

**Technical Protocol for Evaluating Natural Attenuation Parameters  
at Sites with Petroleum Contaminated Groundwater**

**Division of Waste Management  
Petroleum Restoration Program**

**January 2018**

Acknowledgements: Special thanks to Aaron Getchell, CPG, P.G., Jane Anstey Williams, E.I., F. Joseph Ullo, Jr., P.E., Brian Dougherty, Ph.D., and Lynn Walker, P.E. for the development and review of this guidance document.

## INTRODUCTION

The purpose of this technical protocol is to provide a concise reference for evaluating Natural Attenuation Monitoring (NAM) parameters at sites with petroleum-contaminated groundwater. The NAM parameters discussed herein are important to understand as related to Chapter 62-780.690 Florida Administrative Code (F.A.C.). The NAM parameters provide valuable site-specific information that includes: an aquifer's capability to sustain natural attenuation of dissolved-phase petroleum compounds; evidence of plume stability for risk-based closure; identification of new petroleum releases; and when it may be appropriate to discontinue operation and maintenance (O&M) of a constructed remediation system.

NAM has been referred to as "passive" remediation (NGWA, 2001), while a constructed remediation system has been referred to as "active" remediation. However, NAM is not a "passive" or "do nothing" approach, and progress of natural attenuation must be evaluated with the scrutiny of assessing constructed remediation system performance in an O&M report. Thus, a NAM report should be prepared with a level of analysis required to determine the effectiveness of NAM as a site remedy.

A list of common NAM parameters with field and analytical methods is presented in **Table 1**. Some of these NAM parameters can be recorded in the field during groundwater sample collection, and some will be obtained through laboratory analysis. **Table 2** presents these NAM parameters with values, ranges, or observations for use in evaluating the effectiveness and progress of NAM at sites with petroleum-contaminated groundwater.

## MECHANISMS OF NATURAL ATTENUATION AT PETROLEUM SITES

There are two types of NAM mechanisms: (i) non-destructive which does not result in a loss of contaminant mass from the aquifer (dispersion, dilution, and advection); and the focus of this guidance document (ii) destructive, which results in contaminant mass loss from the aquifer (aerobic and anaerobic biodegradation as shown in **Figure 1**) (NGWA, 2001). As a remedial action, both of the destructive NAM mechanisms will result in a stable or shrinking dissolved plume of petroleum in the aquifer. Assessing the suitability and the effectiveness of NAM at a petroleum site will be evaluated by the parameters listed in **Tables 1 and 2**.

Non-destructive mechanisms include dispersion, dilution, and advection, where a plume of petroleum-impacted groundwater migrates through an aquifer along a flow path and the plume is reduced in concentration over time (NGWA, 2001). These non-destructive mechanisms rely on physical processes and aquifer characteristics such as aquifer matrix, effective porosity, hydraulic gradients, groundwater table fluctuations, and other hydraulic considerations (groundwater pumping, seeps, springs, or interaction with surface water bodies). Generally, these non-destructive mechanisms of NAM will be evaluated by the gross reduction of petroleum compounds from groundwater sampling analytical results.

Destructive mechanisms of natural attenuation consist of aerobic and anaerobic biodegradation (shown on **Figure 1**), where a petroleum plume is reduced by naturally occurring aerobic and anaerobic biodegradation activities within an aquifer (NGWA, 2001 and EPA, 2016). Biodegradation is a biological process where the petroleum compounds are consumed and byproducts are respired. Biodegradation processes from aerobic to anaerobic in order of occurrence are: aerobic biodegradation, nitrate reduction (denitrification), manganese reduction, iron reduction, sulfate reduction, and carbon dioxide reduction (methanogenesis) (NGWA, 2001 and EPA, 2016). It is likely that more than one biodegradation process is occurring within a naturally attenuating petroleum plume. The NAM parameters collected in the field or

derived by laboratory analysis listed in **Tables 1 and 2** are a direct measure of the effectiveness and progress of these destructive natural attenuation mechanisms.

Petroleum compounds commonly monitored at gasoline release sites (listed on **Tables 1 and 2**) include benzene, toluene, ethylbenzene, and total xylenes (BTEX); and petroleum compounds commonly monitored at a diesel release site include the polynuclear aromatic hydrocarbons (PAHs): naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene (FDEP, 2016). These petroleum compounds can be reduced by both aerobic and anaerobic biodegradation. Fuel additives commonly found at petroleum-impacted sites include: 1,2-dibromoethane (EDB), 1,2-dichloroethane (DCA), methyl tert-butyl ether (MTBE), tert-butyl alcohol (TBA), and ethanol. These common fuel additives can also be reduced by both aerobic and anaerobic biodegradation (FDEP, 2016).

## MONITORING WELL SELECTION FOR EVALUATING NAM

Within the framework of Chapter 62-780 F.A.C., NAM can be proposed following the approval of a Site Assessment Report (SAR) (Chapter 62-780.600 F.A.C.), or Active Remediation (Chapter 62-780.700 F.A.C.). A site assessment requires horizontal and vertical delineation of a petroleum plume and active remediation requires performance monitoring. Thus, by the time NAM is proposed at a site, there are sufficient monitoring wells to evaluate the effectiveness and progress of NAM. These monitoring wells will also have been installed and developed within the affected aquifer(s) according to common industry practice, with screen-intervals placed according to FDEP regulations (FDEP, 2008).

According to NAM requirements (Chapter 62-780.690 F.A.C.), a minimum of two monitoring wells are required for a monitoring program: one monitoring well installed at the downgradient edge (outside) of a petroleum plume, and one monitoring well installed in the area of the highest groundwater contamination (inside the petroleum plume). This minimum number of wells (illustrated on **Figure 2**) will provide field and laboratory data from both inside and outside of the petroleum plume.

Monitoring well selection is important because, as shown on **Table 2**, many NAM parameters are evaluated by a comparison of inside/outside petroleum plume, and are not directly compared to FDEP-provided default cleanup criteria. Please note that two monitoring wells is a minimum number, and a more robust monitoring well network may be needed depending on the scale, extent, and complexity of the petroleum plume within an aquifer or aquifers.

As shown on **Figure 2**, the monitoring well installed outside the petroleum plume will provide NAM parameters that could represent unaffected concentrations, or areas where biodegradation is not occurring. The monitoring well installed inside the petroleum plume will provide a direct measurement of the concentration of petroleum compounds and NAM parameters from most active area of biodegradation.

## NAM PARAMETER EVALUATION

In order to understand the effectiveness of NAM at a petroleum site, the field data and laboratory data from each NAM sampling event must be critically evaluated. Some sites may have an analyte list that consists of just petroleum compounds, while other sites, depending on complexity, may have an analyte list that includes other physical water quality parameters (FDEP, 2011).

A list of FDEP-requested and more frequently requested NAM parameters has been described below and listed in **Tables 1 and 2**. Following a description of petroleum compound analysis, these NAM parameters are ordered in the progressive stages from aerobic biodegradation through anaerobic biodegradation (illustrated on **Figure 1**): aerobic biodegradation, nitrate reduction (denitrification), manganese reduction, iron reduction, sulfate reduction, and carbon dioxide reduction (methanogenesis) (NFESC, 1999 and EPA, 2016).

### Petroleum Compound Analysis

The greatest evidence of natural attenuation of a petroleum plume is based on laboratory analysis of petroleum compounds (listed **Tables 1 and 2**). Based on characterization of the release, petroleum compound analysis will include a combination of BTEX and PAHs. Laboratory analysis results are compared to the Groundwater Cleanup Target Levels (GCTLs) and Natural Attenuation Default Concentrations (NADCs) listed in Chapter 62-777 F.A.C., Tables I and V, respectively. If NAM is an effective strategy for remedial action, then each NAM sampling event should show a decrease of petroleum compounds towards the GCTLs. Over time, the petroleum plume will either become more dilute (decreasing concentrations) or shrink (the plume will appear to retract towards the source area).

### Dissolved Oxygen - Aerobic Biodegradation

The first step of biodegradation of petroleum compounds is an aerobic process (shown on **Figure 1**) where dissolved oxygen is consumed by the bacteria metabolizing the petroleum plume. Aerobic biodegradation is also the most rapid biodegradation process (EPA, 2016). Aerobic aquifer conditions are dissolved oxygen concentrations of greater than 1 milligram per Liter (mg/L or parts per million); and anaerobic aquifer conditions are dissolved oxygen concentrations of less than 1 mg/L (NFESC, 1999). Depending on conditions observed during NAM sampling, dissolved oxygen concentrations of 0.5 mg/L can also be used as the aerobic/anaerobic benchmark value (EPA, 2016).

When evaluating the effectiveness and progress of NAM, dissolved oxygen will be depressed inside a petroleum plume compared to outside a petroleum plume (shown on **Figure 3**) (NGWA, 2001). This occurs because the biological activity associated with aerobic biodegradation within the petroleum plume is consuming the dissolved oxygen. In an aerobic aquifer environment, naturally occurring groundwater flow will provide a continuous source of dissolved oxygen to the petroleum plume which is favorable for aerobic biodegradation.

### Nitrate and Nitrite – Nitrate Reduction “Denitrification” (Anaerobic Biodegradation)

Following dissolved oxygen consumption, nitrate reduction (denitrification) is the first step for anaerobic biodegradation (shown on **Figure 1**), where nitrate is consumed by the petroleum plume (FDEP, 2016). If denitrification is occurring, nitrate concentrations will be lower within the petroleum plume and higher outside the petroleum plume (shown on **Figure 4**) (NGWA, 2001).

If denitrification is occurring and nitrate is being used, then nitrite is being respired by the biological activity. Therefore, nitrite concentrations will be higher inside the petroleum plume while nitrite concentrations will be lower outside the petroleum plume (also shown on **Figure 4**). In aquifer environments with nitrate concentrations less than 1 mg/L, conditions may be limiting for denitrification (NFESC, 1999). Since denitrification is an anaerobic process, dissolved oxygen may be less than 0.5 mg/L while nitrate may be greater than 1 mg/L (NFESC, 1999).

### Manganese – Manganese Reduction (Anaerobic Biodegradation)

After the naturally occurring nitrate has been depleted in the aquifer, manganese is used to support the anaerobic biodegradation of petroleum compounds (shown on **Figure 1**). If manganese reduction is occurring, dissolved manganese concentrations will be lower within the petroleum plume and higher outside the petroleum plume (shown on **Figure 5**). Since this is an anaerobic process, dissolved oxygen may be less than 0.5 mg/L.

### Insoluble Iron (Iron III) and Dissolved Iron (Iron II) – Iron Reduction (Anaerobic Biodegradation)

After manganese has been depleted, insoluble iron (iron III) is used to support anaerobic biodegradation of the petroleum plume (shown on **Figure 1**) (NGWA, 2001). If iron reduction is occurring, then concentrations

of insoluble iron (iron III) will be lower inside the petroleum plume and higher outside the petroleum plume (shown on **Figure 6**).

If insoluble iron (iron III) is being used; biological activity will reduce it to soluble iron (dissolved iron or iron II). Therefore, soluble iron (dissolved iron or iron II) concentrations will be higher inside the petroleum plume and lower outside the petroleum plume (also shown on **Figure 6**) (FDEP, 2016). Since iron reduction is an anaerobic process, dissolved oxygen may be less than 0.5 mg/L (NFESC, 1999).

#### Sulfate – Sulfate Reduction (Anaerobic Biodegradation)

Following iron reduction, sulfate is used to support anaerobic biodegradation of the petroleum plume (shown on **Figure 1**). If sulfate reduction is occurring, then sulfate concentrations will be lower inside a petroleum plume and higher outside the petroleum plume (shown on **Figure 7**) (FDEP, 2016). Since sulfate reduction is an anaerobic biodegradation process, dissolved oxygen concentrations outside a petroleum plume may be less than 0.5 mg/L while sulfate concentrations may remain greater than 1 mg/L (NFESC, 1999).

#### Methane – Carbon Dioxide Reduction “Methanogenesis” (Anaerobic Biodegradation)

After the naturally occurring sulfate in an aquifer environment is consumed, carbon dioxide is used to support anaerobic biodegradation and methane is respired (as shown on **Figure 1**). If carbon dioxide reduction (methanogenesis) is occurring, methane concentrations will be higher inside the petroleum plume and lower outside the petroleum plume (shown on **Figure 8**) (FDEP, 2016). Since methanogenesis is an anaerobic process, dissolved oxygen may be less than 0.5 mg/L (NFESC, 1999).

#### pH (Water Quality Parameter)

pH is recorded to measure the acidity (generally 4 to 0 Standard Units) or alkalinity (generally 8 to 14 Standard Units) of an aquifer environment. Anaerobic biodegradation of petroleum compounds may cause an increase or decrease in pH in an aquifer environment; therefore, pH above or below background may correspond to a dissolved petroleum plume. An aquifer with a neutral pH (6 to 8 Standard Units) is optimum for biodegradation of petroleum compounds (EPA, 2016).

#### ORP (Water Quality Parameter)

Oxidation Reduction Potential (ORP or redox potential) is the measurement of electron activity and is an indicator of an aquifer environment to accept or transfer electrons (biodegrade petroleum compounds). Groundwater measurements can range from +800 to -400 mV (NGWA, 2001); the lower the value, the more reducing and anaerobic the aquifer environment (as shown on **Figure 1**). ORP measurements will typically be lower inside the petroleum plume than outside the petroleum plume because microbial activity is consuming dissolved oxygen, resulting in an anaerobic and reducing aquifer environment within the petroleum plume.

#### Temperature (Water Quality Parameter)

Microbial activity associated with the biodegradation of petroleum compounds is highest within an aquifer environment at temperatures between 5 Degrees Celsius (°C) and 45°C (EPA, 2016). Optimally, for aerobic or anaerobic biodegradation of petroleum compounds, an aquifer environment should be above 15°C.

### NAM EFFECTIVENESS EVALUATION

By analyzing the NAM parameters discussed above and in accordance with Rule 62-780.690, F.A.C., environmental professionals can determine whether site conditions are conducive to the natural degradation of contaminants. The information from this analysis and potential follow up modeling should be combined to make remedial decisions for sites. For each site, the rate of attenuation should be estimated either quantitatively or qualitatively (Rule 62.780.690(1)(f)2.b, F.A.C.) If the rate of attenuation does not

achieve the protection of human health, public safety, and the environment and result in the best value to the state, recommendations should be made as to more aggressive remedial steps. In making such recommendations, professionals should consider whether or what enhancements could be part of the remedy if a biological or chemical treatment is the preferred remedy. This may be the case if natural attenuation occurred on the site, but was rate limited. For instance, if aerobic metabolism of contaminants was effective, but dissolved oxygen was depleted, bio-sparging or an oxygen releasing amendment may be proposed. In contrast, if natural attenuation is shown to be ineffective at the site based on the analysis, more physical contaminant removal methods are likely to garner greater consideration.

## CONCLUSIONS

As described in this technical protocol, evaluating the effectiveness and progress of NAM at a petroleum site is more than a “passive” or “do nothing” approach to remediation. Understanding the evaluation process of these parameters is critical to characterize the suitability of a site for a NAM program, but also serves as an important step to optimize existing NAM programs. A 2011 FDEP Memorandum indicated that after 42 months, a site in NAM was expected to show a 20% to 30% reduction in petroleum concentrations, and that evaluation of these NAM sites should be managed with flexibility (FDEP, 2011).

In a 2016 study conducted by an FDEP Petroleum contractor, NAM sites were evaluated for NAM optimization for cost savings. Cost savings were shown to be realized by better characterization of the site that leads to: alternative sample collection methods; a reduced monitoring well network; reduced sample frequency; and a reduced analyte list. 86 petroleum sites were evaluated using statistical methods; only 11 of these (17%) were expected to reach GCTLs in less than two years, where 43 of these sites (66%) were expected to take greater than ten years to reach GCTLs (Applegate, 2016). Natural attenuation of contaminants is always occurring, and it is hoped that through more considered analysis and aquifer characterizations, we can derive solutions that fully take advantage of and enhance nature’s work.

The FDEP accepted sites into the Petroleum Cleanup Program beginning in the late 1980s, and site assessments have been conducted based on FDEP’s ranking of a site’s risk to human health and the environment. Therefore, assuming a hypothetical low ranking with a score of 25; a site has had approximately 30 years of “un-monitored NAM”. Therefore, following remediation of a source, it becomes crucial to evaluate the effectiveness of NAM within a reasonable timeframe so that NAM can be evaluated as a cost-effective remedial action. This protocol was prepared as a concise reference to assist in these evaluations.

## REFERENCES

Applegate, Joe, 2nd Annual Winter Water Seminar, Session IV Groundwater Remediation: Natural Attenuation Monitoring, February 16, 2016.

Florida Department of Environmental Protection, Bureau of Water Facilities Regulation, Monitoring Well Design and Construction Guidance, 2008.

Florida Department of Environmental Protection, Chapter 62-777 Florida Administrative Code, Contaminant Cleanup Target Levels, April 17, 2005.

Florida Department of Environmental Protection, Chapter 62-780 Florida Administrative Code Contaminated Site Cleanup Criteria, February 4, 2017.

Florida Department of Environmental Protection, Standard Operating Procedures for Field Activities, DEP-SOP-001/01, March 1, 2014.

Florida Department of Environmental Protection, Waste Cleanup Program, Mechanisms of Monitored Natural Attenuation, Biodegradation of Petroleum Hydrocarbons and Fuel Additives, December 19, 2016.

Florida Department of Environmental Protection, Bureau of Water Facilities Regulation, Monitoring Well Design and Construction Guidance Manual, 2008.

Florida Department of Environmental Protection, Bureau of Petroleum Storage Systems, Procedures for Implementation of the Natural Attenuation Monitoring Provisions of Section 376.3071, F.S. in the Petroleum Cleanup Program, Effective February 1, 2011.

National Ground Water Association, Natural Attenuation for Remediation of Contaminated Sites, Nashville, Tennessee, May 7-9, 2001.

Naval Facilities Engineering Service Center, Natural Attenuation General Data Guide, User's Guide UG-2035-ENV, February 1999.

United States Environmental Protection Agency, How to Evaluate Alternative Cleanup Technologies For Underground Storage Tank Sites, A Guide For Corrective Action Reviewers, EPA 510-B-16-005, November 2016.

**Table 1**  
**Field and Laboratory Analytical Methods Summary**  
**Technical Protocol for Evaluating Natural Attenuation at Sites with Petroleum Impacted Groundwater**

	Parameter	CAS	Laboratory Analysis Method and/or FDEP SOP	Field Method
Petroleum Compound Analysis	Benzene	71-43-2	FS 2200 EPA Method 8260B	NA
	Toluene	108-88-3	FS 2200 EPA Method 8260B	NA
	Ethylbenzene	100-41-4	FS 2200 EPA Method 8260B	NA
	Xylenes (total)	1330-20-7	FS 2200 EPA Method 8260B	NA
	Naphthalene	91-20-3	FS 2200 EPA Method 8260B and/or EPA Method 8270B or EPA 8270 with SIM	NA
	1-Methylnaphthalene	90-12-0	FS 2200 EPA Method 8270B or EPA 8270 with SIM	NA
	2-Methylnaphthalene	91-57-6	FS 2200 EPA Method 8270B or EPA 8270 with SIM	NA
Fuel Additives Analysis	1,2-Dibromoethane (EDB)	106-93-4	FS 2200 EPA Method 8011	NA
	1,2-Dichloroethane (DCA)	107-06-2	FS 2200 EPA Method 8260B	NA
	Methyl tert-Butyl Ether (MTBE)	1634-04-4	FS 2200 EPA Method 8260B	NA
	Ethanol	64-17-5	FS 2200 EPA Method 8260B	NA
Aerobic Biodegradation	Dissolved Oxygen	NA	FS 2200	Membrane-type polarographic or galvanic electrode sensor with dedicated meter or configured with multi-parameter sonde.
Anaerobic Biodegradation	Nitrate "Denitrification"	14797-55-8	FS 2200 EPA Method 300.0	NA
	Nitrite "Denitrification"	14797-65-0	FS 2200	NA
	Manganese	7439-96-5	FS 2200 EPA 6010C	NA
	Insoluble Iron (Iron III)	NA	FS 2200 EPA Method 365.1 or SM3500	NA
	Dissolved Iron (Iron II)	NA	FS 2200 EPA Method 6010C	NA
	Sulfate	14808-79-8	FS 2200 EPA Method 9035	NA
	Methane "Methanogenesis"	74-82-8	FS 2200 RSKSOP-147/175	NA
Water Quality Parameters	pH	NA	FS 2200 FT 1100 EPA 150.1	For routine fieldwork use a pH meter accurate and reproducible to at least 0.2-unit in the range of 0.0 to 14.0 units, and equipped with temperature-compensation adjustment. Record the pH value in pH units to one decimal place.
	ORP	NA	FS 2200	Electronic sensor within a multi-meter array within a flow-through cell.
	Temperature	NA	FS2200 FT 1500	Membrane-type polarographic or galvanic electrode sensor with dedicated meter or configured with multi-parameter sonde. Select instrument assemblies that provide minimum precision of +/- 0.2 mg/L and a minimum accuracy of +/- 0.2 mg/L.

Notes:  
CAS = Chemical Abstracts Service  
EPA = Environmental Protection Agency  
mg/L = milligrams per Liter (parts per million)  
NA = not available or not commonly utilized for this application  
PAH = Polynuclear Aromatic Hydrocarbon  
SIM = Selective Ion Monitoring  
VOA = Volatile Organic Aromatic



**Table 2**  
**NAM Parameter Values and Ranges Interpretation**  
**Technical Protocol for Evaluating Natural Attenuation at Sites with Petroleum Impacted Groundwater**

	Parameter	NAM Parameter Values and Ranges Interpretation
Petroleum Compound Analysis	Benzene	GCTL 1 µg/L; NADC 100 µg/L
	Toluene	GCTL 40 µg/L; NADC 400 µg/L
	Ethylbenzene	GCTL 30 µg/L; NADC 300 µg/L
	Xylenes (total)	GCTL 20 µg/L; NADC 200 µg/L
	Naphthalene	GCTL 14 µg/L; NADC 140 µg/L
	1-Methylnaphthalene	GCTL 28 µg/L; NADC 280 µg/L
	2-Methylnaphthalene	GCTL 28 µg/L; NADC 280 µg/L
Fuel Additives Analysis	1,2-Dibromoethane (EDB)	GCTL 0.02 µg/L; NADC 2 µg/L
	1,2-Dichloroethane (DCA)	GCTL 3 µg/L; NADC 300 µg/L
	Methyl tert-Butyl Ether (MTBE)	GCTL 20 µg/L; NADC 200 µg/L
	Ethanol	GCTL 10,000 µg/L; NADC 100,000 µg/L
Aerobic Biodegradation	Dissolved Oxygen	An aquifer under aerobic conditions will have dissolved oxygen concentrations above 1 mg/L outside of the petroleum plume (upgradient or background). Dissolved oxygen concentrations within the petroleum plume may be depressed to below 1 mg/L as the dissolved oxygen is consumed by micorbial activity during aerobic biodegradation. Groundwater flow provides a continuous source of dissovod oxygen to the petroleum plume.
Anaerobic Biodegradation	Nitrate "Denitrification"	During denitrification, nitrate is consumed by microbial activity within the petroleum plume. Nitrate concentrations will be lower within the petroleum plume and higher outside the petroleum plume.
	Nitrite "Denitrification"	If denitrification is occurring and nitrate is being consumed by microbial activity inside the petroleum plume; then nitrite is being respired by the biological activity. Nitrite concentrations will be higher inside the petroleum plume.
	Manganese	If manganese reduction is occurring, manganese concentrations will be lower within the petroleum plume, and higher outside the petroleum plume.
	Insoluble Iron (Iron III)	If iron reduction is occurring, then concentrations of insoluble iron (iron III) will be lower inside the petroleum plume and higher outside the petroleum plume.
	Dissolved Iron (Iron II)	Biological activity will reduce insoluble iron (iron III) yo soluble iron (dissolved iron or iron II). Therefore, soluble iron (dissolved iron or iron II) concentrations will be higher inside the petroleum plume, and lower outside the petroleum plume
	Sulfate	If sulfate reduction is occurring, then sulfate concentrations will be lower inside a petroleum plume and higher outside the petroleum plume. Dissolved oxygen concentrations may be less than 0.5 mg/L while sulfate concentrations may remain greater than 1 mg/L.
	Methane "Methanogenesis"	During methanogenesis, carbon dioxide is consumed to support anaerobic biodegradation of petroleum compounds and methane is respired. Methane concentrations will be higher inside the petroleum plume and lower outside the petroleum plume.
Water Quality Parameters	pH	Optimum range for biodegradation is 6-8 SU. pH may be increased within a plume due to anaerobic conditions during biodegradation.
	ORP	Negative ORP suggests a reducing to strongly reducing environment capable of anaerobic biodegradation. ORP values will be lower inside the petroleum plume as dissolved oxygen is being consumed, and ORP will be higher outside the petroleum plume.
	Temperature	The optimum range for microbial activity between 5°C and 45 °C, ideally, temperatures should be above 15 °C. Extreme hot or cold temperatures inhibit microbial activity.

Notes:  
µg/L = micrograms per Liter (parts per billion)  
GCTL = Groundwater Cleanup Target Level, Chapter 62-777 Florida Administrative Code, Table I, 4/17/2005  
mg/L = milligrams per Liter (parts per million)  
NADC = Natural Attenuation Default Concentration, Chapter 62-777 Florida Administrative Code, Table V, 4/17/2005  
°C = Degrees Celsius  
SU = Standard Units

**FIGURE 1**  
**Oxidation Reduction Potentials**  
**for Electron Receptors**

AEROBIC BIODEGRADATION	Aerobic Biodegradation ORP = 820 mV	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
ANAEROBIC BIODEGRADATION	Nitrate Reduction "Denitrification" ORP = 740 mV	$2NO_3 + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$
	Manganese Reduction ORP = 520 mV	$MnO_2 (s) + HCO_3 + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_2O$
	Iron Reduction ORP = -50 mV	$FeOOH(s) + HCO_2^- + 2H^+ + e^- \longrightarrow FeCO_3 + 2H_2O$
	Sulfate Reduction ORP = -220 mV	$SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS + 4H_2O$
	Carbon Dioxide Reduction "Methanogenesis" ORP = -240 mV	$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$

**Notes:**

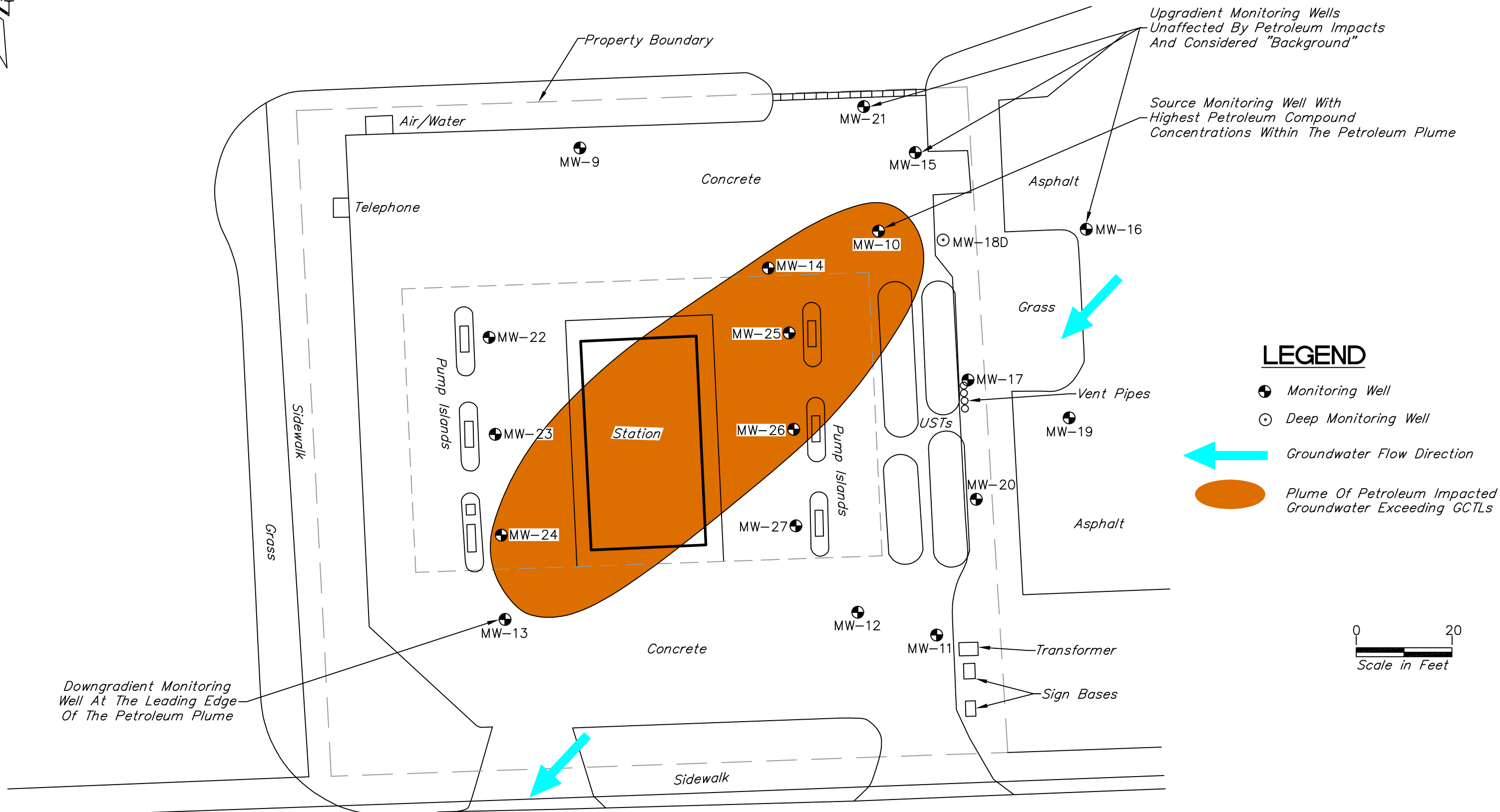
mV=Millivolts

ORP = Oxidation Reduction Potential

Oxidation Reduction Potential assuming groundwater is 25° Celsius

Modified from: United States Environmental Protection Agency, How to Evaluate Alternative Clean-up Technologies For Underground Storage Tank Sites, A Guide For Corrective Action Reviewers, EPA 510-B-16-005, November 2016

FIGURE 2



Upgradient Monitoring Wells  
Unaffected By Petroleum Impacts  
And Considered "Background"

Source Monitoring Well With  
Highest Petroleum Compound  
Concentrations Within The Petroleum Plume

Downgradient Monitoring  
Well At The Leading Edge  
Of The Petroleum Plume

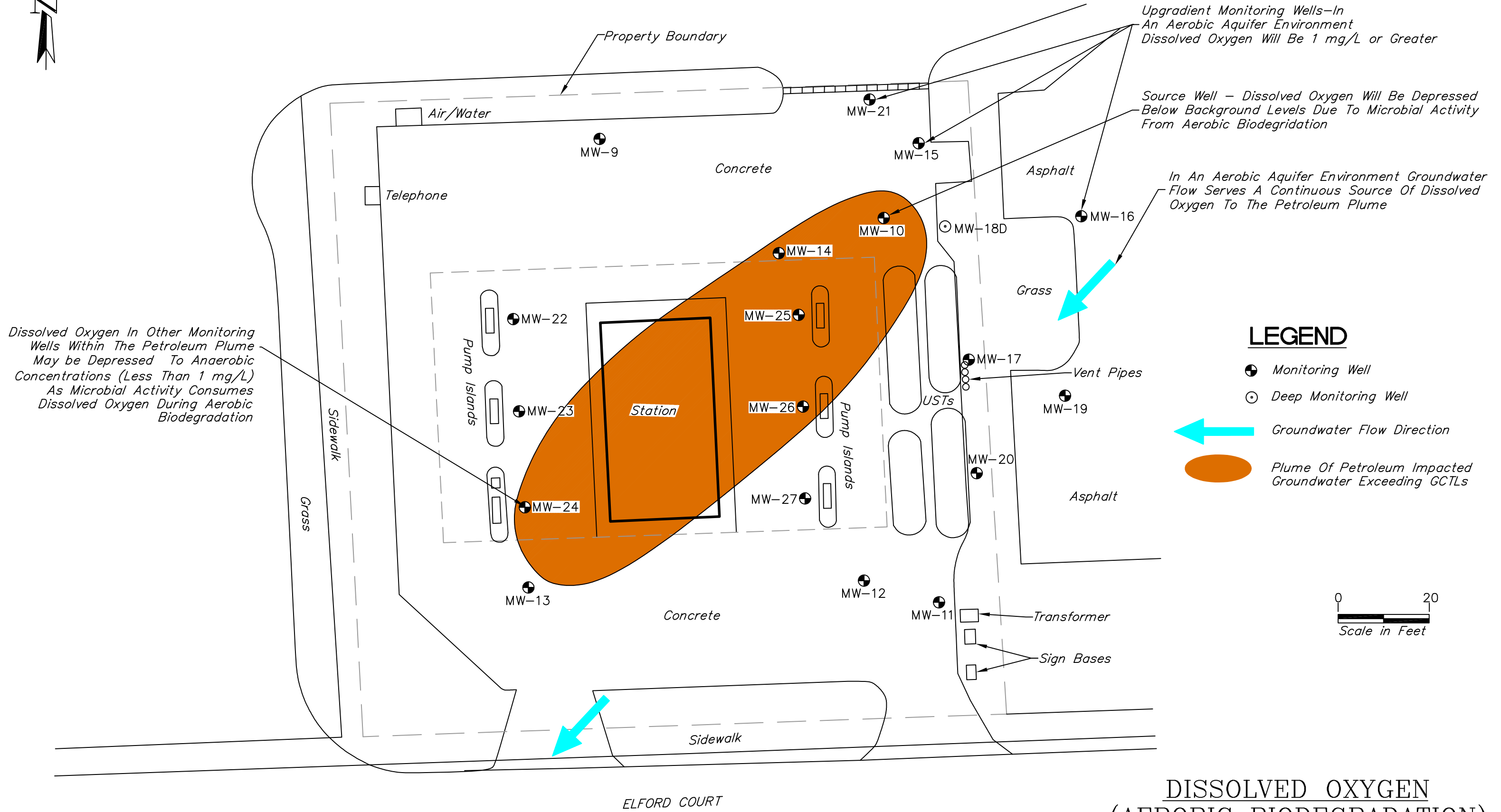
**LEGEND**

- Monitoring Well
- ⊙ Deep Monitoring Well
- ← Groundwater Flow Direction
- Plume Of Petroleum Impacted Groundwater Exceeding GCTLs



**MONITORING WELL  
LOCATIONS**  
AARON'S DODGE & DATSUN  
1160 ELFORD COURT  
DELRAY BEACH, FLORIDA

FIGURE 3



Upgradient Monitoring Wells—In An Aerobic Aquifer Environment Dissolved Oxygen Will Be 1 mg/L or Greater

Source Well — Dissolved Oxygen Will Be Depressed Below Background Levels Due To Microbial Activity From Aerobic Biodegradation

In An Aerobic Aquifer Environment Groundwater Flow Serves A Continuous Source Of Dissolved Oxygen To The Petroleum Plume

Dissolved Oxygen In Other Monitoring Wells Within The Petroleum Plume May be Depressed To Anaerobic Concentrations (Less Than 1 mg/L) As Microbial Activity Consumes Dissolved Oxygen During Aerobic Biodegradation

**LEGEND**

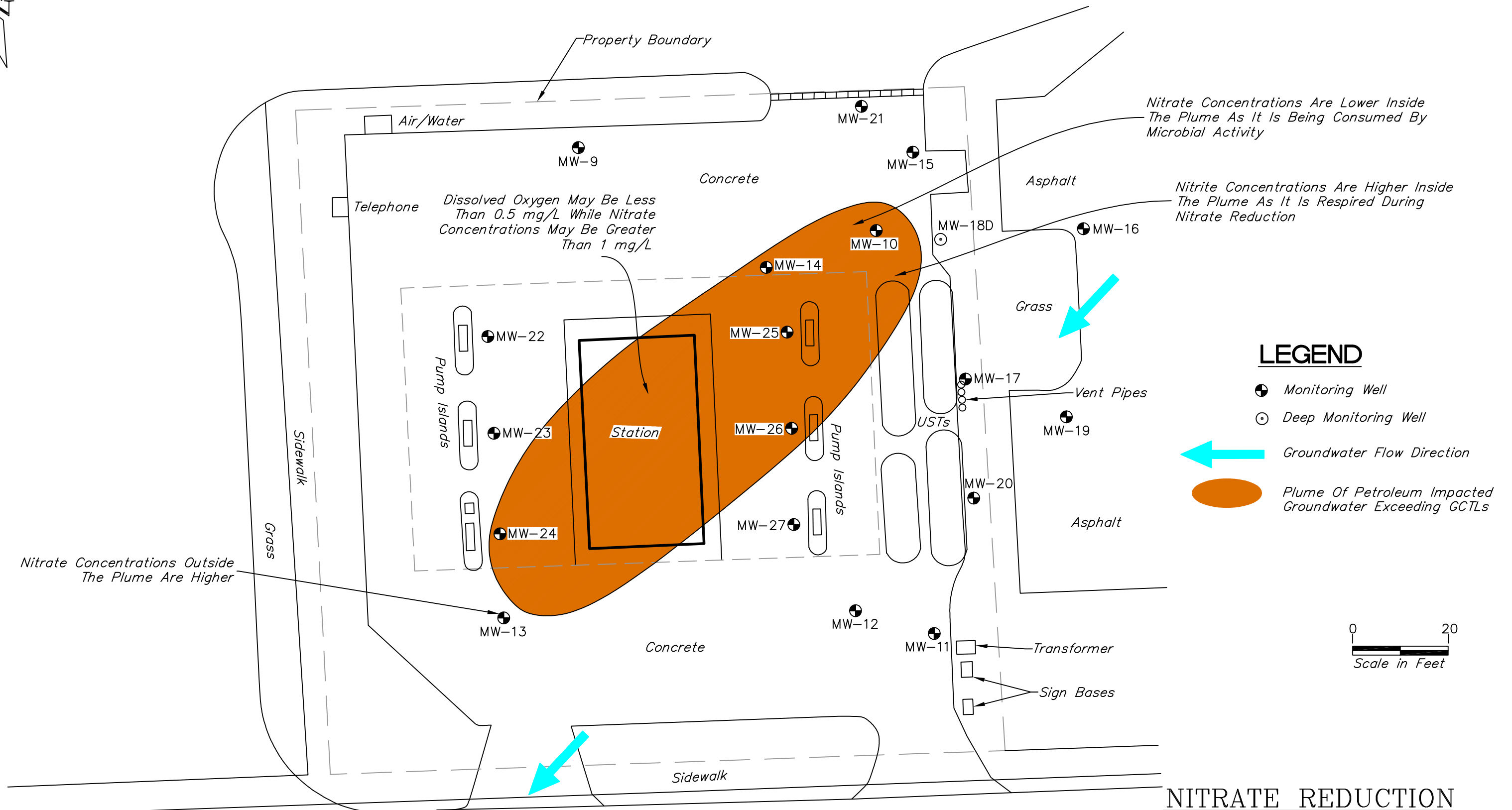
- Monitoring Well
- ⊙ Deep Monitoring Well

- ← Groundwater Flow Direction
- Plume Of Petroleum Impacted Groundwater Exceeding GCTLs

**DISSOLVED OXYGEN  
(AEROBIC BIODEGRADATION)**

AARON'S DODGE & DATSUN  
1160 ELFORD COURT  
DELRAY BEACH, FLORIDA

FIGURE 4



**LEGEND**

- Monitoring Well
- ⊙ Deep Monitoring Well

← Groundwater Flow Direction

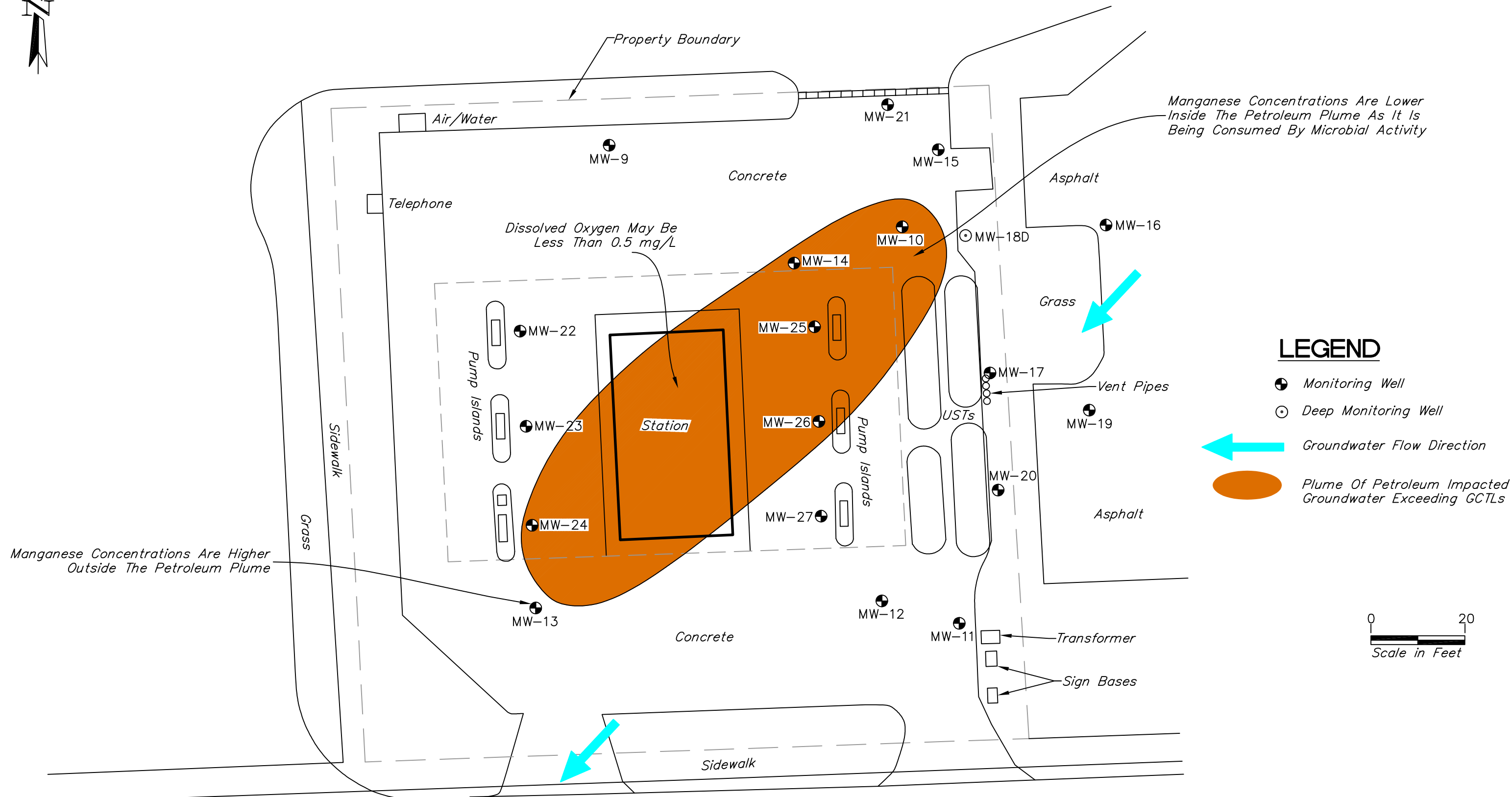
● Plume Of Petroleum Impacted Groundwater Exceeding GCTLs



**NITRATE REDUCTION  
"DENITRIFICATION"  
(ANAEROBIC BIODEGRADATION)**

AARON'S DODGE & DATSUN  
1160 ELFORD COURT  
DELRAY BEACH, FLORIDA

FIGURE 5



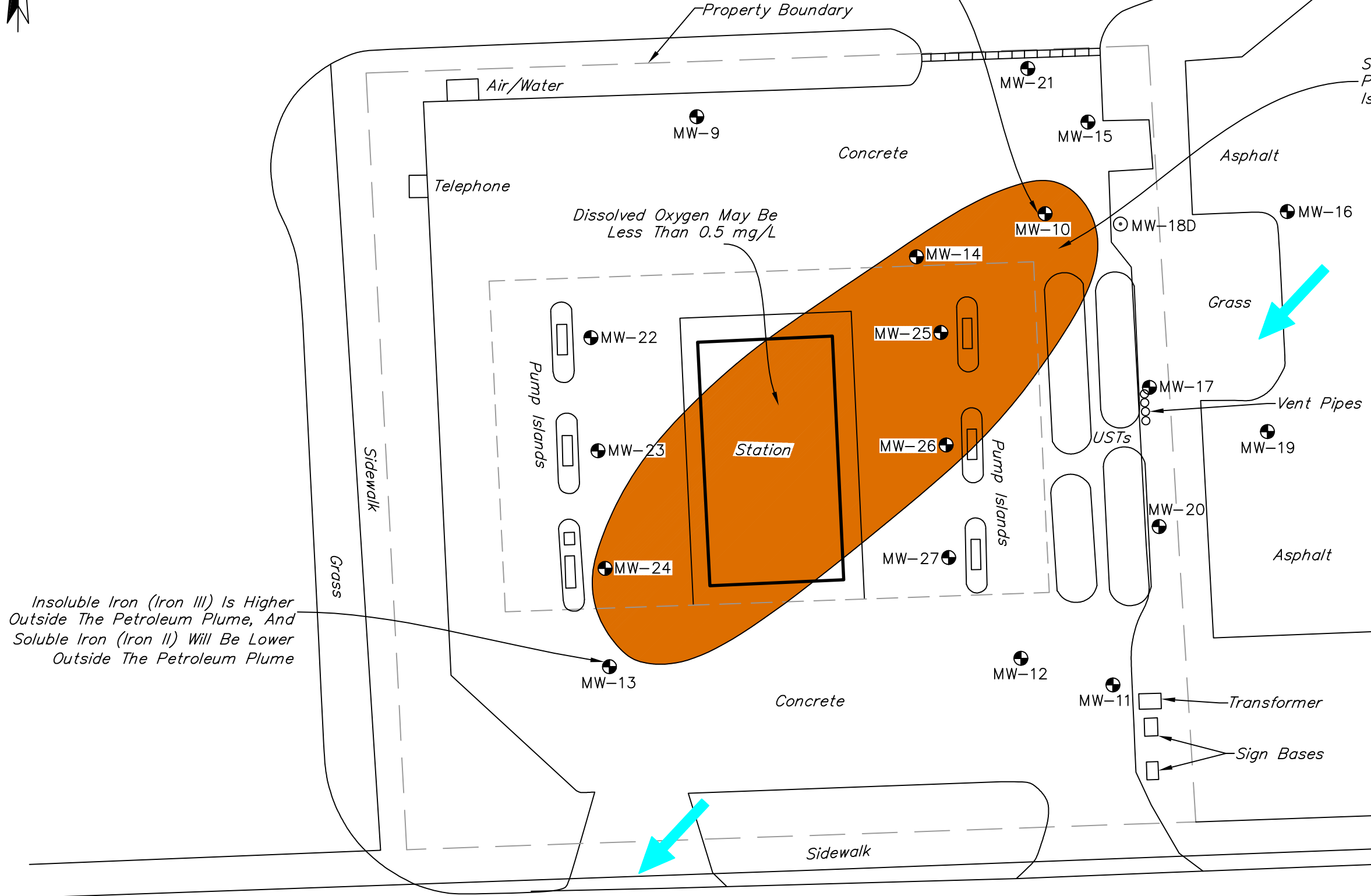
**MANGANESE REDUCTION  
(ANAEROBIC BIODEGRADATION)**  
 AARON'S DODGE & DATSUN  
 1160 ELFORD COURT  
 DELRAY BEACH, FLORIDA

FIGURE 6



*Insoluble Iron (Iron III) Is Lower Inside The Petroleum Plume As It Is Being Consumed By Microbial Activity*

*Soluble Iron (Iron II) Is Higher Inside The Petroleum Plume As Insoluble Iron (Iron III) Is Being Reduced*



*Insoluble Iron (Iron III) Is Higher Outside The Petroleum Plume, And Soluble Iron (Iron II) Will Be Lower Outside The Petroleum Plume*

**LEGEND**

- Monitoring Well
- ⊙ Deep Monitoring Well

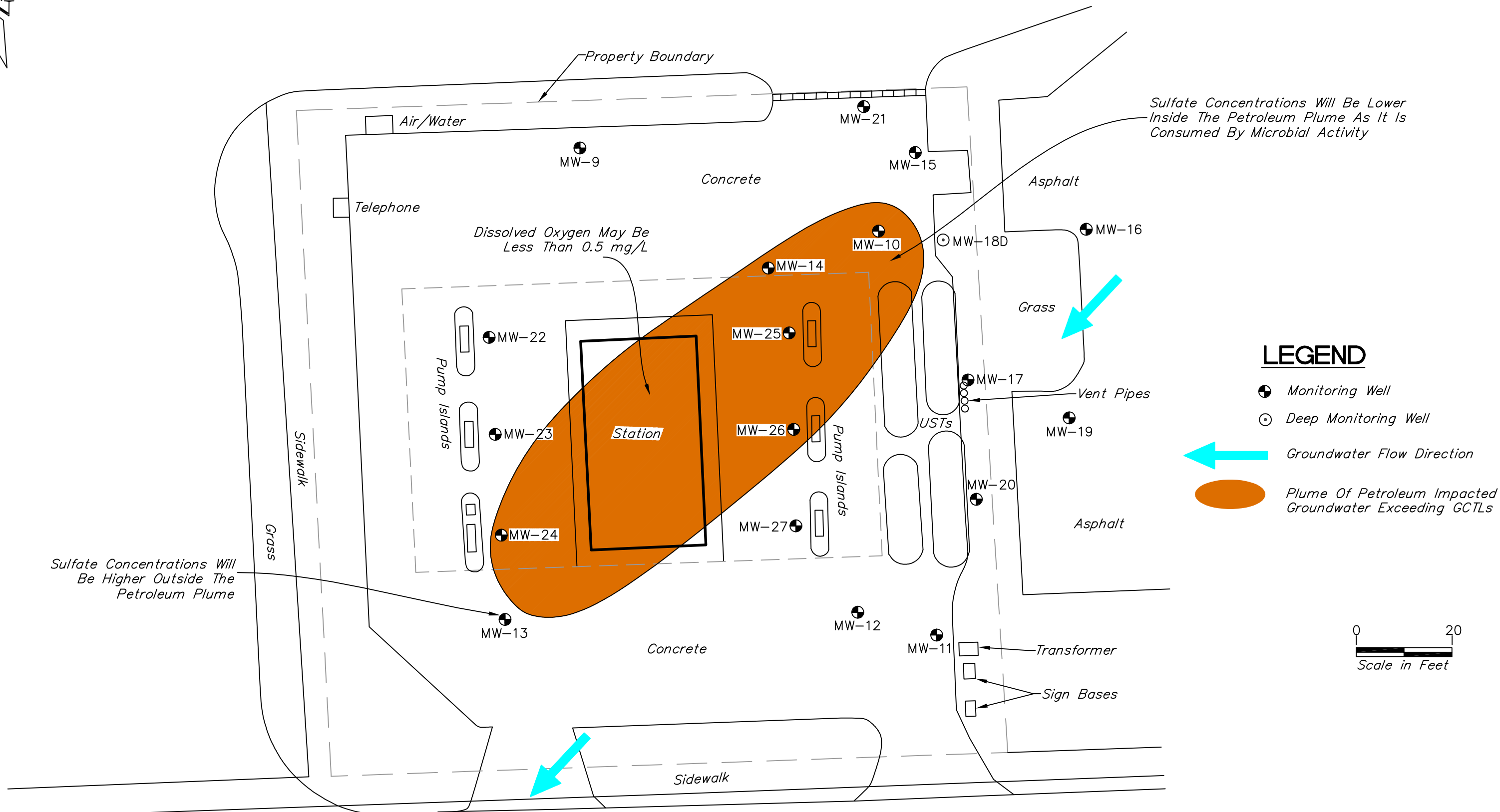
- ← Groundwater Flow Direction
- Plume Of Petroleum Impacted Groundwater Exceeding GCTLs



**IRON REDUCTION  
(ANAEROBIC BIODEGRADATION)**

AARON'S DODGE & DATSUN  
1160 ELFORD COURT  
DELRAY BEACH, FLORIDA





**LEGEND**

- Monitoring Well
- ⊙ Deep Monitoring Well

- ← Groundwater Flow Direction
- Plume Of Petroleum Impacted Groundwater Exceeding GCTLs

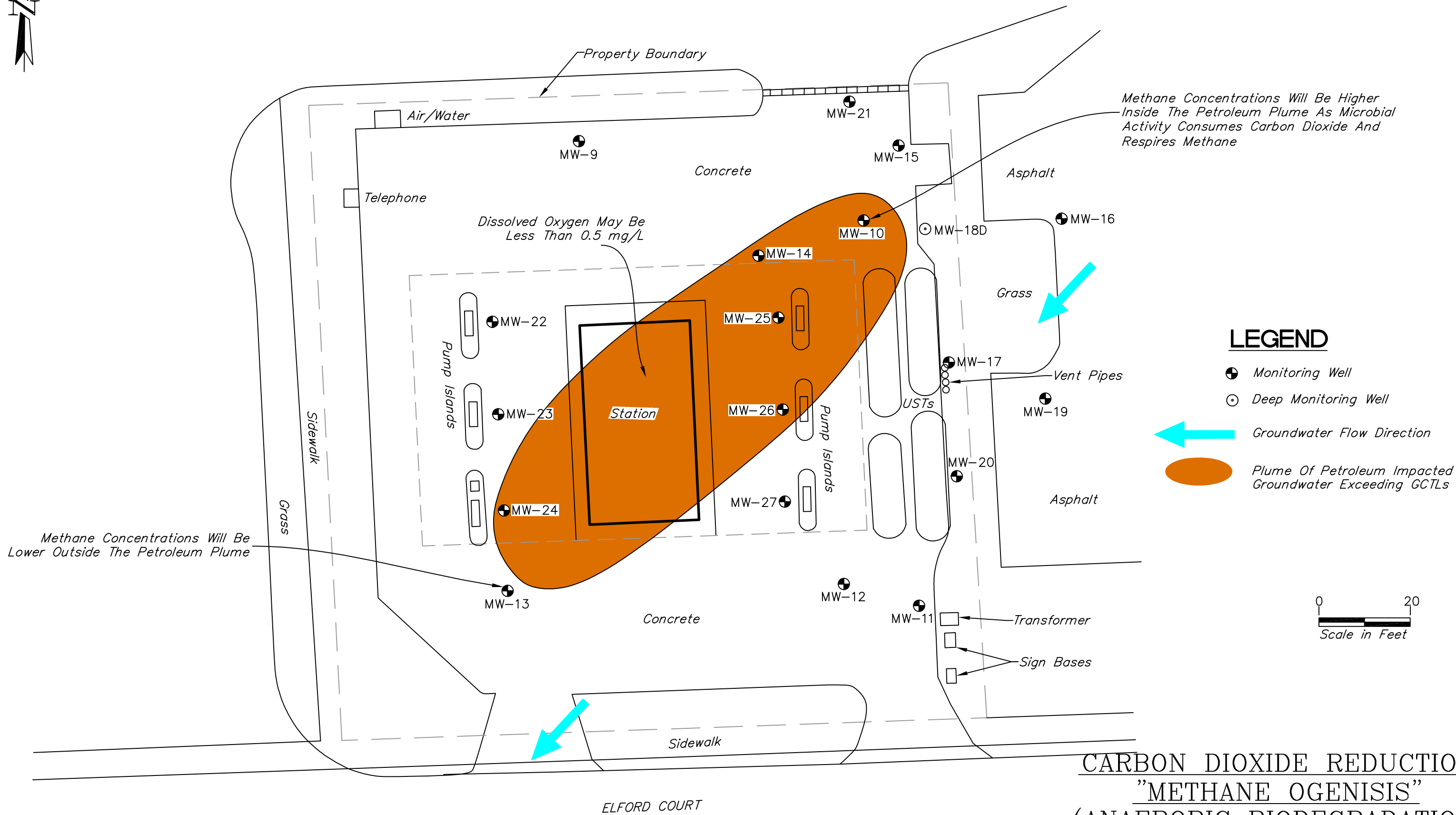


**SULFATE REDUCTION  
(ANAEROBIC BIODEGRADATION)**

AARON'S DODGE & DATSUN  
1160 ELFORD COURT  
DELRAY BEACH, FLORIDA



FIGURE 8



**CARBON DIOXIDE REDUCTION  
"METHANE OGENESIS"  
(ANAEROBIC BIODEGRADATION)**

AARON'S DODGE & DATSUN  
1160 ELFORD COURT  
DELRAY BEACH, FLORIDA