EnviroTrac
Environmental Services

January 21, 2019

Ms. Ainura Doronova
New York State Department of Environmental Conservation
Division of Environmental Remediation
Remediation Section B
Hunters Point Plaza
47-40 21st Street
Long Island City, NY 11101

Re: **Injection Well Installation/Injection Work Plan**
Speedway #7822
401 West 207th Street
New York, NY
NYSDEC Spill # 02-01957

Dear Ms. Doronova:

On behalf of Speedway LLC (Speedway), EnviroTrac Ltd. (EnviroTrac) is submitting this Injection Well Installation/Injection Work Plan to the New York State Department of Environmental Conservation (NYSDEC) for the above-referenced Site. Enclosed as **Figure 1** is an aerial photograph of the Site and enclosed as **Figure 2** is a Site Plan.

The purpose of this Work Plan is to remediate four (4) localized areas of groundwater impact that remain. The plan is to complete five (5) soil borings and install five (5) injection wells to be utilized for the application of BioSolve® Pinkwater® and/or RegenOx. The proposed injection well locations were determined based on the presence of dissolved phase hydrocarbons in the existing monitoring well network. Enclosed as **Table 1** is a Groundwater Gauging and Analytical Data Table and enclosed as **Table 2** is a Summary of Groundwater Sampling Data Table for the VOC STARs List. Enclosed as **Figure 3** is a Water-Table Elevation on November 20, 2018 and Total BTEX/MTBE Concentrations Map.

Well Installations

A review of the historical boring logs indicates that the subsurface lithology consists of medium grained sands and gravels with interbedded clay lenses to a depth of approximately 10 feet below grade surface (bgs). From 10 feet to 20 feet bgs, the lithology consists mainly of silts and sand with cobbles and gravels. Depth to groundwater on-site in November 2018 ranged from 8.17 to 10.41 bgs. Groundwater flow is predominantly towards the east.

Two (2) injection wells will be installed in front of the station building west (up-gradient) of MW-2, one (1) injection well will be installed to the west of MW-4, one (1) injection well will be installed to the west of MW-12 and one (1) injection well will be installed to the west of SVE-4. **Figure 3** includes the proposed well locations. The initial six (6) feet of each borehole will be precleared to reduce the potential for damage to underground utilities. The borings will then be advanced utilizing a hollow stem auger drill rig. Soil from the borings will be screened in the field for volatile organic compounds (VOCs) using a photo-ionization detector (PID). PID readings, soil lithology, and well construction details will be recorded in well logs.

The boreholes will be advanced to a total depth of 20 feet below grade. The injection wells will be constructed of 4-inch diameter, schedule 40 PVC with a fifteen (15) foot 20-slot screened zone and a five (5) foot PVC riser. The annulus will be backfilled with #2 Morie Sand to at least one (1) foot above the screen zone. A two (2) foot layer of bentonite will be placed above the sand and then the remaining borehole will be backfilled with a concrete/bentonite slurry to near grade. The injection wells will be developed after completion.

For this work plan, either PetroCleanze™ or an equivalent product will be used to treat the dissolved phase hydrocarbons.

PetroCleanze™ Product Information

According to Regenesis, PetroCleanze™ is designed for use in conjunction with physical and/or mechanical enhanced recovery systems. PetroCleanze™ is an advanced chemical oxidation technology that destroys contaminants through powerful, yet controlled chemical reactions and not through biological means as part of a two-part integrated system comprised of standard RegenOx™ Part A and PetroCleanze™. A PetroCleanze™ application will remove significant amounts of contamination from the subsurface and is typically applied using direct-injection techniques. The product maximizes in-situ performance while using a silicate-based surface catalyst with a slow-release percarbonate-based peroxide source. PetroCleanze™ is an alkaline surface catalyst system composed of silicic acid, ferrous sulfate, sodium hydroxide and sodium tripolyphosphate that is applied with RegenOx™ Part A as an oxidizer powder, which is composed of sodium per carbonate, sodium carbonate, sodium silicate, and sodium silica gel. When the two parts are mixed together with water and applied to the subsurface under pressure it is expected to react with dissolved phase organic materials in the subsurface, including dissolved phase hydrocarbons. Once in the subsurface, PetroCleanze™ targets sorbed-mass and residual non-aqueous phase liquid (NAPL), bringing each into the recoverable phase from where they may then be extracted. The desorption of contaminants by PetroCleanze™ is driven by action as a wetting agent. It promotes the release and mobility of NAPL and the creation of temporary alkaline conditions, which facilitates desorption and leads to the formation of more soluble species from the target compounds. The reagent is entirely inorganic; it presents no biological oxygen demand (BOD) and in fact releases oxygen. It does not inhibit follow-on biologic activity, and may arguably stimulate it. PetroCleanze™ exhibits good compatibility with the majority of subsurface services and infrastructure and therefore may be widely used in complex source areas including those where buildings, services and structures may restrict the potential for excavation. PetroCleanze™ produces minimal heat and is highly compatible with followed up enhanced bioremediation applications. The Regenesis PetroCleanze™ White Paper is enclosed.

Proposed In-Situ Application

EnviroTrac proposes injecting approximately 40 pounds of PetroCleanze™ and 40 pounds of RegenOx™ Part A into each injection location. Limiting factors such as the formation's ability to accept the injected slurry mix may change the actual amount of product that is injected.

The application process will involve the combination of the two part product and water into a slurry mixture and then pressure injecting the slurry into the zone of contamination through injection wells and out into the aquifer media.

Prior to the initial injection of PetroCleanze™, The injection wells will be sampled for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) as per the NYSDEC CP-51 List of compounds (former STARS List) to establish a baseline. Additionally, a geochemical baseline will be established by measuring dissolved oxygen (DO) and temperature in the injection wells and adjacent monitoring wells.

EnviroTrac will return to the Site approximately one (1) week after each injection event to gauge the wells to confirm if any free phase product has been released. EnviroTrac will then return to the Site within two (2) weeks after the gauging event with a vacuum truck to conduct an enhanced fluid recovery (EFR) event to recover the PetroCleanze™ and any potential free phase product and/or dissolved petroleum hydrocarbons that may have been freed from the soil by the surfactant component. Select wells will be sampled prior to the EFR event to observe any changes in the baseline VOC and/or SVOC concentrations. After two (2) to three (3) weeks of contact time, it is expected that the surfactant component will release sorb-mass and an increase in VOC and/or SVOC concentrations may confirm its effectiveness.

Approximately, five (5) to six (6) weeks after the EFR event is completed, the next injection event will be be completed. The scope will be the same as the initial event. The results of the groundwater sampling will determine if the next injection event will follow with the same PetroCleanze™ application or if there is believed to be no free phase product or significant smear zone remaining, then RegenOx™ may be utilized to treat the residual dissolved petroleum.

Following approval of this plan by the NYSDEC, Speedway will execute the following implementation schedule:

Action Item	Duration (Days)
NYSDEC approval of Work Plan	-
Injection well installations	Within 60 days from above
Preliminary limited baseline groundwater gauging/sampling event. Perform initial PetroCleanze™ injection event.	Within 45 days from above
Gauging event (to assess for free phase product)	Within 7 days from above

Routine EFR event (with limited sampling)	Within 2 weeks from above
Perform second PetroCleanze™ injection event	5 to 6 weeks after EFR event

Reporting

A summary of the well installations and remedial events will be documented in the routine Quarterly Update Reports. Speedway/EnviroTrac will notify the NYSDEC if any significant changes occur between reporting periods.

If you have any questions or need additional information, please do not hesitate to contact me at 631.924.3001.

Sincerely,

Ed Russo
Senior Project Manager

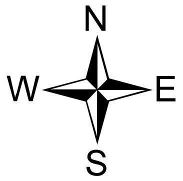
Enclosures

AERIAL PHOTOGRAPH

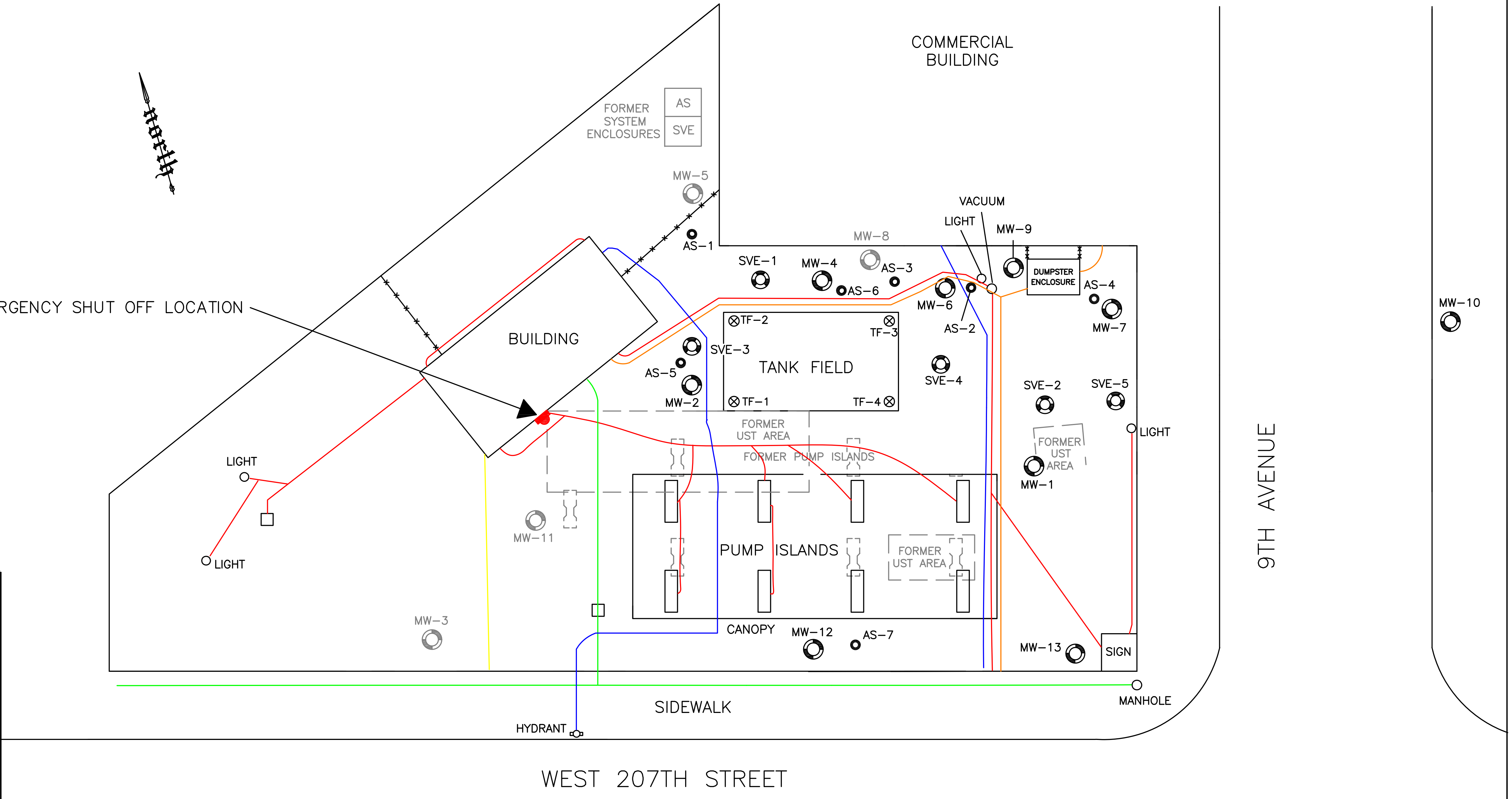
Figure 1
Aerial Photograph

Speedway #7822 (Hess **#**32517**)**
401 W. 207th St.
Inwood, NY

Digital Imagery taken in 2010



EnviroTrac
Environmental Services
5 Old Dock Road
Yaphank, NY 11980
P: 631-924-3001 F:631-924-5001



LEGEND:

- ◎ MONITORING WELL
- ◎ ABANDONED MONITORING WELL
- ◎ AS/SVE CLUSTER WELL
- ○ AIR SPARGE WELL
- ⊗ TANK FIELD WELL
- ⌜ ⌝ = FORMER SITE FEATURE
- 🟥 ELECTRIC
- 🟨 GAS
- 🟦 WATER
- 🟩 SEWER
- 🟧 TELEPHONE / TELECOMMUNICATIONS

EnviroTrac
ENVIRONMENTAL SERVICES
5 OLD DOCK ROAD, YAPHANK, NY 11980
PHONE: (631)924–3001 FAX: (631)924–5001

0 15 FT. 30

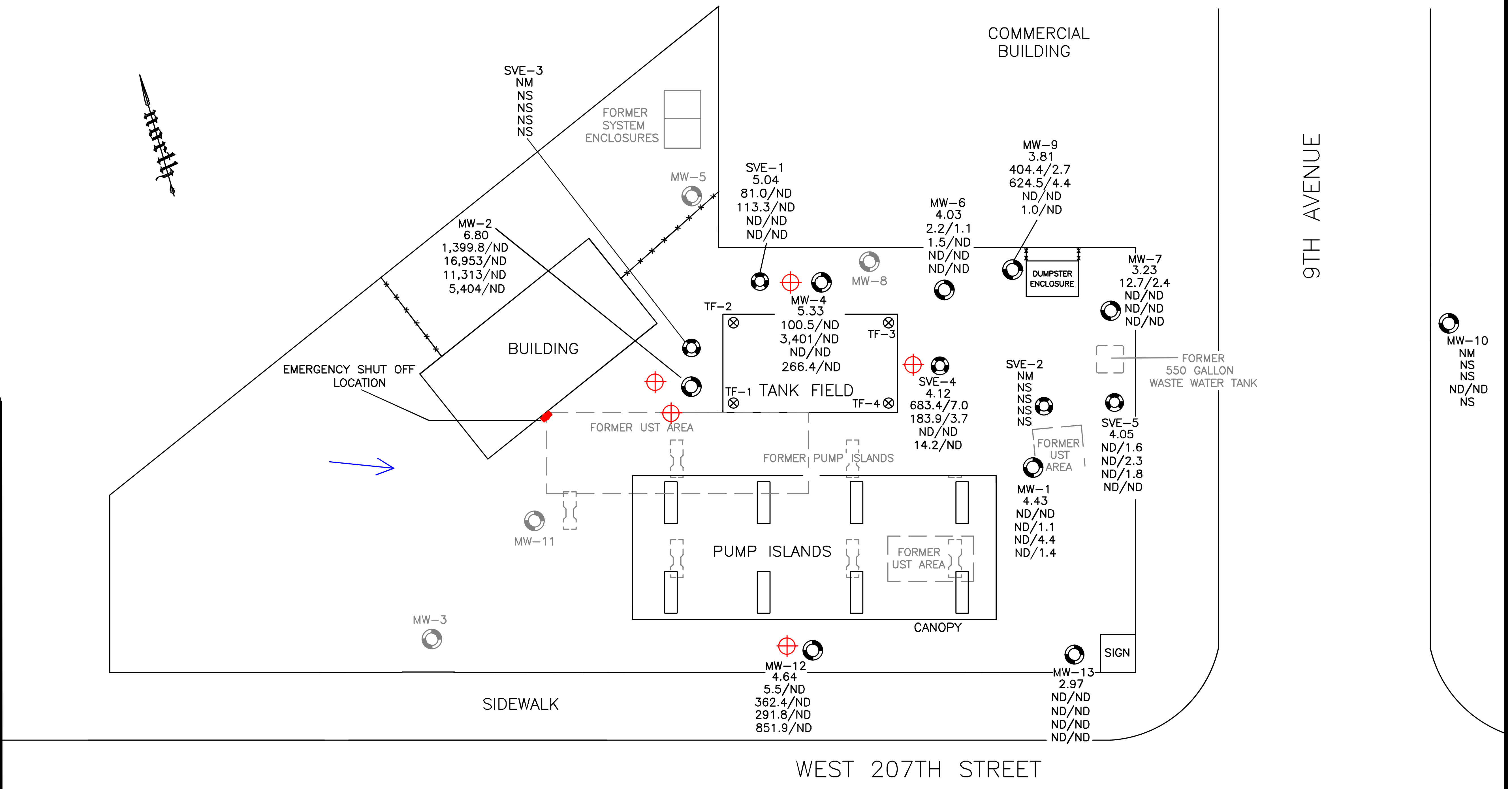
REVISION DATE:	SCALE:	REVISED BY: TB
AUGUST 10, 2018	1" = 30 FEET	

Speedway

SPEEDWAY # 7822
401 W. 207th STREET
NEW YORK, NEW YORK

SITE PLAN

FIGURE #
2



LEGEND:

◎ MONITORING WELL
◎ ABANDONED WELL
◎ AS/SVE CLUSTER WELL
⊕ PROPOSED SOIL BORING/INJECTION WELLL
⊗ TANK FIELD WELL
⌜ ⌝ = FORMER SITE FEATURE

SVE = SOIL VAPOR EXTRACTION
NSVD = NOT SURVEYED
NS = NOT SAMPLED
NM = NOT MEASURED
J = ESTIMATED VALUE
ND = NOT DETECTED
NA = NOT ACCESSIBLE

→ INFERRED GROUNDWATER FLOW DIRECTION

SAMPLE WELL:

◎ MW–1 = WELL ID
4.43 = WATER–TABLE ELEVATION

ND/ND = FEBRUARY 8, 2018
ND/1.1 = MAY 31, 2018
ND/4.4 = AUGUST 27, 2018
ND/1.4 = NOVEMBER 20, 2018
BTEX/MTBE RESULTS IN ug/L

EnviroTrac
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5 OLD DOCK ROAD, YAPHANK, NY 11980
PHONE: (631)924–3001 FAX: (631)924–5001

0 15 FT. 30

REVISION DATE: JANUARY 7, 2019
SCALE: 1" = 30 FEET
REVISED BY: TB

Speedway

SPEEDWAY # 7822
401 W. 207th STREET
NEW YORK, NY

WATER–TABLE ELEVATION ON NOVEMBER 20, 2018 AND TOTAL DISSOLVED BTEX/MTBE CONCENTRATION MAP

FIGURE #
3

Table 1
Groundwater Gauging and Analytical Data
401 West 207th Street
New York, NY

Well ID (Screen Zone)	Date	Top of Casing (feet)	Depth to Water (feet)	Depth to Product (fbg)	Product Thickness (feet)	Relative GW Elevation (feet)	Dissolved Oxygen (mg/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Total Xylenes (ug/L)	Total BTEX (ug/L)	MTBE (ug/L)
MW-1 (3-23')	2/8/2018	13.21	11.23			1.98	1.43	ND	ND	ND	ND	ND	ND
	5/31/2018	13.21	10.03			3.18	1.06	ND	ND	ND	ND	ND	1.1
	8/27/2018	13.21	9.58			3.63	0.96	ND	ND	ND	ND	ND	4.4
	11/20/2018	13.21	8.78			4.43	0.60	ND	ND	ND	ND	ND	1.4
MW-2 (2-20')	2/8/2018	14.97	10.37			4.60	0.76	854	88.4	36.4	421	1,399.8	ND
	5/31/2018	14.97	9.42			5.55	0.81	2,840	7,910	673	5,530	16,953	ND
	8/27/2018	14.97	9.36			5.61	0.84	3,060	2,630	783	4,840	11,313	ND
	11/20/2018	14.97	8.17			6.80	0.59	579	1,190	155	3,480	5,404	ND
MW-4 (2-20')	2/8/2018	14.80	10.72			4.08	0.84	8.1	25.0	5.4	62.0	100.5	ND
	5/31/2018	14.80	10.09			4.71	0.63	117	331	563	2,390	3,401	ND
	8/27/2018	14.80	10.00			4.80	0.72	ND	ND	ND	ND	ND	ND
	11/20/2018	14.80	9.47			5.33	1.32	14.9	29.9	18.6	203	266.4	ND
MW-6 (3-16')	2/8/2018	13.90	12.42			1.48	1.21	2.2	ND	ND	ND	2.2	1.1
	5/31/2018	13.90	10.55			3.35	3.68	1.5	ND	ND	ND	1.5	ND
	8/27/2018	13.90	10.22			3.68	2.24	ND	ND	ND	ND	ND	ND
	11/20/2018	13.90	9.87			4.03	3.63	ND	ND	ND	ND	ND	ND
MW-7 (4-19')	2/8/2018	12.96	11.88			1.08	0.91	ND	ND	ND	12.7	12.7	2.4
	5/31/2018	12.96	10.84			2.12	4.22	ND	ND	ND	ND	ND	ND
	8/27/2018	12.96	10.46			2.50	3.66	ND	ND	ND	ND	ND	ND
	11/20/2018	12.96	9.96			3.00	3.23	ND	ND	ND	ND	ND	ND
MW-9 (3.5-18.5')	2/8/2018	14.22	12.17			2.05	1.16	377	7.2	2.2	18.0	404.4	2.7
	5/31/2018	14.22	11.25			2.97	1.16	517	16.5	21.4	69.6	624.5	4.4
	8/27/2018	14.22	10.98			3.24	1.05	ND	ND	ND	ND	ND	ND
	11/20/2018	14.22	10.41			3.81	3.08	1.0	ND	ND	ND	1.0	ND
MW-10 (3-18')	2/8/2018	NSVD	NM			NM	NM	NS	NS	NS	NS	NS	NS
	5/31/2018	NSVD	NM			NM	NM	NS	NS	NS	NS	NS	NS
	8/27/2018	NSVD	11.21			NM	0.58	ND	ND	ND	ND	ND	ND
	11/20/2018	NSVD	NA			NM	NM	NS	NS	NS	NS	NS	NS
MW-12 (6-21')	2/8/2018	13.77	11.87			1.90	1.86	1.5	ND	ND	4.0	5.5	ND
	5/31/2018	13.77	10.54			3.23	0.61	11.4	2.0	184	165	362.4	ND
	8/27/2018	13.77	10.08			3.69	0.98	11.5	1.3	159	120	291.8	ND
	11/20/2018	13.77	9.13			4.64	0.66	12.6	1.3	437	401	851.9	1.1
MW-13 (5-20')	2/8/2018	12.29	9.72			2.57	1.31	ND	ND	ND	ND	ND	ND
	5/31/2018	12.29	8.88			3.41	3.70	ND	ND	ND	ND	ND	ND
	8/27/2018	12.29	8.47			3.82	2.92	ND	ND	ND	ND	ND	ND
	11/20/2018	12.29	9.32			2.97	0.50	ND	ND	ND	ND	ND	ND
SVE-1 (2-15')	2/8/2018	15.04	10.78			4.26	1.02	75.8	1.8	ND	3.4	81.0	ND
	5/31/2018	15.04	10.55			4.49	0.70	111	2.3	ND	ND	113.3	ND
	8/27/2018	15.04	10.35			4.69	0.90	ND	ND	ND	ND	ND	ND
	11/20/2018	15.04	10.00			5.04	2.22	ND	ND	ND	ND	ND	ND
SVE-4 (1.5-16.5')	2/8/2018	13.67	11.50			2.17	1.72	643	12.7	2.5	25.2	683.4	7.0
	5/31/2018	13.67	10.81			2.86	0.76	161	6.3	4.8	11.8	183.9	3.7
	8/27/2018	13.67	10.43			3.24	1.11	ND	ND	ND	ND	ND	ND
	11/20/2018	13.67	9.55			4.12	0.68	6.4	ND	4.4	3.4	14.2	ND
SVE-5 (1.5-16.5')	2/8/2018	12.34	10.56			1.78	1.08	ND	ND	ND	ND	ND	1.6
	5/31/2018	12.34	9.59			2.75	1.24	ND	ND	ND	ND	ND	2.3
	8/27/2018	12.34	9.12			3.22	1.20	ND	ND	ND	ND	ND	1.8
	11/20/2018	12.34	8.29			4.05	0.81	ND	ND	ND	ND	ND	ND

Notes:

NA - Not Accessible
ND - Not Detected
NM - Not Measured
NS - Not Sampled

Table 2
Summary of Groundwater Sampling Data for VOC STARs List
Speedway # 7822
401 W. 207th Street
New York, NY

Well ID	Date	Benzene (1)	n-Butylbenzene (5)	sec-Butylbenzene (5)	tert-Butylbenzene (5)	Ethylbenzene (5)	Isopropyl benzene (5)	p-Isopropyltoluene (5)	Methyl Tert Butyl Ether (10)	Naphthalene (10)	n-Propylbenzene (5)	Toluene (5)	1,2,4-Trimethyl benzene (5)	1,3,5-Trimethyl benzene (5)	m,p-Xylene	o-Xylene	Total Xylene (5)	Total VOCs
MW-1	**8/27/2018**	ND	ND	ND	ND	ND	1.7	ND	4.4	ND	1.3	ND	ND	ND	ND	ND	ND	7.4
	11/20/2018	ND	ND	ND	ND	ND	ND	ND	1.4	2.6	ND	ND	ND	ND	ND	ND	ND	4.0
MW-2	**8/27/2018**	**3,060**	**26.1**	**9.4**	ND	**783**	**42.7**	**9.0**	ND	**101**	**78.3**	**2,630**	**1,320**	**333**	**3,660**	**1,180**	**4,840**	13,233.5
	11/20/2018	**579**	**22.5**	4.1	ND	**155**	**9.8**	**7.7**	ND	**80.8**	**11.8**	**1,190**	**999**	**311**	**2,530**	**950**	**3,480**	6,850.7
MW-4	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	14.9	6.6	4.0	ND	**18.6**	**16.5**	1.5	ND	**54.9**	**32.7**	29.9	**330**	40.2	184	18.7	203	752.8
MW-6	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MW-7	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MW-9	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	1.0	ND	ND	ND	ND	ND	ND	ND	1.5	ND	ND	ND	ND	ND	ND	ND	2.5
MW-10	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
MW-12	**8/27/2018**	**11.5**	**28.7**	**20.8**	ND	**159**	**168**	**5.7**	ND	**243**	**444**	1.3	**128**	**94.6**	**119**	1.3	**120**	1,424.6
	11/20/2018	**12.6**	**18.5**	**10.9**	ND	**437**	**91.8**	3.8	1.1	**293**	**221**	1.3	**493**	**149**	**399**	2.4	**401**	2,134.0
MW-13	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
SVE-1	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
SVE-4	**8/27/2018**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	11/20/2018	**6.4**	1.1	ND	ND	4.4	4.8	ND	ND	**6.3**	**10.8**	ND	**14.2**	4.0	2.0	1.4	3.4	55.4
SVE-5	**8/27/2018**	ND	ND	ND	ND	ND	1.0	ND	1.8	ND	ND	ND	ND	ND	ND	ND	ND	2.8
	11/20/2018	ND	ND	ND	ND	ND	ND	ND	ND	1.8	ND	ND	ND	ND	ND	ND	ND	1.8

Notes:

Concentration units = µg/L (micrograms per Liter)
Laboratory analyses via EPA Method 8260 STARs List
ND = Not Detected
NS = Not Sampled
NYSDEC Groundwater Standards are listed in parentheses
Bold values indicate an exceedance of the NYSDEC Groundwater Standards

REGENESIS

Petroleum Hydrocarbon Mass Removal using Reagent Based Enhanced Desorption Combined with Physical Recovery Techniques

***Ph.D Jeremy Birnstingl* [1], *Ph.D Alberto Leombruni* [2], *Ph.D Ben Mork*[3]**

1 Vice President – Environmental Technology, Regenesis, Ph.D 1997 at University of Lancaster (Presenting Author)
2 Engineering Scientist Regenesis Ltd, PhD 2011 at Polimi (IT) – MIT (US)
3 Vice President –Research and Development, Regenesis, PhD at University of California-Berkeley (US)

Keywords: Integrated treatment – enhanced mass–recovery – practical research application – enhanced dual-phase extraction – asymptotic treatment – remediation system closure – European case studies

Objectives: Presentation of technical details, usage scenarios and real-world application experience of a reagent specifically developed to overcome performance limitations and increase the cost-effectiveness of some of the most widely used groundwater treatment approaches in Europe.

Innovative Nature: The presentation presents the science, rationale and principles underpinning the development and application of a new treatment reagent for addressing the widespread challenge of diminishing efficiency of P&T / DPE groundwater treatment systems, supported by case-study examples from full-scale projects across Europe.

Abstract: Dual-phase extraction (DPE) or pump-and-treat (P&T) systems are widely used for the remediation of high concentrations of hydrocarbon nonaqueous phase liquid (NAPL) at contaminated sites. While the initial phase of DPE system operation typically achieves rapid reduction of NAPL the long-term effectiveness diminishes and the system often reaches an asymptote. Further operation of a system in asymptote conditions would provide little incremental benefit in treating soil or groundwater contamination thus negatively impacting both project costs and time.

The leveling off of DPE effectiveness typically arises as a result of hydrocarbon distribution through zones of differential matrix permeability, the presence of slowly dissolving smeared or sorbed hydrocarbon contamination, or a combination of both of these factors. For many remediation practitioners the next logical choice for remediation when DPE operation is asymptotic is to use In Situ Chemical Oxidation (ISCO). While the use of ISCO can be successful in many instances there are still two main limitations to ISCO to treat heavy sorbed phase contamination. The first being that DPE systems are often used in low permeability sites where they achieve greater treatment radii because of the beneficial use of high vacuum flow. These very same soils may prevent efficient distribution and contact of a chemical oxidant. The second point is that while a DPE system may have reached an asymptote the corresponding soil and groundwater concentrations may still be quite high meaning that the number of injections and volume of reagent required would be costly.

The use of surfactants to enhance recovery of sorbed-phase or smeared hydrocarbon is another option, but applications are rare owing to problems of cost, pore-blockage, trapping of residual hydrocarbons by sub-CMC residual surfactant, and high residual surfactant biological oxygen demand (BOD) that inhibit follow-on biodegradation or natural / enhanced attenuation of residual hydrocarbon.

This presentation will provide information on a reagent-based approach which systematically addresses the above issues in order to increase the efficiency and expedite the closure of physical extraction-based clean-up projects (DPE, pump-and-treat, etc.). This technology is entirely inorganic and presents no BOD yet provides combined ISCO and enhanced desorption at contaminated sites to treat bound hydrocarbon and NAPL. This approach can also be used to increase efficiency at failing DPE installations for fast and cost-effective mass reduction. An overview of the results from laboratory and field studies will be presented and the potential modes of usage and anticipated benefits to common remediation projects explored.

(Submitted for oral presentation.)

Petroleum Hydrocarbon Mass Removal using Reagent Based Enhanced Desorption Combined with Physical Recovery Techniques

Background

Remediation of contaminated groundwater using extractive systems has remained the most widely employed interventive remedial approach since the birth of the contemporary remediation sector in the 1980s. The widespread use of the approach is such that it is probably safe to say that the only contaminated regions where it is *not* employed are those in which groundwater clean-up legislation either does not exist or is not enforced.

The extractive approach may include either single or multi-phase systems which may themselves be coupled to a wide range of treatment or disposal approaches ranging from granular activated carbon (GAC) to air-stripping, to direct or indirect disposal to fixed wastewater facilities to a range of other options. Notwithstanding the diversity, extractive groundwater remediation is widely referred to under the shorthand '**Pump-and-Treat**' (P&T), which epithet for convenience, will be adopted for the present paper.

Strengths and Weaknesses of P&T

P&T technologies have a number of powerful strengths, most notably their utility for contaminant mass reduction – especially at high-concentrations up to and including free-product – and for plume control (hydraulic containment). It also has the advantage, especially compared to later technologies, of being simple in concept (even if not in engineering).

However, whilst the widespread utilization of P&T may arguably be cited as testimony to its utility, the shortcomings of the technology quickly became clear following its initial uptake and have long been documented (McKay and Cherry, 1989). Principal among these are:

- Recovery frequently becomes asymptotic – diminishing efficiency
- Rebound post shut-down is common – within weeks or months
- Operation may be necessary for many years – often open-ended

Given these shortcomings, what may commence as an efficient and appropriate remediation technology selection for a given site, may over a relatively short time become increasingly inefficient and ineffectual, with the prospect of on-going operation and associated costs with negligible incremental return – the 'pump for ever trap' as it has sometimes been termed (Figure 1). Given that operational costs remain broadly static, the incremental cost of each unit mass removed increases as recoveries diminish (Figure 2).

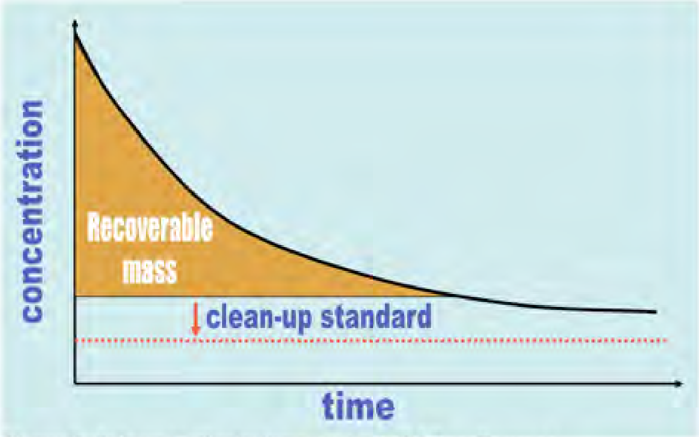

Figure 1. Schematic illustrating asymptotic P&T performance

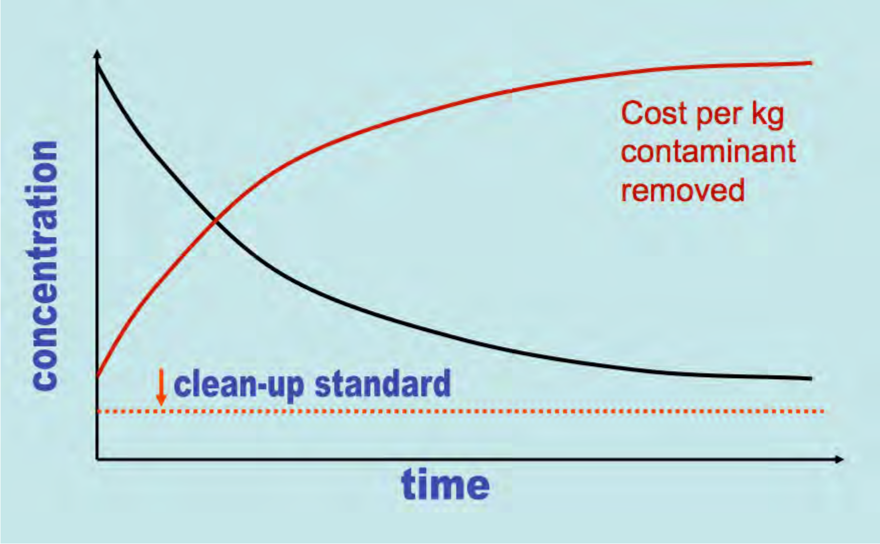

Figure 2. Schematic illustrating impact on efficiency of diminishing recoveries in a fixed-cost system. (Efficiency as cost per unit mass of contaminant removed.)

Contaminant Hydrogeology – Basis of the Problem

In essence, the aquifer-specific design variables for a P&T system relate solely to extraction rate and extraction location, the vertical and horizontal placement of extraction points and their spacing. Beyond these factors, systems will differ only in engineering quality, post-extraction treatment mechanism, and monitoring, communication and control capabilities. However, the principal challenges to P&T have their basis in contaminant hydrogeology rather than the engineering of the systems, irrespective of the growing complexity and sophistication of the latter.

P&T performance and efficiency – of even a well-engineered system – will be governed by the distribution within the aquifer of **recoverable vs. non-recoverable contaminant mass**. Specifically, the mass of a target groundwater-contaminant within an aquifer will comprise:

- **Mobile mass** – (recoverable). Dissolved-phase and non-aqueous-phase liquid (NAPL) contamination within the *mobile porosity*.

- **Sorbed mass** – (non-recoverable). Contamination partitioned onto sorption sites plus trapped NAPL / smear within the aquifer matrix that may *slowly* equilibrate with the dissolved-phase. A source of performance tailing / rebound.

- **Mass in low-permeability zones** – (non-recoverable). Mass diffused into the *immobile porosity* that may *slowly* equilibrate with the mobile porosity. A source of performance tailing / rebound.

The high initial efficiency of a P&T system therefore relates to its capacity to rapidly recover mobile mass. However, once this mass has been removed, contaminant extraction rate is governed by the relatively slow dissolution and desorption rates of NAPL and sorbed-mass, and the diminishingly slow diffusion of mass from the immobile porosity. Adjustments in rate or placement of abstraction will have negligible effect on these – they are largely independent of the system's engineering capacity.

The characteristic outcome is therefore a fast initial mass recovery followed by diminishing returns and eventually an asymptotic, long-term tailing. This may be followed by a slow increase in concentration ('rebound') should the system ever be switched off as a result of slow concentration equilibration between mobile, immobile and sorbed / NAPL phases.

Addressing the Problem

For the most part, continued operation of P&T systems beyond the point of optimal efficiency remains the norm. The reasons for this are manifold, but can include the nature of the contractual model, inflexibility or cost of change of the permitting arrangement or in some cases a paucity of cross-discipline engineering skills. Coupled with this can simply be the erroneous perception that changing technology implies a technical failure rather than a recognition that each technology has its principal strengths which may be leveraged to greatest efficiency as part of a treatment train rather than employ the technology as standalone approach beyond it's niche of efficiency irrespective of the changing conditions it has itself brought about as remediation proceeds. That said, with respect to P&T specifically, the principal enhancement approaches that have been explored may broadly be encapsulated within two principal categories. These are:

- **Thermal Enhancement** – the raising of the ambient aquifer temperature by a variety of means to increase contaminant solublity, dissolution and diffusions rates.

- **Surfactant Enhancement** – use of surface-active agents ('surfactants') to increase the effective solubility of sorbed and NAPL contamination.

These approaches remain relatively uncommon however. **Thermally enhanced extraction**, whilst very effective in the right circumstance, requires considerable energy and thus comes with an increased price tag, which may or may not be offset by improved performance or time saved. This challenge is exacerbated on larger sites. Moreover, the approach presents issues of potential incompatibility around certain infrastructure such as tanks, buildings and services. It presently remains more commonly employed for treatment of tightly defined source zones rather than plumes, and also in the unsaturated rather than saturated zone, where in both circumstances effectiveness and net benefit are typically higher and the challenges lower.

Surfactant enhanced extraction, although explored for more than 20 years (Sabatini et al, 1995), has not experienced wide uptake across the industry. This may be attributed variously to the propensity of surfactants to clog formations and thereby limit distribution in some zones (even if enhancing recovery in others), to the challenge the surfactant itself may pose to the treatment system, and finally, to the simple cost of the surfactants added. Moreover, surfactants by their nature are only effective for recovery enhancement when present in solution above their respective critical micelle concentrations, and below this, may actually increase the binding of hydrophobic contaminant species (Edwards et al, 1994). In addition, surfactants will characteristically leave significant residues within the formation, the degradation of which presents a major biological oxygen demand (BOD) thus inhibiting the biodegradation / attenuation of the remaining hydrocarbon through competition for available oxygen / electron acceptors.

Development of a New Reagent

The present paper focuses on a new reagent for enhancing and extending the effectiveness of P&T systems. The reagent is sold under the commercial name **PetroCleanze™**, developed by Regenesis, San Clemente, CA. The product combines a silicate-based surface catalyst with a slow-release percarbonate-based peroxide source that may be applied as a liquid amendment to enhance contaminant mass recovery of petroleum hydrocarbon and other contaminants in a number of usage scenarios.

PetroCleanze targets sorbed-mass and residual NAPL, bringing each into the recoverable phase from where they may then be extracted through a variety of means. Whereas the reagent's utility extends through a range of target contaminant species including chlorinated and partially chlorinated organics, its most striking efficacy is with weathered, highly adsorbed petroleum hydrocarbons (TPH) and 'smear'.

The product's function is to **enhance recoverable mass**, enabling:

- Shorter P&T duration;
- Elimination of post P&T rebound;
- Increased removal of higher molecular weight (lower solubility) hydrocarbons;
- Removal of smear-zone;
- *In Situ* vadose zone treatment (including low vapour-pressure species inaccessible to Soil Vapour Extraction (SVE)).

The reagent is entirely inorganic – it presents no BOD and in fact releases oxygen. It does not inhibit follow-on bio., and may arguably stimulate it. It exhibits good compatibility with the majority of subsurface services and infrastructure and therefore may be widely used in complex source areas including those where buildings, services and structures may restrict the potential for excavation.

Principles of Action

The desorption of contaminants by PetroCleanze is driven by:

- Action as a **wetting agent** (promoting release / mobility of NAPL);
- Creation of temporary **alkaline conditions** (promoting desorption);
- **Formation of surfactants** *from* the target contaminants (TPH);
- **Formation of more soluble species** from the target contaminants.

The contaminants themselves are therefore not only released but also transformed (through partial oxidation) into species that may further enhance the solublisation, desorption and mobilization of further contamination (Figure 3). Soil-bound contamination is thus powerfully transferred into the recoverable phases (dissolved-phase and free-phase) (Figures 4a and 4b) where it may then be captured and removed through a variety of means[1]. These range from existing P&T installations to mobile vacuum extraction tankers ('vac trucks') or surface-mopping in excavations.

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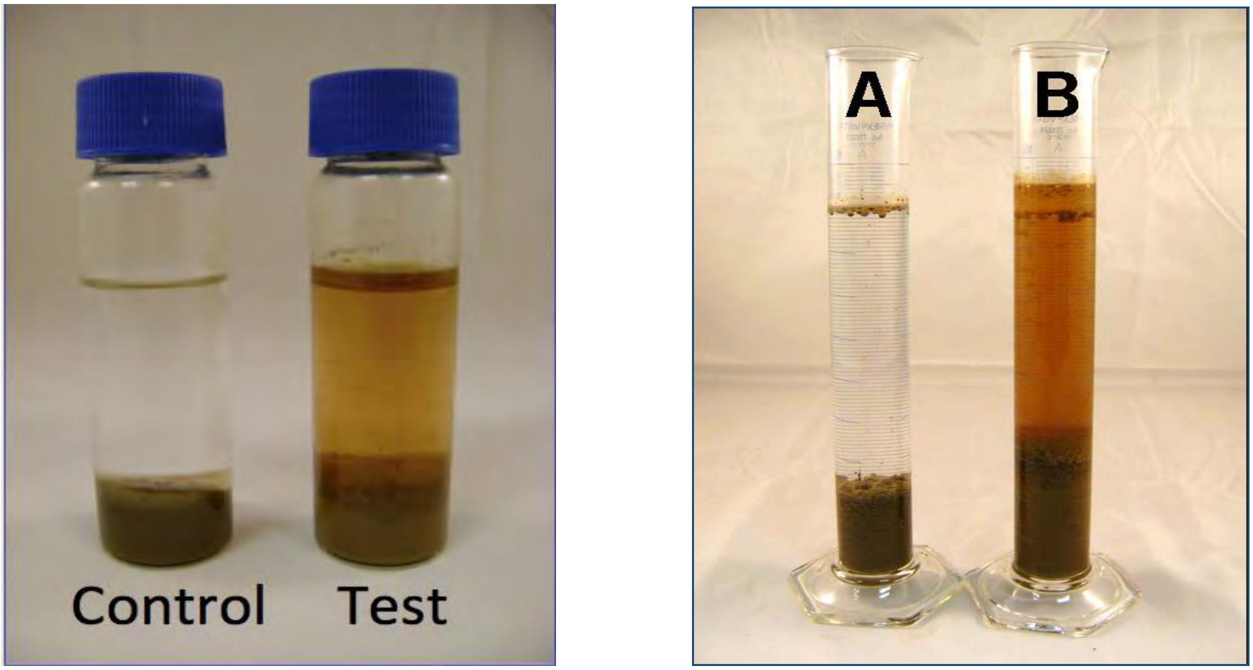
[1] It is important to apply the technology within a suitably defined capture zone so as not to unintentionally exacerbate the formation of a free plume beyond the zone of control.

Chemical Name	Chemical Structure	Solubility in H_2O(g/L)
Heptane		0
Heptanol		3.3
Heptanoic Acid		241.9

Figure 3. Example of the partial oxidation of the alkane heptane to form more soluble species that may themselves act co-solvents and surfactants.



Figures 4a and **4b**. Visual comparison of soil-water systems with PetroCleanze added ("test" left, and "B" right) and without ("control" left, "A" right). Note the floating separate-phase hydrocarbon in the treated systems and accompanying discoloration arising from increased desorption of organics from soil into water.

Field Performance

Field experience with PetroCleanze is consistent with laboratory observations, and can often be particularly striking.

__Case One:__ Figures 3a and 3b depict groundwater ('bailer') samples pre and post PetroCleanze application at a **commercial yard in the southern United Kingdom**. Despite a known loss of hydrocarbon of several thousand liters at the site, recoverable separate-phase hydrocarbon (SPH, 'free-product') was negligible. Following PetroCleanze application, recoverable SPH increased from a few millimeters (Figure 5a) to over a meter (Figure 5b) after one week. This was recovered by vacuum tanker and the application-extraction cycle repeated a further two times, the final event yielding no visible NAPL. Post treatment groundwater monitoring has shown no rebound above site target at the time of writing (three months post application). The project required no resident equipment as was completed within two months.

Figures 5a and **5b**. Visible separate-phase hydrocarbon pre-PetroCleanze (left) and post-PetroCleanze (right) application. Commercial yard, southern UK.

<u>Case Two:</u> Data for chlorinated hydrocarbons illustrate similar efficacy. On a site in **Northern England**, PetroCleanze-enhanced P&T secured a reduction in **monochlorobenzene** (MCB) of more than two orders of magnitude (>99.9%) in a mixed solvent plume within four months, taking MCB concentrations in the treatment zone from a baseline of more than 18,000 µg/L to an average of 16 µg/L (Figure 6). Abstracted solvent concentrations were approximately ten-times the background (pre-PetroCleanze) concentrations. Following this bulk-mass reduction phase, the project progressed by design into an enhanced bioremediation phase to address residual mixed solvents in the immobile-porosity and wider plume.

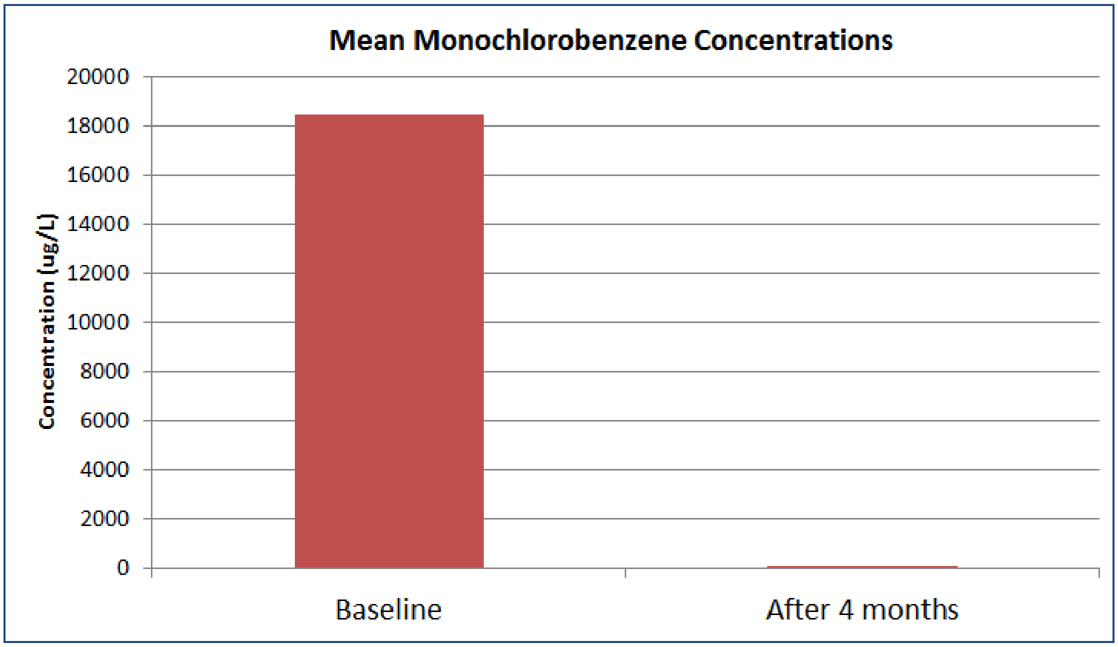


Figure 6. North of England site. Monochlorobenzene concentrations at baseline and at four months following PetroCleanze-enhanced P&T.

Summary

- The PetroCleanze reagent is designed as a commercially available product for enhancing recovery of sorbed-phase and NAPL contaminants by physical extraction systems (P&T etc).

- Contaminant desorption occurs immediately upon application increasing to a peak approximately one to two weeks post-application.

- The reagent is designed to support integrated treatment (combined remedy) remediation programs. It has good compatibility with physical systems (both hardware and sorption media) and site infrastructure, and is entirely inorganic presenting no competing oxygen demand or electron acceptor residue that may inhibit follow-on aerobic or anaerobic bio-treatment.

- The efficacy of the reagent is leveraged by 'performance feedback' – desorbed / solublised contaminants which are transformed by the reagent themselves increase the desorption / solublisation of further contamination.

- The reagent provides a means of both accelerating the rate and range (of accessible contaminants) of pump-and-treat programs and avoiding / eliminating performance tailing or post-treatment rebound.

- In field use, the reagent has proved effective with both chlorinated and non-chlorinated species.

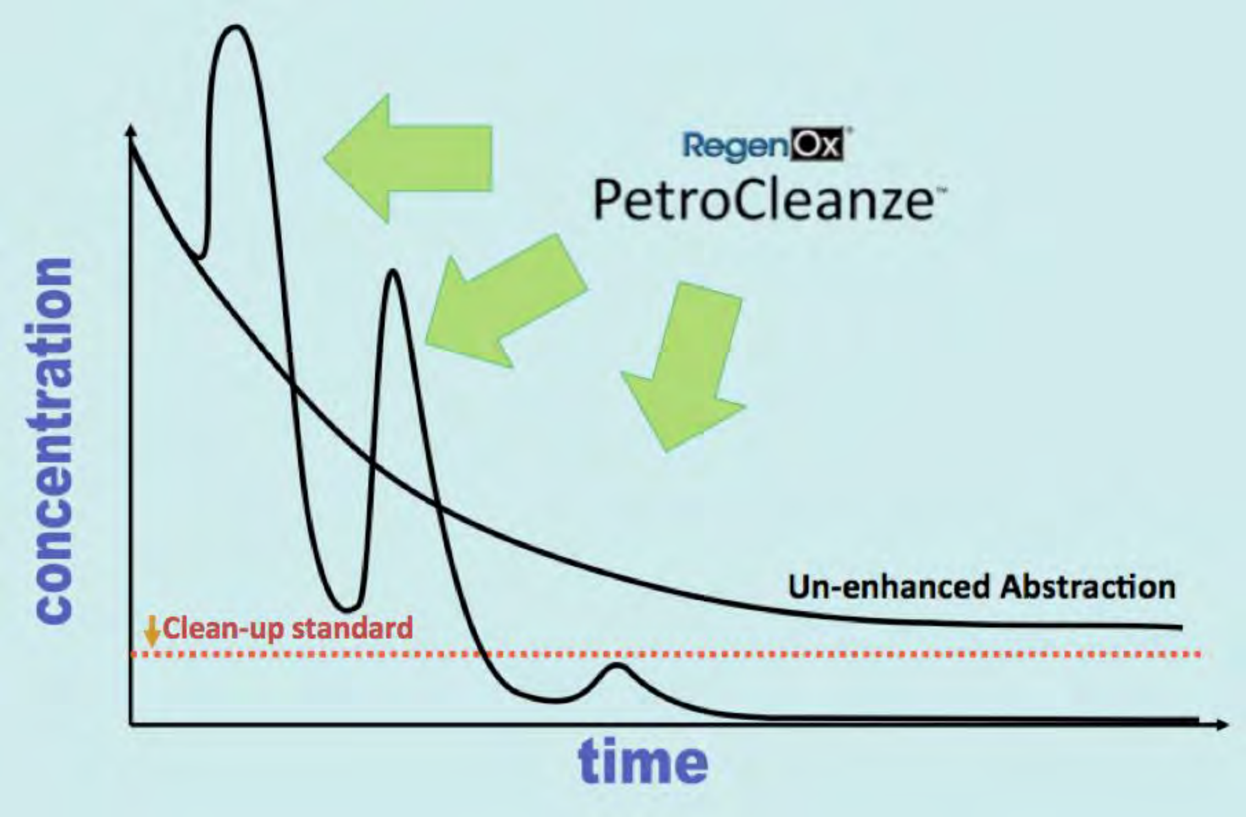


Figure 7. Schematic illustration of PetroCleanze Utility.

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