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An Evaluation of the Department of Energy Naval Petroleum Reserve No. 3 Produced Water Bio-Treatment Facility

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Abstract

The Department of Energy (DOE) Naval Petroleum Reserve No. 3 (NPR-3) produced water bio-treatment facility effectively treats an average of 35,000 barrels of water per day. All discharge limits are met. The functional component parts of the bio-treatment facility consist of cooling, blending, oil/water separation and biological treatment. The bio-treatment facility replaced subsurface injection saving \$175,000 per year on utilities (\$3.5MM over the 20-year life expectancy). The surface discharge of the treated produced water benefits wildlife by keeping a normally dry streambed wet year-round with an abundance of wetland plants for forage.

This bio-treatment facility evaluation is based on site observations over the past four years, review of historical discharge data and a one-time sampling event at eight locations within the facility in September of 1999. The suite of analytical tests include BOD₅, COD, TOC, TIC, TPH, O&G, GRO, DRO, BTEX, Ca, Mg, SO₄, TKN, NH₃, NO₃, Alkalinity, pH, EC, hardness, H₂S, P (total), PO₄ (ortho), TDS, TSS, turbidity and VS. In addition, selected temperature and flow measurements were collected. Hach Biological Activity Reaction Tests (BARTs) were used to measure microbial activity in the water and soil columns and to demonstrate the “substrate effect.” The sampling event occurred shortly after an upset event that resulted in a hydraulic surge, elevated temperatures and skimming difficulties. In spite of the upset, the bio-treatment facility’s removal rates were >90% for nearly all analytes. The extent of hydrocarbon removal ranged from 95% to 100%.

The areas identified for potential improvement to the bio-treatment facility include cooling capacity, solids handling/removal, skimming operations, flow control and water control structures, replanting of the wetland (free-water surface and/or subsurface), future discharge limits and water reuse.

Introduction

Recent advances in produced water treatment technology have led to the use of wetlands, the oldest natural water treatment process, to meet discharge limits. In contrast to highly engineered water treatment facilities, wetlands provide good treatment at low cost and create wildlife habitat (both flora and fauna). This paper evaluates the performance of a produced water treatment wetland in a Wyoming oilfield.

Objectives. The objectives of this evaluation:

- Determine the efficacy of treatment by the Department of Energy (DOE) Naval Petroleum Reserve No. 3 (NPR-3) produced water bio-treatment facility.
- Determine microbial activity in the water and sediment columns.
- Suggest possible improvements for the bio-treatment facility.

Scope. The scope of this evaluation:

- Review existing operational data.
- Measure flowrates.
- Conduct a one-time sampling event on the bio-treatment facility encompassing influent, intermediate and effluent sampling points.
- Test for BOD₅, COD, TOC, TIC, TPH, O&G, GRO, DRO, BTEX, Ca, Mg, SO₄, TKN, NH₃, NO₃, alkalinity, pH, EC, hardness, H₂S, P (total), PO₄ (ortho), TDS, TSS, turbidity, VS and temperature. (**Appendix A, C**)
- Measure microbial activity in the water and sediment columns using Hach Biological Activity Reaction Tests (BARTs).

Background. The Naval Petroleum Reserve No. 3 (NPR-3) is located in Natrona County in east central Wyoming, 32 miles north of Casper, and 8 miles south of Midwest, Wyoming.

The DOE NPR-3 bio-treatment facility is one of the first produced water treatment wetlands in the US, and the second to be permitted by Wyoming Department of Environmental Quality. In January 1996, NPR-3 opened a bio-treatment facility for produced water. Justifications for building the facility were twofold: (1) to save operating expenses attributed to re-injecting produced water and (2) to benefit wildlife.

Prior to installing the bio-treatment facility, three disposal wells handled 10,000 barrels per day of produced water at an annual operating cost of \$185,000. Today, NPR-3 treats as much as 50,000 barrels of produced water per day. Maintenance and operating expenses for the facility are less than \$10,000 per year. Over the 20-year life of the facility, NPR-3 will realize savings in operating costs upwards of \$3.5MM (\$175,000/year). Since the start-up period, all National Pollutant Discharge Elimination System (NPDES) limits have been met.

The bio-treatment facility is based on the treatment wetland concept. Wetlands are more commonly known as nurseries for hundreds of species of flora and fauna, but wetlands are also thin-film biological reactors that nature has used for eons to remove organic and inorganic compounds from water. The wetland combination of plants, microbes and soils helps to purify the water. The removed compounds create a nutrient rich environment for plants and wildlife. Recently, man has started to mimic nature by building wetlands to treat a variety of waters, wastewaters, storm waters, acid-mine drainage waters, irrigation waters, aquaculture waters, feedlot runoff waters, and produced waters. As a new water treatment technology, we are still learning how to design and operate treatment wetlands for specific applications.

Materials And Methods

Bio-treatment Facility Description. The bio-treatment facility process (**Figure 1**) begins at tank battery B-Tp-10. Water from all producing formations is routed to the tank battery and discharged onto a cooling tower. The water then flows through the stepped cooling trench No. 1 into the netted pond (or skimming pond). From the pond, the water flows into a series of six canals (cooling trench No. 2) designed to keep the water level shallow and to aid in cooling. From the canals, the water flows onto a series of vertical stair-steps. The stair-steps add oxygen to the water and further cool the water. The stair-steps discharge into a cooling trough that flows through a series of spigots into the bio-treatment pond (wetland). By design, biological treatment occurs in this pond. An adjustable valve allows the water level of this pond to be increased or decreased according to fluctuations in the flowrate to ensure optimal holding time and treatment. Microorganisms break down most of the hydrocarbons in the water before it moves through to the polishing lagoon. The treated produced water is discharged under an NPDES permit into an unnamed tributary of the Little Teapot Creek.

Sampling was done under upset conditions (or a "worst case" scenario). The bio-treatment facility met discharge

limits even with increased hydraulic loading, elevated temperatures and skimming difficulties. A total of eight of the fourteen sampling points identified in **Figure 1** were selected. The points included cooling tower (produced water side), cooling tower (Tensleep water side), cooling trench No. 1, netted pond, cooling trench No. 2, wetland (bio-treatment pond) below trough, out of lagoon, and creek.

Analytical Tests. Common analytical tests were selected to evaluate treatment performance based on removal of carbon, nitrogen, phosphorous, and sulfur; identification of hydrocarbon species; quantification of solids; characterization of salts and ions; and measurement of biological activity. The tests performed are presented in **Appendix C**.

The carbon tests included BOD₅, COD, TOC and TIC. The nitrogen tests included NH₃, NO₃ and TKN. The phosphorus tests include both total P and ortho PO₄. The sulfur tests included H₂S and SO₄. Hydrocarbon species were characterized based on TPH, O&G, BTEX, GRO and DRO. In addition to EC, hardness and alkalinity, selected major ions included Mg and Ca. Solids tests included TSS, TDS, VS and turbidity. To measure microbial activity, a series of BARTs were used.

Sampling and Testing. RMOTC and Texaco personnel conducted sampling of the bio-treatment facility on September 28, 1999. On February 21, 2000, Tensleep water was sampled a second time and analyzed only for TIC and TOC. A certified contract environmental laboratory (Energy Laboratories Inc.) supplied sampling containers with preservatives. The samples were hand delivered by RMOTC personnel to the laboratory in ice chests. The laboratory conducted the analyses according to Standard Methods and EPA test procedures.

Results And Discussion

Data from the NPR-3 bio-treatment facility evaluation are listed below and graphically represented in the form of charts in **Appendix D**.

Flowrates. Flowrates were measured with a portable Global Flow Probe, model FP101 flow meter and cross-checked with daily Tensleep and produced water pumping records measured by a 3-inch Halliburton flow totalizer, model no. 991.40523 and a 4-inch Halliburton flow totalizer, model no. 458.8628, respectively.

The DOE NPR-3 produced water bio-treatment facility is designed and permitted to treat a maximum 1,458 gpm (50,000 bwpd). Historical flowrates have averaged 1,021 gpm (35,000 bwpd).

The bio-treatment system is designed to cool the water, drop out solids, skim oil, and biologically treat water-soluble organic compounds (WSO). As in most producing oilfields, the produced water is a blend of waters from various formations. In this case, the typical produced water blend is 1:4 (other formation produced waters to Tensleep formation produced water).

The NPR-3 field produces both sweet and sour crude oil. The sour crude is produced from the Tensleep formation. It is approximately 31°API and is produced with a 99.75% water cut. For every one-barrel of oil produced, 400 barrels of water are produced from this formation. The water is of fair quality although it is not considered potable because of its high sodium content.

Sweet crude is produced from six other producing formations. The gravity weight of the crude oil ranges between 32-40°API. Approximately 20 bbl of water are produced for every one barrel of sweet crude oil produced. The sodium content of the other produced waters is considerably higher than the sodium content of the Tensleep water.

Blending. The first step in the bio-treatment facility process is the blending of the produced waters. The 1:4 blending is needed to meet the NPDES limit for electrical conductivity (EC) of 7,500 umho/cm. The unblended produced waters frequently exceed the NPDES EC limit, but they do meet the limit when blended with Tensleep water. Another reason for blending is to compensate losses from the average pan evaporation rate of 37 inches annually. Blending helps to offset the evaporation of the produced water as it passes through the bio-treatment facility and lowers the temperature.

Table 1 is a compilation of the performance of the treatment facility. It is a comparison of predicted and actual concentrations of test parameters based on 1:4 blending ratio. For inorganic test parameters, the predicted and measured concentrations match closely. The measured values for the ion group matches very well for the predicted value. Therefore, the blending operation is fulfilling one of the treatment objectives, lowering the concentration of solids and salts of the produced water.

The water soluble organic tests and hydrocarbon parameters tend not to match the predicted concentrations as well as the inorganic parameters. Microbial degradation of the organic compounds and attachment of organic compounds to solids that settle out are the likely reasons for the differences in actual v. predicted 1:4 blending concentrations.

Table 1. Predicted 1:4 Blending and Actual Concentrations and Effluent Concentrations.

Test Parameter	Units	Sampling Site ID #1 Produced water	Sampling Site ID #2 Tensleep water	Predicted 1:4 Blend For ID #3	Sampling Site ID #3	% Difference Actual v. Predicted*	Effluent concentration	Bio-treatment Facility Overall % Removal
CARBON								
BOD	mg/L	28.0	20.0	21.6	15.0	44%	2.3	92%
COD	mg/L	48.0	26.0	30.4	28.0	9%	29	40%
TOC	mg/L	32.7	9.5	14.1	4.2	236%	3.6	89%
TIC	mg/L	85.6	32.3	43.0	39.4	1%	22.8	73%
NITROGEN								
TKN	mg/L	1.8	0.6	0.8	0.8	0%	<0.5	>72%

Test Parameter	Units	Sampling Site ID #1 Produced water	Sampling Site ID #2 Tensleep water	Predicted 1:4 Blend For ID #3	Sampling Site ID #3	% Difference Actual v. Predicted*	Effluent concentration	Bio-treatment Facility Overall % Removal
NH ₃	mg/L	2.03	0.79	1.04	1.0	4%	0.54	73%
NO ₃	mg/L	<0.1	<0.1		<0.1		<0.1	-
PHOSPHORUS								
Total Phosphorus	mg/L	1.83	0.87	1.06	1.1	4%	0.46	75%
Orthophosphate	mg/L	<0.5	<0.5		<0.5		<0.5	-
SULFUR								
SO ₄	mg/L	678	903	858.0	878.0	-2%	890	-31%
H ₂ S	mg/L	<1.0	<1.0		<1.0			
HYDROCARBON								
TPH	mg/L	112.0	56.1	67.3	341.0	-80%	5.8	95%
O&G	mg/L	71.9	49.1	53.7	216.0	-75%	4.2	94%
GRO	mg/L	1.44	0.3	0.56	0.8	-30%	0.0	100%
DRO	mg/L	98.0	35.0	47.6	43.0	11%	2.0	98%
BTEX								
Benzene	ug/L	143.0	18.1	43.1	37.8	14%	<1.0	100%
Toluene	ug/L	135.0	19.5	42.6	42.3	1%	<1.0	100%
Ethylbenzene	ug/L	33.6	5.2	10.9	14.2	-23%	<1.0	100%
Xylene	ug/L	162.0	26.0	53.2	69.0	-23%	<1.0	100%
SOLIDS								
Turbidity	mg/L	45.4	29.5	32.7	14.2	130%	4.76	90%
TDS	mg/L	4380	3490	3668	3680	0%	4010	9%
TSS	mg/L	111.0	53.0	64.6	73.0	-12%	4	96%
VS	mg/L	2.79	4.06	3.81	4.1	-7%	3.23	-16%
IONS								
Hardness	mg/L	549.0	771.0	726.6	734.0	-1%	732	-28%
Calcium	mg/L	177.0	253.0	237.8	240.0	-1%	236	-33%
Magnesium	mg/L	25.9	33.9	32.3	32.8	2%	34.7	-34%
Alkalinity	mg/L	713.0	269.0	357.8	328.0	9%	190	73%
PH	s.u.	8.0	7.9	7.9	7.9		8.0	-
Conductivity	umh o/cm	7490	5540	5930	5860	12%	6270	16%
Predicted = (1*Site#1 + 4*Site#2)/(1+4) %Difference = (Predicted-Actual)/(Actual)*100 %Removal = (Inlet-Outlet)/(Inlet)*100								

As seen in **Table 1** many of the test parameters were only affected by the blending of the produced waters. For that reason no further discussion will be made of the bio-treatment facilities impact on pH, hardness, calcium, magnesium, , electrical conductivity and TDS. While there may be some movement of some of these analytes among water, sediments and biomass, there is no net change observed in these compounds. Data for the compounds are in **Appendix D**.

Temperature. The NPR-3 oilfield is a test site for a variety of oil production methods and equipment for secondary and tertiary recovery. Steam flooding and the natural hot springs of Wyoming frequently generate produced water around 180-200°F. Surface temperature for the Tensleep formation water

averages 180°F. The objective of the cooling tower and trenches is to lower the temperature from 180-200°F to <100°F to protect the wetland plants.

Table 2 and **Figure 2** detail temperatures across the bio-treatment facility on September 28, 1999. The Tensleep water had a higher temperature than the producing field water. The temperature in the wetland was 124°F. No living plants were seen in the wetland. Only vestiges of old plants remained. The wetland water did not drop to <100°F until it reached the lagoon. Plants were growing along the banks of the lagoon. A thriving community of wetland plants exists at the discharge point where the water temperature is <100°F.

Table 2. Bio-treatment Facility Temperatures for September 28, 1999.

Sampling Location No.*	Description	Sample ID No.	Temperature (°F)
1	Base of cooling tower (produced water side)	1	132
3	Base of cooling tower (Tensleep water side)	2	157
4	Cooling trench No. 1	3	149
6	Netted pond	4	147
8	Cooling trench No. 2	5	140
9	Wetland below trough	6	124
13	Out of lagoon	8	98
15	Creek	9	98

*See Figure 1.

Hydrocarbon. For the bio-treatment facility evaluation, hydrocarbon was measured based on total petroleum hydrocarbons (TPH), oil & grease (O&G), gasoline range organic compounds (GRO), diesel range organic compounds (DRO), and benzene, toluene, ethylbenzene, and xylene (BTEX) (**Table 3**).

TPH and O&G measure similar hydrocarbon fractions but use different analytical methods. Both use a solvent to extract hydrocarbon. TPH uses IR spectroscopy following a silica-gel cleanup step. O&G lacks the cleanup step and uses gravity for separation. GRO and DRO are gas chromatographic tests, which identify a suite of compounds based on differential boiling points through a simulated distillation. The GRO fraction boils off at lower temperatures than the DRO fraction. The BTEX test quantifies Benzene, Toluene, Ethylbenzene and Xylene.

Petroleum hydrocarbons are compounds that occur naturally and readily biodegrade. The results of this section indicate that the bio-treatment facility is very effective in removing the petroleum components in the produced water.

Table 3. Hydrocarbon Data Summary.

Test Parameter	Units	Influent	Effluent	NPDES Limit	% Removal
HYDROCARBON					
TPH	mg/L	112.0	3.1	-	97%

Test Parameter	Units	Influent	Effluent	NPDES Limit	% Removal
O&G	mg/L	71.9	3.5	10	95%
GRO	mg/L	1.44	0.0	-	100%
DRO	mg/L	98.0	2.0	-	98%
BTEX					
Benzene	ug/L	143.0	<1.0	-	100%
Toluene	ug/L	135.0	<1.0	-	100%
Ethylbenzene	ug/L	33.6	<1.0	-	100%
Xylene	ug/L	162.0	<2.0	-	100%

Total Petroleum Hydrocarbon and Oil & Grease. Sample No. 4 was collected at the netted pond (or skimming pond). Large amounts of both TPH and O&G were found in these water samples due to an upset (**Figures 3 and 4**). The concentration increased from 112 and 56 mg/L TPH for the produced water and Tensleep water to over 6000 mg/L at the netted pond. The bio-treatment facility removed 97% and 95% of the TPH and O&G, respectively. It is not known how much of the TPH and O&G removal is the result of skimming, volatilization and/or biodegradation.

Gasoline Range Organics and Diesel Range Organics. Both GRO and DRO are known to be readily biodegradable. The bio-treatment facility removed 100% and 98% of the GRO and DRO, respectively (**Figures 5 and 6**).

Benzene, Toluene, Ethylbenzene, Xylene. BTEX represents a group of low molecular weight compounds that both readily biodegrade and volatilize. The BTEX concentrations are measured in ug/L (or ppb) (**Figure 7**). These are extremely low levels. The bio-treatment facility reduced the BTEX to even lower levels. The effluent contained non-detectable concentrations of BTEX (**Table 3**).

Conclusion. Hydrocarbons were effectively removed by the bio-treatment facility. Depending on the family of compounds, petroleum hydrocarbons were removed with a greater than 95% efficiency by the bio-treatment facility.

Carbon. A suite of standard tests (BOD₅, COD, TOC and TIC) measured the content of water-soluble carbon (**Table 4**). Each test measures carbon content a little differently. BOD₅ is the biochemical oxygen demand that is exerted by the materials contained in water over a five-day period. It is a measure of the biologically degradable compounds by a standard inoculum of microbes. Therefore, the BOD₅ is an indirect measurement of biodegradable carbon as well as the other soluble compounds such as ammonia. COD is the chemical oxygen demand. It is a test which chemically oxidizes organic (and some inorganic) compounds with a strong acid. Therefore, the test measures both the biodegradable compounds and the compounds that are biorefractory (not readily biodegradable). TOC is the total organic carbon, and TIC is the total inorganic carbon. The five-minute test converts carbon to CO₂. The organic forms of carbon are usually degradable.

Table 4. Carbon Data Summary.

Test Parameter	Units	Influent	Effluent	NPDES Limit	% Removal
CARBON					
BOD ₅	mg/L	28.0	1.4	-	95%
COD	mg/L	48.0	25.0	100	48%
Ratio BOD ₅ :COD	Unitless	0.58	0.06	-	90%
TOC	mg/L	32.7	2.4	-	93%
TIC	mg/L	85.6	23.6	-	72%
Ratio BOD ₅ :TOC	Unitless	0.85	0.58	-	32%

Biochemical Oxygen Demand and Chemical Oxygen Demand. The concentration of BOD₅ was lowered at each sampling point tested in the bio-treatment facility (**Figure 8**). The initial low concentration of BOD₅ (28 mg/L) was lowered by an order of magnitude (1.4 mg/L) at the discharge point. The stepwise reduction in BOD₅ indicates that biodegradation occurs in all stages of the bio-treatment facility. The overall BOD₅ removal was 95%.

The COD numbers are in agreement with the BOD₅ numbers (**Figure 9**). The “easy to biologically degrade” fraction (48% removal from 48 mg/L to 25 mg/L) of the COD corresponds to the loss of BOD removal (21.4 mg/L). The remaining COD fraction was biorefractory. The NPDES permit limit for COD is 100 mg/L. The COD concentration exiting the bio-treatment facility is well below that limit.

The ratio of BOD₅ to COD is indicative of the amount of biodegradation that can be further attained in the bio-treatment facility. The influent BOD₅:COD ratio of 0.58 is consistent with what is found in municipal wastewater facilities (Metcalf and Eddy). The low effluent BOD₅:COD ratio (0.06) indicates that almost all of the biodegradation that could occur did occur.

Total Organic Carbon and Total Inorganic Carbon. The TOC of the water is removed at a rate similar to the removal of the BOD₅ (**Figure 10**). The influent BOD₅:TOC is 0.85. The effluent BOD₅:TOC is 0.58. The slight change in these ratios indicates that the biologically available carbon was organic carbon.

TIC represents the inorganic forms of carbon. The bio-treatment facility reduced the TIC concentration by 72% (**Figure 11**). The residual TIC is likely to be in the form of a carbonate and bound to a salt.

Conclusion. A number of direct and indirect measures of carbon were performed. Each measure of carbon confirmed that the treatment was successful in removing more than 90% of the carbon.

Nitrogen. Nitrogen is an essential element for carbon based life forms. It is used to build proteins. Ammonia is readily biodegradable and can be incorporated into cell mass. Nitrifying organisms convert ammonia into nitrate. Nitrate is also used as a nitrogen source by microorganisms. Plants and microorganisms require nitrogen for growth. Wetlands remove nitrogen by incorporating it into biomass or as a substrate for generating energy (ammonia into nitrate by

denitrifying organisms and nitrate into ammonia for denitrifying organisms).

The three forms of nitrogen measured include TKN, NH₃ and NO₃. TKN is Total Kjeldahl Nitrogen. TKN is the sum of all forms of nitrogen commonly found in water. The TKN test digests organic matter at an elevated temperature with a strong acid to convert nitrogen to the -3 oxidation state (ammonia). The ammonia is then quantified to generate the TKN number. NH₃ is ammonia. There are four NH₃ test methods (two colorimetric, a volumetric and an ion specific electrode). NO₃ is nitrate (an oxidized version of ammonia). Analytical methods include UV spectrophotometry, IC, ion specific electrode, and Cd reduction. NO₃ is also a fertilizer.

Table 5 is a summary of the nitrogen data. There are low levels of nitrogen entering the bio-treatment facility and lower levels exiting. TKN and NH₃ were in close agreement, although normally the concentration of TKN is greater than the concentration of NH₃. No detectable levels of NO₃ were found.

Table 5. Nitrogen Data Summary.

Test Parameter	Units	Influent	Effluent	% Removal	NPDES Limit	Comment
NITROGEN						
TKN	mg/L	1.8	<0.5	>72%	-	Below limit of detection.
NH ₃	mg/L	2.03	0.5	75%	-	
NO ₃	mg/L	<0.1	<0.1		-	Below limit of detection.

Total Kjeldahl Nitrogen. The TKN concentrations are low (**Figure 12**). Blending decreases the concentration of TKN (**Table 1**). The concentration of TKN increases in the skimming pond and then gradually decreases to below the limit of detection. The overall TKN removal is >72%.

Ammonia. The ammonia concentrations are low (**Figure 13**). The trend in ammonia concentrations is similar to the trend in TKN concentrations. Blending decreases the concentration of ammonia (**Table 1**). The concentration of ammonia does not increase in the skimming pond but does decrease in subsequent treatment stages. The overall ammonia removal is 75%.

Nitrate. The concentration of nitrate is below the limit of detection entering and leaving the bio-treatment facility (**Table 5**).

Conclusion. Nitrogen was a minimal component of the produced water at the NPR-3 field. None of the water samples contained more than 2 mg/L of nitrogen, measured either as NH₃ or as TKN.

Phosphorus. Trace quantities of phosphorus are required to create nucleic acids. At the cellular level, ATP/ADP and NAD/FAD require phosphorus. Orthophosphate is the form that is readily utilizable by microorganisms and plants. Orthophosphate can be removed from water by incorporation into biomass or precipitated as insoluble salts.

Table 6 is a summary of the phosphorus data. The concentrations of total phosphorus entering and leaving the bio-treatment facility are low. The 71% removal rate is likely

due to solids settling. The concentration of orthophosphate was below the limit of detection throughout the treatment system. The lack of orthophosphate is not surprising since the high calcium and magnesium concentrations are suitable conditions to form insoluble calcium and magnesium phosphates.

Table 6. Phosphorus Data Summary.

Test Parameter	Units	Influent	Effluent	% Removal	NPDES Limit	Comment
PHOSPHORUS						
Total Phosphorus	mg/L	1.83	0.53	71%	-	Degrades and settling.
Orthophosphate	mg/L	<0.5	<0.5	-	-	Below limit of detection.

Conclusion. Orthophosphate, the biologically available form of phosphorous, was not present in the water. The concentration of total phosphorous dropped by approximately one half, following the initial dilution due to blending of the produced. Whether this is caused by biological activity or physical settling is not known.

Sulfur. Sulfur is an essential element to life. It is incorporated into amino acids. Two forms of sulfur were measured in the produced water, sulfate (SO_4) and hydrogen sulfide (H_2S) (**Table 7**). In addition to forming the building blocks for biomass, sulfur can be used by microorganisms in the generation of energy. Sulfate reducing bacteria (SRB) can convert SO_4^- into H_2S under environmental conditions where the REDOX is low (-200 to -400 mV) and adequate biodegradable carbon is present. This reaction occurs in the absence of oxygen and is usually found in the sediments. Conversely, sulfur-oxidizing bacteria can regenerate sulfate from hydrogen sulfide in the presence of oxygen.

Table 7. Sulfur Data Summary.

Test Parameter	Units	Influent	Effluent	% Removal	NPDES Limit	Comment
Sulfur						
SO_4	mg/L	678	890	-31%	-	Seawater level of sulfate.
H_2S	mg/L	<1.0	<1.0	-	-	SRB are C-limited.

Sulfate. The 1:4 blending (produced water:Tensleep water) closely predicted the actual concentration of SO_4 (-2.3%) (**Table 1** and **Figure 14**). The increase in SO_4 is attributed to blending, evapotranspiration and solids settling. Some microbial activity by SRB is present where solids have accumulated. The SO_4 concentration is high (close to seawater) and characteristic of the mineral waters of the hot springs found in Wyoming.

Hydrogen Sulfide. The overall net gain/loss of H_2S was zero from influent to effluent (**Figure 15**). H_2S was generated by SRB where solids accumulated (netted (skimming) pond and oxidation lagoon). Very little of the SO_4 that could be

converted in the netted pond into H_2S was converted due to a relatively low concentration of carbon as measured by BOD_5 and TOC. Removal of the solids would likely minimize the generation of H_2S .

Conclusion. There is no net gain or loss of H_2S across the bio-treatment facility. H_2S is generated where in the wetland pond and oxidation lagoon where carbon is available for SRB to convert SO_4 into H_2S . Removal of the settled solids would prevent H_2S formation.

Solids. Solids can be measured in a number of ways. For this discussion there are the solids associated with particulate matter (TSS and turbidity), and there are completely soluble solids (TDS and VS). The TSS and turbidity decreased significantly throughout the bio-treatment facility (96% and 85%, respectively) (**Table 8**). The loss of these solids is attributed to a long retention time. This time allows the particles to drop out in the quiescent sections such as the netted pond and oxidation lagoon, and to attach to the “sticky sites” created by the sediments, rocks and surviving plants. All of these components facilitate the removal of particulates. The soluble solids, TDS and VS, did not settle out as well as the particulates. TDS decreased by 8%. VS increased by 16%. Instead, they acted like ions in solution.

Conclusion. Insoluble solids were removed by the bio-treatment facility. The soluble components were not effected following initial blending.

Table 8. Solids Data Summary.

Test Parameter	Units	Influent Produced water	Predicted from water blends	Effluent	% Removal Influent v. Effluent	% Removal predicted co-mingling the streams v. Effluent	Comment
SOLIDS							
TSS	mg/L	111	64.6	4.00	96%	94%	TSS settles out.
TDS	mg/L	4380	3668	4010	8%	-9%	TDS act like ions.
VS	mg/L	2.79	3.81	3.23	-16%	15%	VS act like ions.
Turbidity	mg/L	45.4	32.7	4.76	90%	85%	Turbidity settles out.

Biological Activity Reaction Tests

The BART work was done at the Texaco laboratories in Bellaire, Texas using the manufacturer’s instructions. Interpretation of the results used Cullimore, 1993, “Practical Manual of Groundwater Microbiology”, Lewis Publishers, Ann Arbor.

Water and sediment column samples were collected and evaluated for the microbial populations using BARTs. These are rapid tests, which semi-quantitatively evaluate the relative activity of microbial populations. Differential media within the BART tube indicates the presence or absence of that population of microorganisms in the sample. The time required for the indicator to confirm the presence is

proportional to the number of microorganisms present in the sample. The advantages of BARTs are that they are cost effective, require only limited amounts of training and are simple to interpret. However, the method is not as rigorous as a full microbiological screen.

Tables 9 and 10 compare relative concentrations of different microorganism populations in the waters and sediments of the bio-treatment facility. The results of this evaluation indicate that there are significant populations of microorganisms capable of metabolizing organic and inorganic compounds throughout the bio-treatment facility. The populations are diverse and flourished throughout the facility despite the high temperatures in the cooling trenches and through the bio-treatment (wetland) pond (**Table 2**). The BART data confirm that the removal of organic compounds is due primarily to biological activity.

Table 9. BART Data Summary for Water Column Samples. (Log concentration of organisms.)

Sample	HAB	SLYM	FLUOR	SRB	IRB	NIT, ALG	DN
Cooling Trench	5.6	5.6	2	4.6	3.6	-	1
Entrance Stairway Trough	3	4.6	3	0	3	-	1
Wetland	3	4.6	3	1	3	-	1
Exit Oxidation Lagoon	5.6	5.6	1	2	3	-	1
Creek Downstream	5.6	5.6	1	4	3.6	-	0
Creek Upstream	5.6	5.6	0	5	3.6	-	0
Inlet to lagoon	3	6.6	0	1	3	-	1

Note:
 1) No Significant concentration of nitrifying organisms or algae was detected through the wetland with the BART tubes.
 2) Reported values are log concentrations of the microbial population.
 3) HAB – Heterotrophic bacteria. SLYM – Slime forming organisms. FLUOR – Fluorescent microorganisms. SRB – Sulfate reducing bacteria. IRB – Iron related bacteria. NIT – Nitrifying bacteria. DN – Denitrifying bacteria. ALG – Algae.

Table 10. BART Data Summary for Sediment Column Samples.

Sample	HAB	SLYM	FLUOR	SRB	IRB	NIT	DN
Cooling Trench	5	6	3	4	6	-	<2
Inlet Lagoon	5	6	3	4	5.6	-	3
Stairway Trough	3	6	3	3	4	-	<2
Wetland	5	5.6	<2	3	5.6	-	3
Exit Shoreline	7.6	6	<2	5.6	6	-	<2
Creek Downstream	8.6	8.6	<2	6.6	6	-	<2
Creek Upstream	8.6	6.6	<2	3	4	-	<2

Note:
 1) Reported values are log concentrations of the microbial population.
 2) HAB – Heterotrophic bacteria. SLYM – Slime forming organisms. FLUOR – Fluorescent microorganisms. SRB – Sulfate reducing bacteria. IRB – Iron related bacteria. NIT – Nitrifying bacteria. DN – Denitrifying bacteria.

The bio-treatment facility is a complex microbial ecosystem based on the BARTs and water quality data. BARTs provide a “snapshot” of the microbial flora in the water and sediment columns. The facility has a healthy and diverse population of microorganisms, which is in line with the good treatment of biodegradable components indicated by

the water chemistry data. The concentration and location of specific populations are consistent with what was seen with the water chemistry. The matching of microbial populations to food sources is known as the “substrate effect.”

Heterotrophic Bacteria and Slime Forming Organisms. Heterotrophic bacteria (HAB) and slime forming organisms (SLYM) are present throughout the facility. Heterotrophs metabolize BOD₅ and hydrocarbons under aerobic conditions. These organisms are consistent with the degradation of BOD₅ throughout the facility.

Fluorescent Microorganisms. Fluorescent microorganisms (FLUOR) are those microbes that produce a fluorescent pigment when growing. Fluorescent pigment producers include the members of the genus *Pseudomonas*. The family of pseudomonads can metabolize a broad range of hydrocarbons. This metabolic flexibility allows over 100 types of petroleum hydrocarbons to be biodegraded by some species in this genus. The FLUOR BARTs detected fluorescent microorganisms in the upper end of the treatment facility, the cooling trench, stairway trough and in the wetland. These are the areas of the facility with the highest concentration of petroleum hydrocarbons as measured by the water quality data. The elevated concentrations of petroleum allowed for the enrichment for these organisms in the sediments and waters.

Sulfate Reducing Bacteria. Sulfate reducing bacteria (SRB) are present throughout the facility’s sediments and waters. The water chemistry suggests that conditions are well suited for these organisms to thrive in all parts of the treatment facility. The high concentration of sulfate in the produced water ensures that there is a readily available electron acceptor. The BOD₅ data indicates that there is an oxidizable carbon source throughout the treatment facility. The only exceptions to the universal presence of SRB are in the stairway trough and the wetland water column. The aeration through the stairway may inhibit the water-borne SRB and limit population growth. The low SRB population in the wetland water column may be a function of the quiescent water allowing microorganisms to settle with the particulate matter, since the wetland sediment column contained elevated concentrations of SRBs (log concentration is 5.6) and a carbon source.

Nitrifying and Denitrifying Bacteria. The nitrifying bacteria (NIT) and denitrifying bacteria (DN) BARTs detect nitrogen-metabolizing bacteria. The water chemistry data indicate that there are very few to no concentrations of free ammonium and no nitrate. Therefore there are few nitrogen compounds available for those microbes that use that use nitrogen compounds in the production of energy. No nitrifying organisms are present. The denitrifying organisms are present at about the limit of detection of the BARTs. (log 1 for waters and <2 for sediments).

Iron Related Bacteria. Iron-related bacteria (IRB) are present in the bio-treatment facility. The IRB population is high throughout the bio-treatment (wetland) pond. Since iron was not measured in the water quality data, the interpretation of IRB data is somewhat speculative. It is reasonable to suggest however that the high ionic content of the produced water includes iron that is in the water and is available for metabolism in either an iron oxidizing or reducing environment. The IRB test is one of the more complex BARTs to interpret with or without the iron water chemistry data. However, the IRB are a significant component in the bio-treatment facility ranging from log 3 to 3.6 in the water, and they are an order of magnitude or more higher in the sediment column than in the water column.

Algae. Algae (ALG) were not present as measured by BART tests. The high temperature and the low concentrations of nitrogen and phosphorus of the produced water may be inhibiting algal growth. One might consider retesting for ALG after the water has been cooled and after the bio-treatment facility has equilibrated.

Conclusion. Since this work represents the first reported use of BART tubes for the evaluation of microbial populations in a produced water bio-treatment facility; we have no data for comparison. The BARTs are cost effective and simple to run. They provide a view of the microbial populations of this treatment facility. The BART data are consistent with the water chemistry data.

The results of the BARTs indicate that there are significant populations of microorganisms capable of metabolizing organic and inorganic compounds throughout the bio-treatment facility. The populations are diverse and flourished throughout the facility despite the high temperatures in the cooling trenches and bio-treatment (wetland). The BART data suggest that WSO removal is primarily due to biological activity.

Summary of Treatment Performance

The bio-treatment facility is successful in its four basic NPDES treatment objectives:

- Blend produced waters to meet EC discharge limit.
- Cool down the water for skimming and wetland plant survival.
- Drop out solids.
- Biologically degrade WSO.

The 1:4 blending of produced waters meets EC discharge limits. The cooling tower and trenches work but could be improved. Solids are removed. Organic carbon (WSO) is removed throughout the bio-treatment facility (**Table 11**).

Table 11. Performance Summary of Bio-treatment Facility.

Test Parameter	Units	Sampling Site ID #1 Produced Water	Effluent Concentration	% Removal
CARBON				
BOD ₅	mg/L	28.0	2.3	92%
COD	mg/L	48.0	29	40%
TOC	mg/L	32.7	3.6	90%
TIC	mg/L	85.6	22.8	73%
NITROGEN				
TKN	mg/L	1.8	<0.5	>72%
NH ₃	mg/L	2.03	0.54	73%
NO ₃	mg/L	<0.1	<0.1	-
PHOSPHORUS				
Total Phosphorus	mg/L	1.83	0.46	75%
Orthophosphate	mg/L	<0.5	<0.5	-
SULFUR				
SO ₄	mg/L	678	890	-31%
H ₂ S	mg/L	<1.0	<1.0	-
HYDROCARBON				
TPH	mg/L	112.0	5.8	95%
O&G	mg/L	71.9	4.2	94%
GRO	mg/L	1.44	0.0	100%
DRO	mg/L	98.0	2.0	98%
BTEX				
Benzene	ug/L	143.0	<1.0	100%
Toluene	ug/L	135.0	<1.0	100%
Ethylbenzene	ug/L	33.6	<1.0	100%
Xylene	ug/L	162.0	<1.0	100%
SOLIDS				
Turbidity	mg/L	45.4	4.76	90%
TDS	mg/L	4380	4010	8%
TSS	mg/L	111.0	4.0	96%
VS	mg/L	2.79	3.23	-16%
IONS				
Hardness	mg/L	549.0	732.0	-33%
Calcium	mg/L	177.0	236.0	-33%
Magnesium	mg/L	25.9	34.7	-34%
Alkalinity	mg/L	713.0	190.0	73%
pH	s.u.	8.0	8.0	-
Conductivity	umho/cm	7490	6270	16%

Potential Bio-treatment Facility Improvements

As with any water treatment facility, there are potential opportunities for improvement. **Table 12** lists some possible improvements for the bio-treatment facility.

Table 12. Potential Improvements for the Bio-treatment Facility.

Potential Improvement	Comment
Cooling capacity	Need water <100°F to protect wetland plants. Oil/water separates better at lower temperatures.
Solids handling/removal	Need convenient "wide spot in the line" to remove solids. Eliminates carbon source for SRB.
Skimming operations	Better skimming would minimize emulsion formation, entrainment of solids, WSO content and production of H ₂ S in the produced water.
Flow control and water control structures	Better control of the flowrate would help to dampen out hydraulic surges and improve treatment. Flashboard riser water control structures would help to set and maintain water depths in the lagoon and wetland.
Replanting of wetland (free-water surface and/or sub-surface)	Fully vegetated wetlands will provide better treatment than the current system delivers. Use local plants for replanting. If evapotranspiration is increasing the salt content of the water, consider using a sub-surface wetland.
Future discharge limits	Future discharge limits will be more restrictive. TMDL may play a part. What tests and limits are likely? Can they be met? What improvements might be needed?
Water reuse	Consider going to zero discharge. Look at irrigation. Look at silviculture. What can be done for wildlife?

Conclusions

The DOE NPR-3 produced water bio-treatment facility successfully treats an average of 35,000 bwpd. The functional component parts of the bio-treatment facility consist of cooling, blending, oil/water separation and biological treatment. The facility meets NPDES discharge limits. It saves \$175,000 per year on utilities (\$3.5MM over the projected 20-year life expectancy) and it benefits wildlife by keeping a normally dry streambed wet year-round with an abundance of wetland plants for forage.

- Sampling was done under upset conditions (or a "worst case" scenario). The bio-treatment facility met discharge limits even with increased hydraulic loading, elevated temperatures and skimming difficulties.
- Elevated temperatures (>100°F) have wiped out the bio-treatment facilities wetland plants twice. At the point of discharge where the water is <100°F, there is a thriving community of wetland plants.
- Blending of NPR-3 oilfield produced waters is used to control the electrical conductivity to meet discharge limits.
- Hydrocarbon treatment is good as measured by TPH, O&G, GRO, DRO and BTEX. The removal rates are 97%, 95%, 100%, 98% and 100%, respectively.
- Carbon treatment is good as measured by COD, BOD₅, TOC and TIC. The removal rates are 48%, 95%, 93% and 72%, respectively. About half of the COD is biorefractory.
- Nitrogen treatment is good as measured by TKN, NH₃ and NO₃ ranging from 72% to 100% removal. The microbial population may be nitrogen limited.
- Phosphorus treatment is good as measured by P_{total} and PO_{4(ortho)}. The removal rate for P_{total} was 71% and PO_{4(ortho)} was below the limit of detection for all samples.

- The bio-treatment facility is carbon limited based on comparisons of influent and effluent BOD₅:COD and BOD₅:TOC ratios.
- Most of the sulfur in the system is in the form of SO₄.
- H₂S is produced by sulfate reducing bacteria (SRB) in the bio-treatment facility where anaerobic conditions, SO₄ and a carbon source (solids) are present. The H₂S is rapidly oxidized after formation and none is discharged.
- There are low levels of solids entering and leaving the bio-treatment facility.
- The produced water contains low concentrations of WSO.
- The produced water is a "very hard" water due to calcium and magnesium content.
- The BARTs worked well in demonstrating the "substrate effect."
- The areas identified for potential improvement to the bio-treatment facility include:
 - Cooling capacity.
 - Solids handling/removal.
 - Skimming operations.
 - Flow control and water control structures.
 - Replanting of the wetland (free-water surface and/or subsurface).
 - Future discharge limits.
 - Water reuse.

Appendix A-Acronyms and Abbreviations

ALG – Algae
 ADP – Adenosine Diphosphate
 API – American Petroleum Institute
 ATP – Adenosine Triphosphate
 BART – Biological Activity Reaction Test
 BOD₅ – Biochemical Oxygen Demand
 BTEX – Benzene Toluene Ethylbenzene Xylene
 bwpd – barrels water per day
 C – Carbon
 Ca – Calcium
 Cd – Cadmium
 COD – Chemical Oxygen Demand
 DN – Denitrifying Bacteria
 DRO – Diesel Range Organics or Diesel Range Organic Compounds
 DO – Dissolved Oxygen
 DOE – Department of Energy
 EC – Electrical Conductivity
 FAD – Flavin Adenine Dinucleotide
 FLUOR – Fluorescent microorganisms
 GRO – Gasoline Range Organics or Gasoline Range Organic Compounds
 H₂S – Hydrogen Sulfide
 HAB – Heterotrophic Bacteria
 HRT – Hydraulic Retention Time
 IC – Ion Chromatography
 IRB – Iron Related Bacteria
 Mg – Magnesium
 N – Nitrogen

- NAD – Nictotinamide Adenine Dinucleotide
- NH₃ – Ammonia-Nitrogen
- NIT – Nitrifying Bacteria
- NO₃ – Nitrate
- NPDES – National Pollution Discharge Elimination System
- NPR-3 – Naval Petroleum Reserve No. 3
- O&G – Oil & Grease
- P – Phosphorus
- pH = -Log[H⁺]
- PO₄ – Phosphate
- REDOX – Oxidation-Reduction Potential
- RMOTC – Rocky Mountain Oilfield Testing Center
- S – Sulfur
- S₂⁼ – Sulfide
- SH&E – Safety, Health & Environment
- SIM DIS – Simulated Distillation
- SLYM – Slime Forming Organisms
- SO₄ – Sulfate
- SRB – Sulfate Reducing Bacteria
- SRT – Solids Retention Time
- TAB – Total Aerobic Bacteria
- TC – Total Carbon
- TDS – Total Dissolved Solids
- TIC – Total Inorganic Carbon
- TKN – Total Kjeldahl Nitrogen
- TMDL – Total Daily Maximum Loading
- TN – Total Nitrogen
- TOC – Total Organic Carbon
- TPH – Total Petroleum Hydrocarbons
- T&P – Travel & Personnel
- TSS – Total Suspended Solids
- UV - Ultraviolet
- VS – Volatile Solids
- VSS – Volatile Suspended Solids
- WSO – Water Soluble Organic Compounds

Appendix B-References

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Appendix C-Analytical Test Methods

Analytical Tests* Selected for Bio-treatment Facility Evaluation

Analytical Test	Comment
Carbon BOD SM5210 B COD EPA 410.4 TOC SM 2340-B TIC SM 2320-B	Carbon can be measured in many forms. BOD measures the oxygen required to biodegrade water. COD is the chemical oxidation demand. COD includes the biodegradable (BOD) and components which are solely chemically oxidizable. TOC is a measure of the organic carbon. TIC is the inorganic carbon.
Nitrogen NH ₄ SM4500-NH3G NO ₃ EPA 353.2 TKN EPA 351.3	Nitrogen also can be answered in multiple forms. Ammonia (NH ₄) and nitrate (NO ₃) are forms of nitrogen that are readily metabolized. Total Kjeldahl Nitrogen (TKN) is a measure of all forms of nitrogen.
Phosphorous PO ₄ (total) EPA 200.7 PO ₄ (ortho) EPA 300.0	Phosphorous is typically measured as phosphate (PO ₄). The ortho form is biologically available. PO ₄ (total) is not necessarily biologically available.
Sulfur H ₂ S EPA 376.1 SO ₄ EPA 200.7	The two dominant forms of sulfur found in produced waters are hydrogen sulfide and sulfate.
Hydrocarbon Species TPH EPA 418.1 O&G EPA 413.1 BETX EPA 8020 GRO EPA 8015 DRO EPA 8015	TPH and O&G are spectrographic measures of hydrocarbon content. They differ by the extent of sample cleanup. BETX represents the light ends of hydrocarbons (short carbon chains). GRO is a GC measure of the gasoline range organic compounds. DRO is a GC measure of the diesel range organic compounds.
Ions Ca EPA 200.7 Mg EPA 200.7 EC EPA 120.1 Alkalinity SM 2320-B Hardness SM 2340-B pH SM4500-H-B	Ions are important to biological systems. Freshwater and Saltwater organisms have evolved to handle the presence or absence of ions (cations and anions). Too many salts and ions can be detrimental to biological systems. Optimum biodegradation is between 5-8.
Solids TSS EPA 160.2 TDS SM2540-C-Mod VS USDA # 60/26 Mod Turbidity EPA 180.1	Solids have many forms. Solids are sticky sites for organic and inorganic compounds. Well-run wetlands filter out solids producing crystal clear waters.
BARTs Dyncorp SRB SLYM HAB DN IRB FLUOR ALG	BARTs measure biological activity based on the microbial ability to consume certain substrates (food). The microbes are classified according to which substrates they can consume. The amount of substrate consumed is proportional to the microbial population.

*Cullimore, 1993. “Practical Manual of Groundwater Microbiology”, Lewis Publishers

Appendix D – Figures and Data

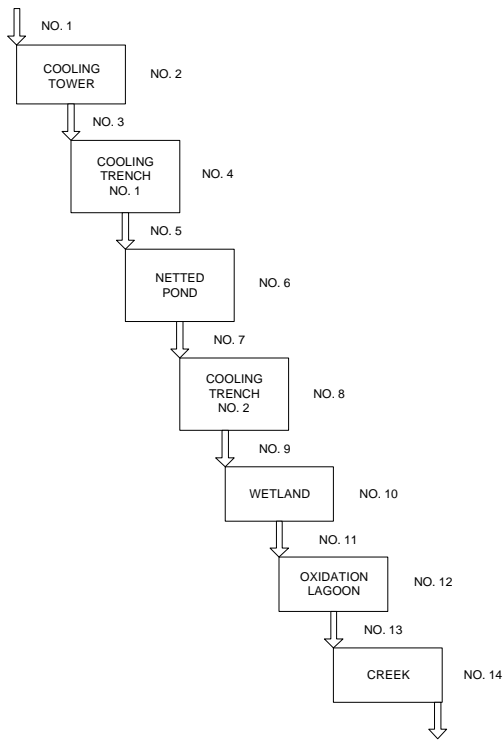


Figure 1. DOE RMOTC Bio-treatment Facility PFD with Potential Sampling Points Nos. 1-14.

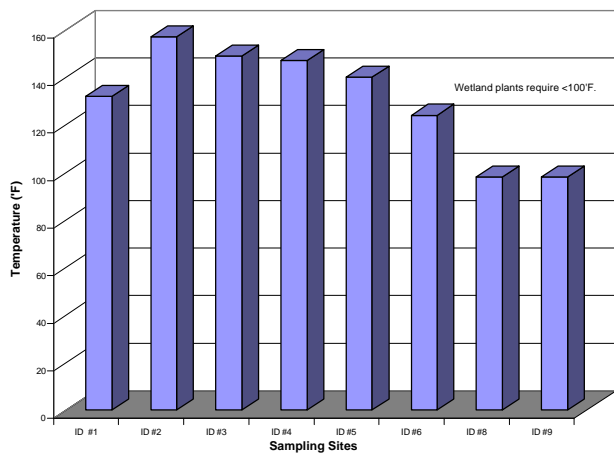


Figure 2. Bio-treatment Facility Temperatures on September 28, 1999.

Total Petroleum Hydrocarbons

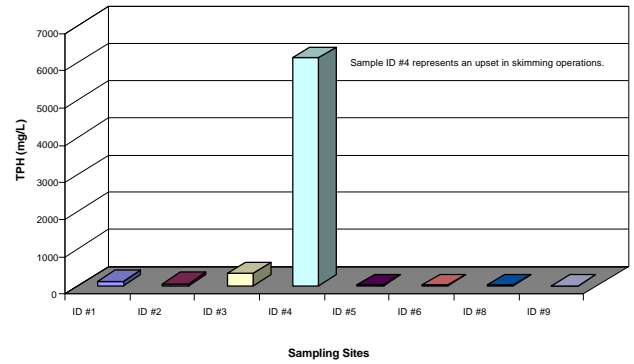


Figure 3. Total Petroleum Hydrocarbons (TPH) Data.

Oil & Grease

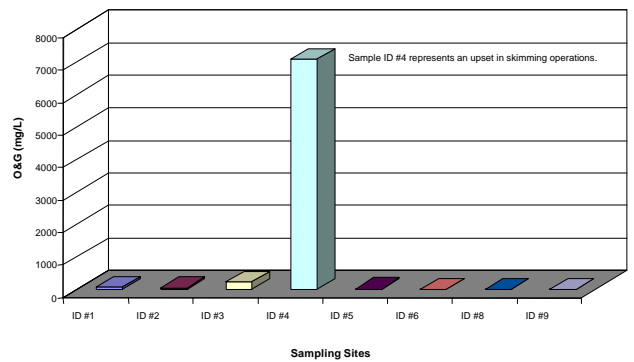


Figure 4. Oil & Grease (O&G) Data.

Gasoline Range Organic Compounds

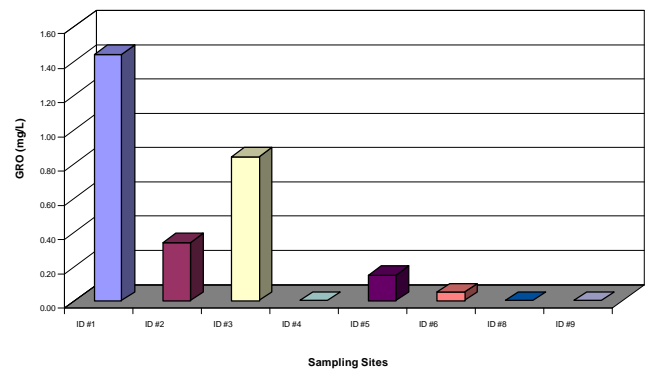


Figure 5. Gasoline Range Organic Compounds (GRO) Data.

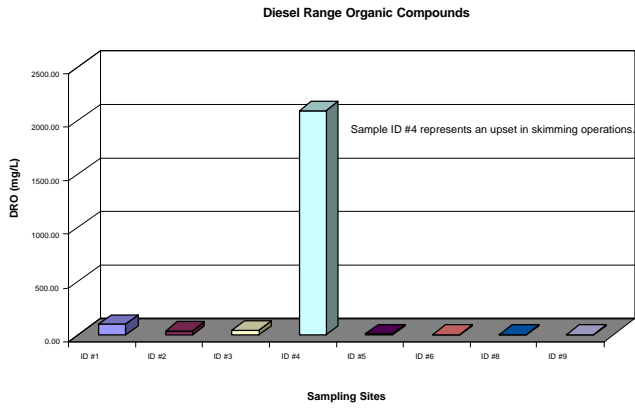


Figure 6. Diesel Range Organic Compounds (DRO) Data.

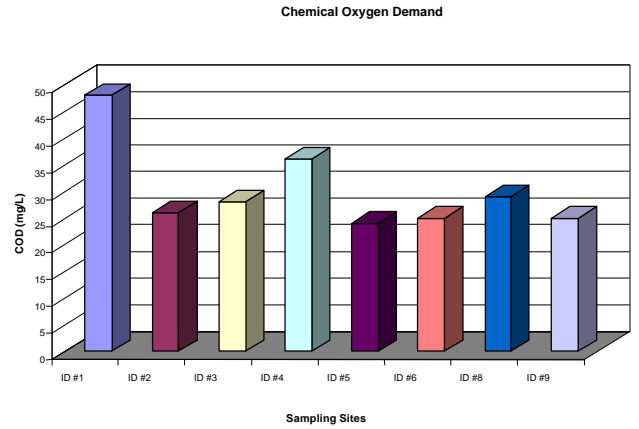


Figure 9. Chemical Oxygen Demand (COD) Data.

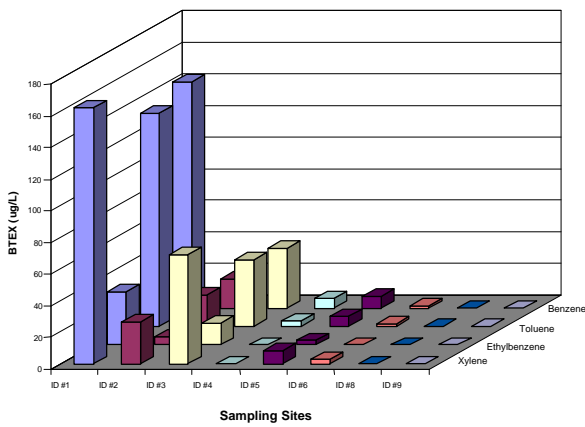


Figure 7. Benzene, Toluene, Ethylbenzene, Xylene (BTEX) Data.

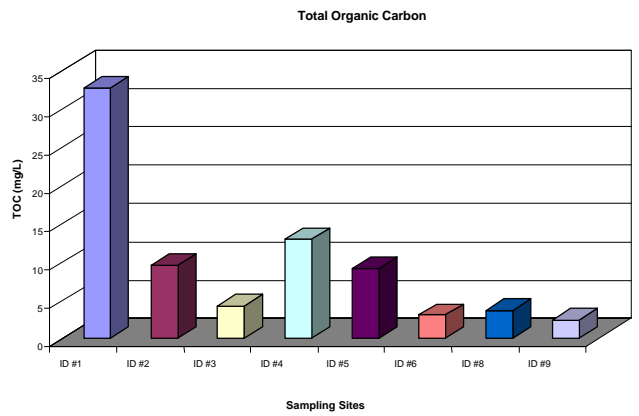


Figure 10. Total Organic Carbon (TOC) Data.

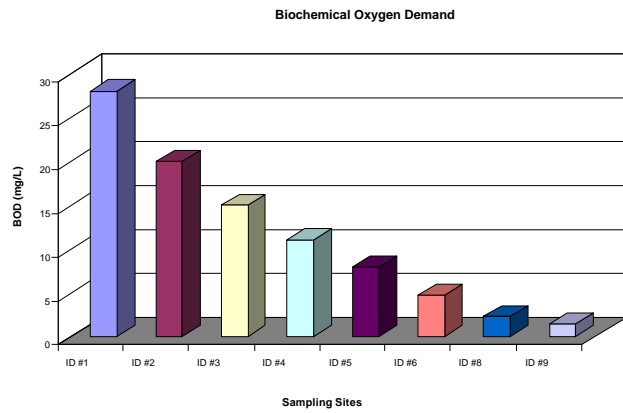


Figure 8. Biochemical Oxygen Demand (BOD₅) Data.

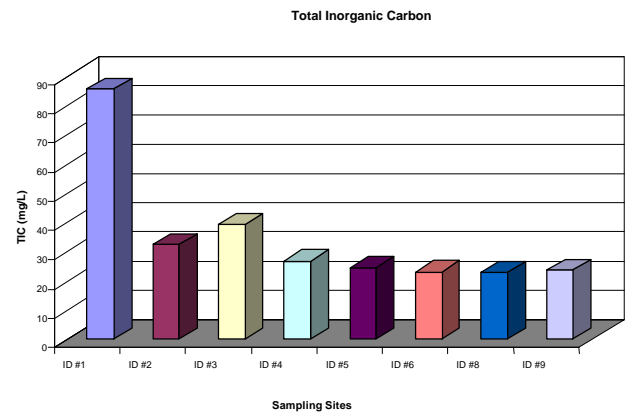


Figure 11. Total Inorganic Carbon (TIC) Data.

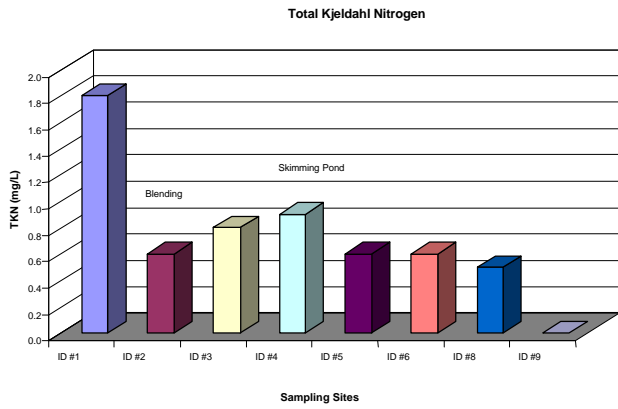


Figure 12. Total Kjeldahl Nitrogen (TKN) Data.

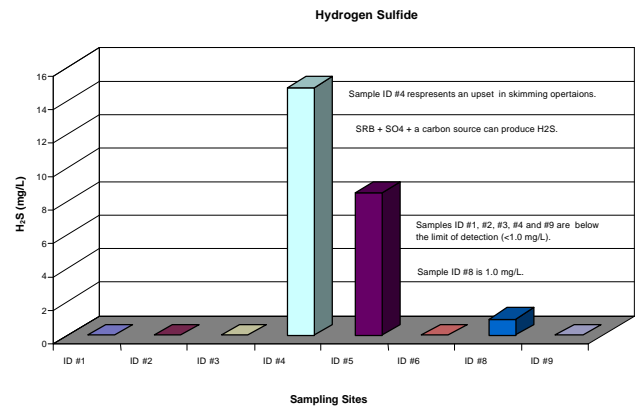


Figure 15. Hydrogen Sulfide (H₂S) Data.

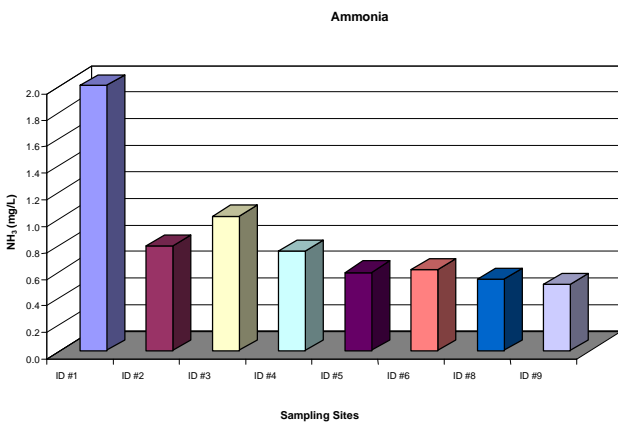


Figure 13. Ammonia (NH₃) Data.

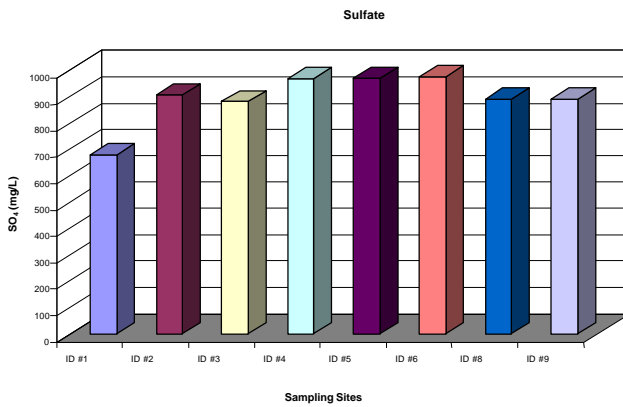


Figure 14. Sulfate (SO₄) Data.