesium								
Barium								
Platinum			0.01					
Mercury								
Lead	0.40	0.09	0.12	0.34	0.01			
Bismuth								
Lanthanum	0.02	0.02		0.01	0.02	0.02	0.02	0.01
Oxygen (calc.)	27.0	42.6	40.0	31.0	30.5	30.3	30.4	30.2

Table G3 –X-Ray Fluorescence for Scale Samples from Retail Sites (Weight %) (continued)

Site ID	**CA-1**	**CA-1**	**CA-1**	**CA-1**	**CA-2**	**CA-2**	**CA-2**	**CA-3**
Sample ID	**53609-11-09C**	**53609-11-04**	**53609-11-09B**	**53609-11-11E-Split**	**53609-14-05**	**53609-14-06B**	**53609-14-09-Split**	**53609-17-03B**
Sodium								
Magnesium		0.06		0.05	0.06	0.05	0.18	0.90
Aluminum	0.01	0.09	0.007	0.09	0.04	0.09	0.26	0.11
Silicon	0.005	0.13		0.13	0.11	0.16	0.25	1.5
Phosphorus				0.008			0.04	
Sulfur		0.04		0.05	0.01	0.03	0.16	0.02
Chlorine		0.007		0.10	0.01		0.14	
Potassium		0.005		0.005			0.008	
Calcium		0.05		0.08	0.03	0.04	0.20	0.17
Scandium								
Titanium		0.02		0.01	0.01	0.01	0.01	0.28
Vanadium								
Chromium	0.02		0.02	0.02	0.01	0.009	0.01	
Manganese	0.17	0.41	0.27	0.36	0.28	0.21	0.36	0.53
Iron	69.6	68.4	69.6	68.3	69.12	69.0	67.8	64.9
Cobalt				0.04	0.02	0.01		0.03
Nickel		0.01	0.02	0.04	0.01		0.009	0.02
Copper		0.10		0.04		0.008	0.04	0.08
Zinc	0.01	0.54		0.06	0.02	0.04	0.19	0.06
Gallium								
Germanium								
Arsenic								
Zirconium								
Molybdenum	0.005	0.007	0.009	0.01	0.009	0.01	0.009	0.006
Silver								
Cadmium								
Indium								
Tin								
Antimony								
Iodine								
Cesium								
Barium								
Platinum		0.02						
Mercury								
Lead								0.16
Bismuth								
Lanthanum	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02
Oxygen (calc.)	30.2	30.1	30.1	30.6	30.2	30.3	30.3	31.3

Table G3 –X-Ray Fluorescence for Scale Samples from Retail Sites (Weight %) (continued)

Site ID	**CA-3**	**CA-3**	**CA-3**
Sample ID	**53609-17-06**	**53609-17-07B**	**53609-17-11-Split**
Sodium			
Magnesium			
Aluminum	0.03	0.007	0.04
Silicon	0.01	0.01	0.15
Phosphorus			0.006
Sulfur	0.02	0.04	0.07
Chlorine			0.03
Potassium			
Calcium			0.05
Scandium			
Titanium	0.005		0.005
Vanadium			
Chromium	0.03	0.05	0.04
Manganese	0.39	0.34	0.35
Iron	69.2	69.1	68.3
Cobalt	0.02	0.02	0.05
Nickel	0.05	0.07	0.06
Copper	0.07	0.17	0.12
Zinc			0.03
Gallium			
Germanium			
Arsenic			
Zirconium			
Molybdenum	0.02	0.02	0.01
Silver			
Cadmium			
Indium			
Tin			
Antimony			
Iodine			
Cesium			
Barium			
Platinum			
Mercury			
Lead			0.011
Bismuth			
Lanthanum	0.02	0.02	0.01
Oxygen (calc.)	30.1	30.2	30.7

Table G4 – X-Ray Fluorescence on Particulate Filtered from Retail Site Fuel and Water Samples

Site ID	**NC-1**	**NY-1**	**NY-2**	**CA-1**	**CA-2**	**CA-3**	**blank filter**	**NC-1**	**NY-1**	**NY-2**	**CA-1**	**CA-2**	**CA-3**
Matrix	Fuel	Fuel	Fuel	Fuel	Fuel	Fuel		Water	Water	Water	Water	Water	Water
Particulate Content, mg/L	55	87	91	115	69	122		115	542	604	161	74	114
Sodium	Major	Major	Major	Minor	Minor	Minor		Major	Minor	Minor	Minor		
Magnesium	Trace	Minor	Trace	Trace				Trace	Minor	Trace	Trace	Minor	Trace
Aluminum	Trace	Minor	Trace	Trace	Trace	Trace		Minor	Trace	Minor	Minor	Minor	Trace
Silicon	Trace	Minor	Trace	Trace	Trace	Trace	**Trace**	Minor	Trace	Minor	Minor	Minor	Minor
Phosphorus	Trace	Trace	Trace	Trace	Trace	Trace		Minor	Trace	Minor	Trace	Minor	Trace
Sulfur	Minor	Minor	Minor	Minor	Minor	Trace		Major	Minor	Major	Minor	Minor	Minor
Chlorine	Minor	Minor	Minor	Minor	Minor	Trace	**Minor**	Major	Major	Major	Minor	Minor	Trace
Potassium	Trace	Trace	Trace	Trace	Trace	Trace		Trace	Trace	Trace	Trace	Trace	
Calcium	Trace	Minor	Minor	Trace	Trace	Trace	**Trace**	Minor	Minor	Minor	Minor	Minor	Trace
Titanium	Trace	Trace	Trace	Trace	Trace	Trace	**Trace**	Trace	Trace	Trace	Trace	Minor	Trace
Chromium	Trace	Trace	Trace	Trace	Trace	Trace	**Trace**	Trace	Trace	Trace	Trace	Trace	Trace
Manganese	Trace	Trace	Trace	Trace	Trace	Minor		Minor	Trace	Trace	Trace	Trace	Minor
Iron	Minor	Minor	Minor	Major	Major	Major	**Minor**	Major	Minor	Major	Major	Major	Major
Cobalt													Trace
Nickel	Trace	Trace	Trace	Trace	Trace	Trace	**Trace**	Minor	Trace	Trace	Trace	Trace	Trace
Copper	Trace	Trace	Trace	Trace	Trace	Trace		Trace	Trace	Major	Trace	Minor	Trace
Zinc	Trace	Trace	Trace	Trace		Trace		Trace	Minor	Major	Minor	Minor	Trace
Strontium													Trace
Molybdenum	Trace		Trace	Trace	Trace	Trace	**Trace**	Trace	Trace	Trace	Trace	Trace	Trace
Cadmium												Trace	
Tin										Trace			
Antimony						Trace							
Cesium	Minor		Minor	Trace	Minor	Minor	**Trace**		Minor	Trace	Minor	Minor	Minor
Barium	Minor		Minor	Minor	Minor	Minor	**Minor**	Trace	Minor	Minor	Minor	Minor	Minor
Lead								Trace		Trace			Trace

Values are reported as Major (shaded), Minor, or Trace when detected above blank filter levels.

Table G5 – GC-MS Results of Scraping and Sediment Samples

Site ID	Sample ID	Sample Description	GC-MS Results Summary
NC-1	08Feb12-3B	Cap of Ball Float Riser	H2O, acetic acid, traces of BTX, C8 through C19 boiling range hydrocarbons
NC-1	08Feb12-4B	Inside Ball Float Riser	H2O, C10 through C17 boiling range hydrocarbons
NC-1	08Feb12-05	White Crust Top of ATG Probe	H2O, C8 through C24 boiling range hydrocarbons
NC-1	08Feb12-11B	Inside STP Riser and Bowl	H2O, acetic acid, traces of BTX, C8 through C20 boiling range hydrocarbons
NY-1	53609-06-03	Spare Riser Cap Near Fill/ATG	Methanol, H2O, acetic acid, N,N-dimethyl formamide, C7 through C20 hydrocarbons
NY-1	53609-06-10A	STP Pump Shaft	Methanol, H2O, acetaldehyde, acetone, acetic acid, C6 through C27 boiling range hydrocarbons, N,N-dimethyl benzenemethanamine, N,N-dimethyl formamide, 4-methyl mopholine, C16- and C18-FAME
NY-1	53609-06-10B	Pump Shaft	Methanol, H2O, acetic acid, trimethylamine, N,N-dimethyl formamide, traces of BTX, C8 through C20 boiling range hydrocarbons
NY-1	53609-06-11	Inside Pump - Wetted Head	Methanol, H2O, acetaldehyde, 1-hydroxy-2-propanone, large acetic acid, N,N-dimethyl benzenemethanamine, C9 through C27 boiling range hydrocarbons, C16- and C18-FAME
NY-1	53609-06-12	Inside STP Riser - Dry Part	Methanol, H2O, acetaldehyde, acetone, acetic acid, traces of BTX, N,N-dimethyl benzenemethanamine, C11 through C28 boiling range hydrocarbons
NY-2	53609-08-03B	Brass Plug on Ball Float Riser	H2O, acetaldehyde, large acetic acid, methyl ethyl disulfide, 1,2-ethanediol monoacetate, 1,2-ethanediol diacetate, C10 through C27 boiling range hydrocarbons
NY-2	53609-08-04B	Cast Iron Plug on Brass Plug from Ball Float Riser	H2O, acetaldehyde, acetone, acetic acid, heptanal, 2-octanone, C10 through C27 boiling range hydrocarbons
NY-2	53609-08-05B	Inside Spare Other Riser	H2O, acetaldehyde, acetone, acetic acid, traces of BTX, C9 through C24 boiling range hydrocarbons
NY-2	53609-08-06B	Outside Fill Pipe	H2O, Large Acetic Acid, C8 through C24 boiling range hydrocarbons
NY-2	53609-08-07	Inside Riser Pipe Groove	H2O, traces of BTX, C9 through C25 boiling range hydrocarbons
NY-2	53609-08-09E split b	Bottom Sediment from 53609-08-09	H2O, acetone, acetic acid, cyclohexylamine, C10 through C25 boiling range hydrocarbons
NY-2	53609-08-14	Bottom of STP Head	H2O, traces of acetic acid and acetone, traces of BTX, C10 through C26 boiling range hydrocarbons
NY-2	53609-08-15	STP Shaft	H2O, acetic acid, 2-butanone, 1,3-cyclohexadiene, C9 through C28 boiling range hydrocarbons
NY-2	53609-08-16	STP Bowl	H2O, acetaldehyde, acetone, acetic acid, C9 through C28 boiling range hydrocarbons
CA-1	53609-11-04	Inside ATG Riser	H2O, traces of acetone and acetic acid, C9 through C25 boiling range hydrocarbons