Integrated Biogeochemical / Electrochemical Method for Remediation of Contaminated Groundwater

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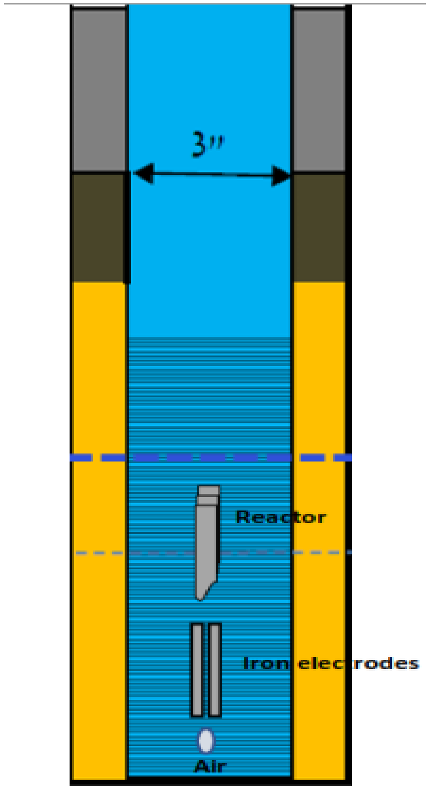
Presentation Outline

- Problem Statement
  - Overview of Available ISCO Technologies
  - Why Do We Need Another?
- What is Provect-"EBR®"?
  - What is Provect-EBR?
  - How does it Work / Mode of Action?
  - Remote System Control and Real-Time Monitoring
  - Applications to Date
- Case Studies
  - CHCs: Confidential Site (Tel Aviv, Israel)
  - MTBE: Operating Gas Station, Sonol Kiryon Site
  - MTBE/BTEX: Operating Gas Station, Neve Tdizek Site
- Summary and Conclusions / R&D Needs

provect "EBR®"
ISCO GENERATOR



ISCO = Breaking Chemical Bonds

- Oxidant must be able to accept electrons
  - Capacity = Equivalent weight (MW / No. electrons)

- Ultimate end point is mineralization
  - Partial oxidation is common

Bond Type	Volts (eV)
Carbon-Carbon (single) Long chain hydrocarbons PAHs, DRO, GRO	2.5
Carbon-Carbon (one and a half) Aromatic Type - BTEX and PCP	2.0
Carbon-Carbon (double) HVOCs, PCE, TCE, DCE, VC	1.5
Carbon-Hydrogen (Alkanes)	1.0

Summary of ISCO Technologies

stronger oxidizer

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical (OH●)	2.80
Persulfate radical (SO_4●)	2.60
Ferrate (Fe^{+6})	2.20
Ozone (O_3)	2.08
Persulfate ($S_2O_8^{-2}$)	2.01
Hydrogen peroxide (H_2O_2)	1.78
Permanganate (MnO_4^-)	1.68
Chlorine (Cl_2)	1.49
https://sites.google.com/site/ecpreparation/ferrate-vi	

Fenton's
- Treats wide range of contaminants
- Short subsurface lifetime
- Difficult to apply in reactive soils

Persulfate
- Treats wide range of contaminants
- Sulfate radical forms slower than the hydroxyl radical, allowing a larger radius of influence

Provect-OX
- Generates Ferrate (Fe IV, V, VI possible)
- Treats wide range of contaminants
- Extended *in situ* lifetime w/ continual production
- Avoids Rebound

Ozone
- Treats wide range of contaminants
- Short subsurface lifetime
- Limited use in saturated zone

Permanganate –
- Treats limited range of contaminants
- Partial oxidation of TPHs, etc
- Long subsurface lifetime
- Potential effects on hydrogeology

Reactive Oxidant Species (ROS)

Higher oxidation potential = stronger the oxidizer

Why We Need A New ISCO Technology

- **Longevity**: Conventional ISCO amendments and means of generating ROS are limited by distribution, kinetics, and short environmental half-lives ($10E^{-9}$ to $10E^{-6}$ seconds) = need to be continuously generated / applied.
- **ISCO PRBs**: PRB applications using existing ISCO (candles, KPS, etc) are limited
- **Sustained, *In Situ* Production of ROS could yield effective PRBs** especially for COIs not conducive to ISCR/ZVI such as 1,4-dioxane, MTBE/TBA, perchlorate, (PFAS?) plumes.

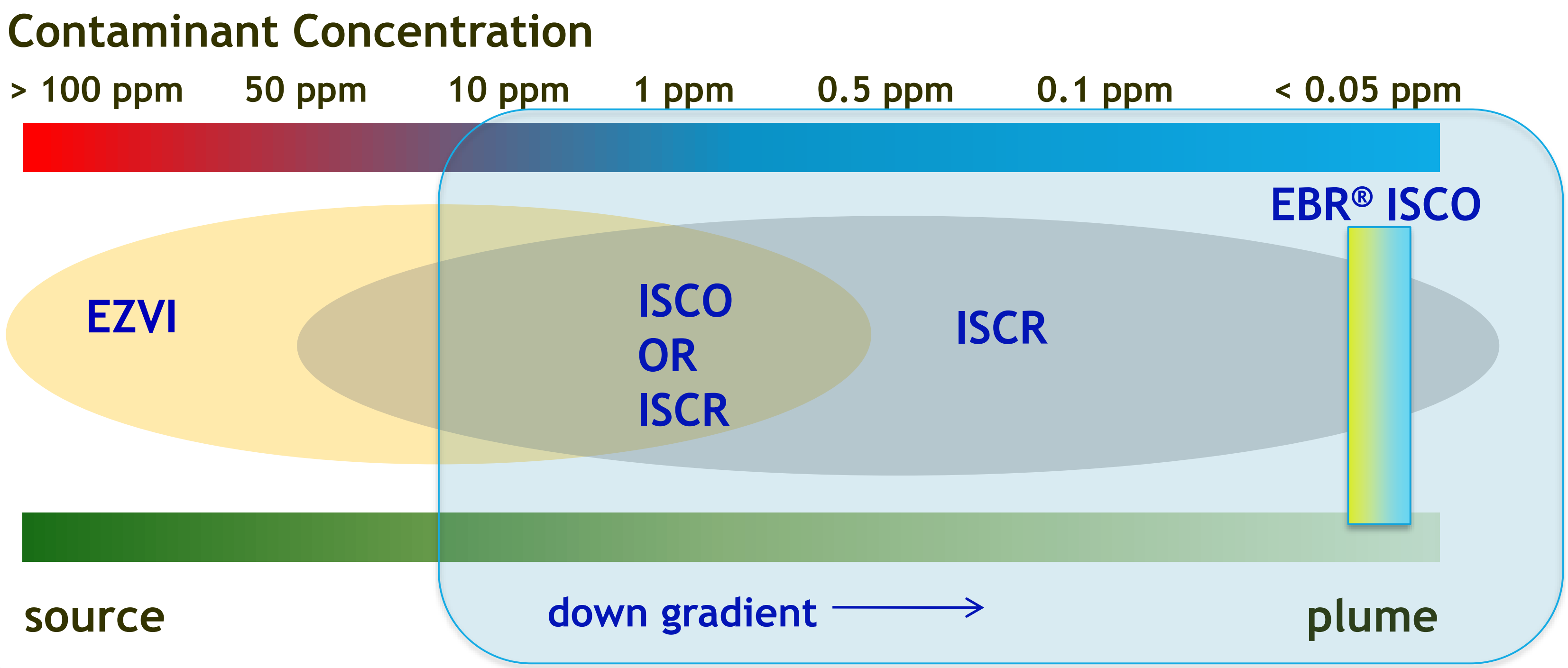
APPENDIX A. Comparative Analysis of Various Options for an Example PRB @ 50 m long x 5 m deep (4 to 9 m bgs) x 3 m wide.

Technology	Process	Benefits	Detriments	Materials	Example Construction O&M&M costs (USD)
Provect-EBR	*In situ* ISCO (Fenton's) generator	Longevity 5 to >7 years; Treats COIs without intermediates; Remote monitoring control panel and software included	Limited application outside Israel; Mostly used to date for MTBE and refined petroleum products	8 EBR wells spaced 5.5 m apart	8-well EBR system, installed = $125K 8x, 4-inch diam wells = $24K Engineering/startup = $30K Annual OMM = $30/yr TOTAL = $209

Provect-”EBR®” ISCO PRB

***In Situ* ISCO Generator** to continuously produce Fenton’s type ROS yields an effective PRB technology for:

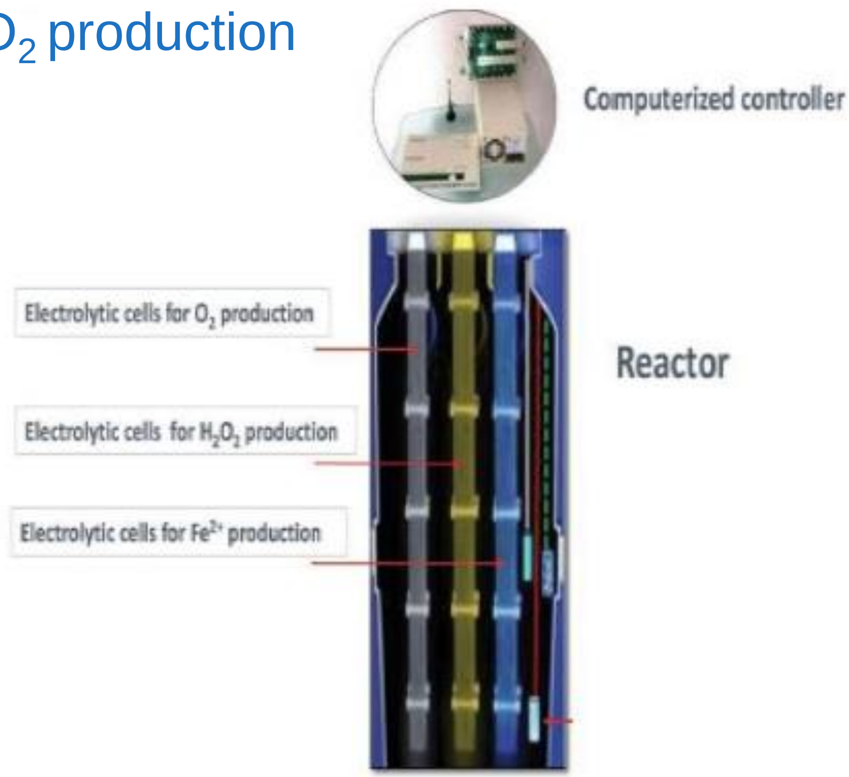
- Challenging lithologies (deep aquifers, clayey soils, fractured rock)
- Situations where sorption/sequestration is not considered an effective response
- Alternatives to hydraulic containment (long term O&M&M)



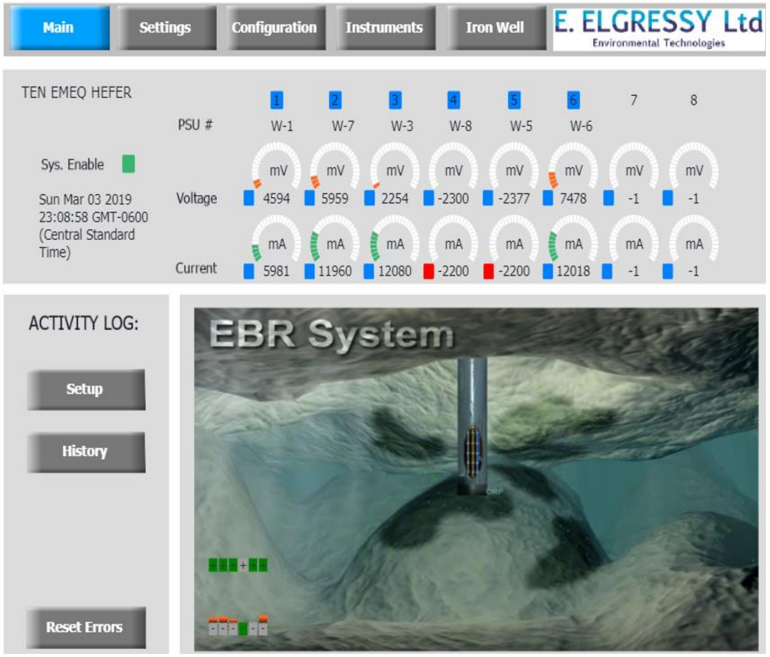
What is Provect-”EBR®”

Electro Bioremediation (EBR) well(s) contain an air sparge plus 3 electrodes:

- H_2O_2 production
- Fe^{2+} release
- O_2 production



Computerized control panel for remote system / adjustment and real-time performance monitoring



US Patent No. 9,975,156 B2

How Does EBR Work?

The EBR Well Generates Reactive Oxidant Species (ROS) in a manner similar to other Electro-Fenton's (EF) type systems (Nazari *et al*., 2019; Rosales, *et.al,* 2012; Sires *et al*., 2014; Yuan et al., 2013):

Production of O_2: electrolytic reduction of water on a catalytic electrode yields molecular oxygen, O_2

Production of H_2O_2: two-electron reduction of oxygen on a cathode surface generates H_2O_2

Release of Iron: H_2O_2 interacts with ferrous iron (Fe^{2+}) released from a third cell to yield hydroperoxyl ($HO_2\cdot$)/superoxide ($O_2\cdot$) and hydroxyl radicals ($OH\cdot$), and likely ferrates

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$$

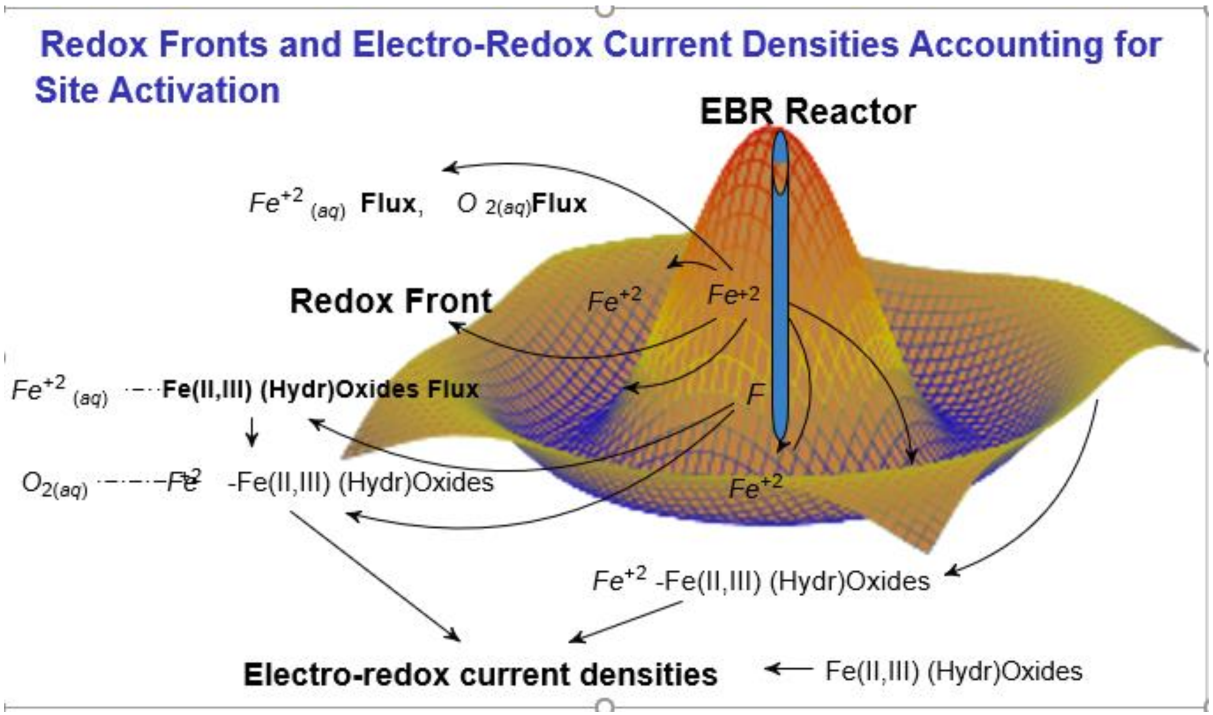
How Does EBR Differ From EF?

$Fe^{2+/3+}$ Nanoclusters: At neutral pH EBR uniquely generates "low" Fermi Level (highly oxidized) FeII/III oxyhydroxide nanoclusters (2 nM) as the sacrificial Fe source corrodes within the well (Ai *et al.,* 2013; Elgressy 2019).

Subsurface distribution of Fe nanoclusters throughout the aquifer is driven by:

- Induced redox fronts
- Electro-redox current densities
- Electroosmosis
- Electrophoresis
- Dynamic coupling between EBR wells

- **Equilibration of differences in Fermi level energies self-generated self-propagated**



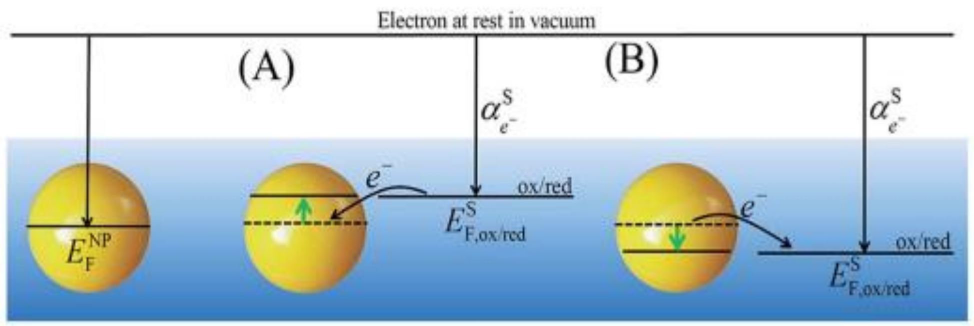
How Does EBR Differ From EF?

$Fe^{2+/3+}$ Nanoclusters: A critical and unique feature of the EBR is use of geophysical mechanisms to enhance subsurface distribution of low Fermi level Fe nanoclusters and propagate catalysis *in situ* to continuously generate reactive oxidants throughout its effective ROI.

Electrochemical Potential of an e- is the difference in potential between the oxidized and reduced species (Peljo *et al.*, 2017; Scanlon *et al.*, 2015)

Fermi Level is a thermodynamic “value” to define the electrochemical potential of an electron in a redox couple in solution

At +850mV (“low” Fermi Level electrochemical potential) electrons are essentially freely transferred from Fe^{3+} to Fe^{2+}

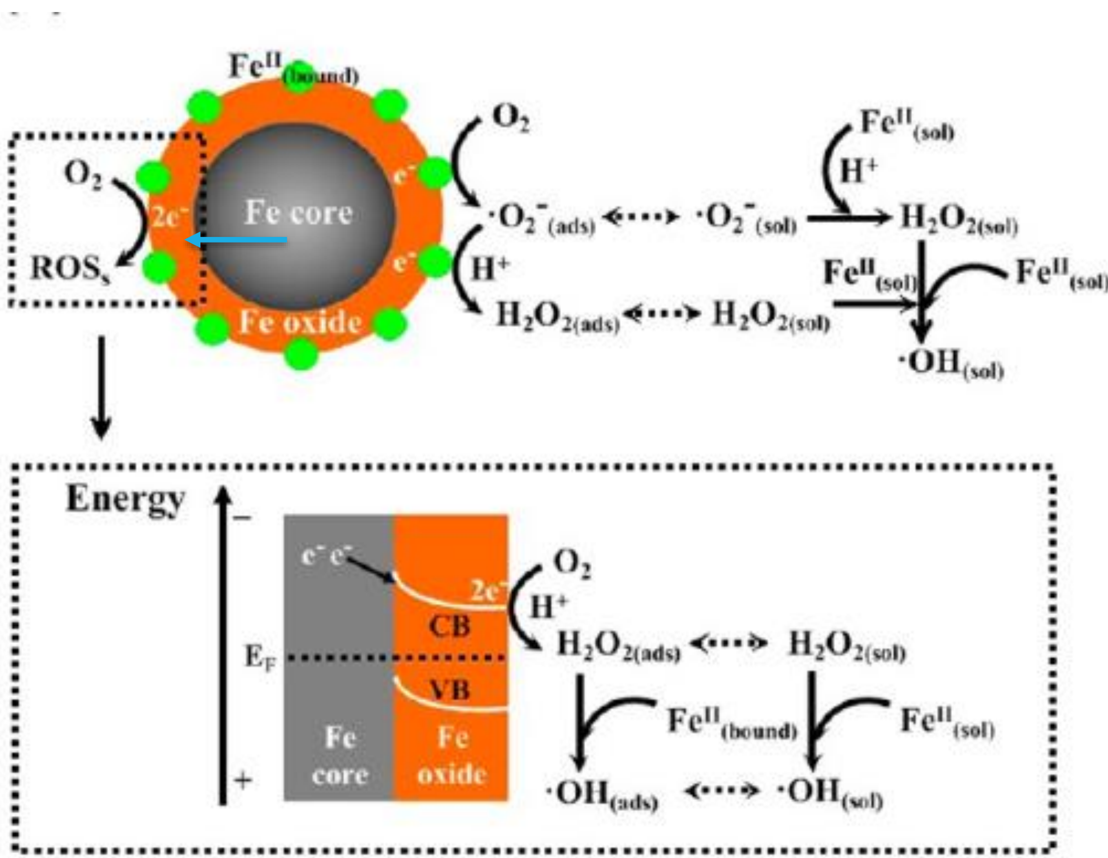


Scheme 3 Redox equilibria for metallic NPs in solution showing the capabilities of metallic NPs to be (A) charged and (B) discharged upon Fermi level equilibration with an excess of a single dominant redox couple in solution.

In Situ Generation of ROS

As Fe (hydro)oxides within the aquifer ROI equilibrate their Fermi level electrochemical potentials they continuously catalyze *in situ* generation of new ROS from dissolved molecular O_2 via two kinds of molecular oxygen activation pathways (Ai *et al*., 2013):

- On the Fe core via rapid two-electron-reduction molecular oxygen activation (may eventually be blocked by the formation of iron oxide coatings), then
- Surface bound ferrous ions catalyze the single-electron-reduction molecular oxygen activation pathway

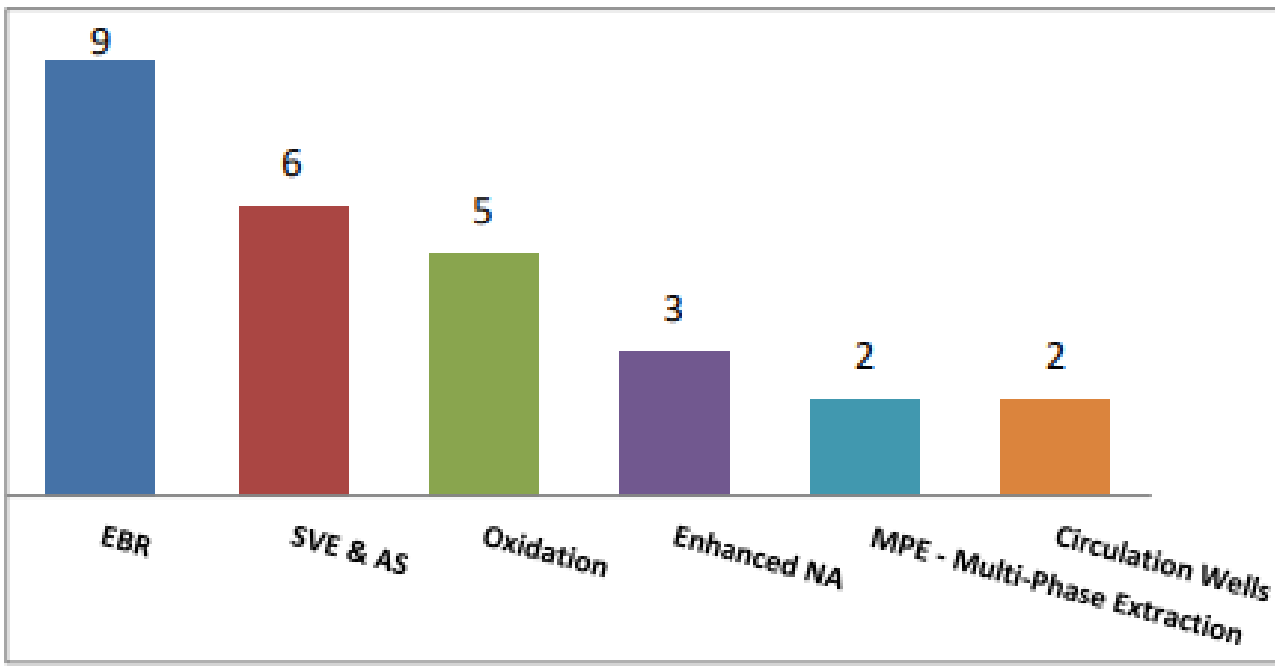


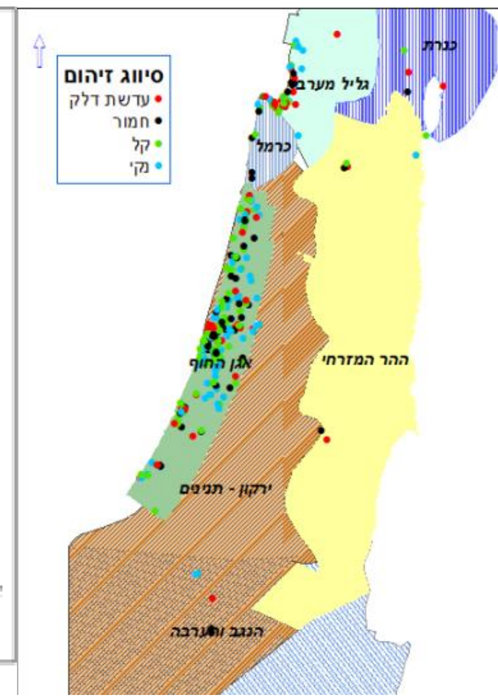
Summary of EBR Reactions

- Generation of H_2O_2
- Release of Fe^{2+}
- H_2O_2 interacts Fe^{2+} to yield ROS $HO_2\cdot/O_2\cdot$ and $OH\cdot$ (ferrate?)
- Release of O_2 and low Fermi Level Fe^{2+}/Fe^{3+} nanoclusters
- Self-propagation throughout ROI (less confined by lithology)
- Continuous *in situ* production of ROS catalyzed by O_2 activation from equilibration of Fermi levels of Fe
  - Transition from ISCO to bioremediation (using oxygen and iron as electron acceptors) and RNA using abiotic transformations.
  - Process controlled remotely with real-time monitoring

Where has it been Used?

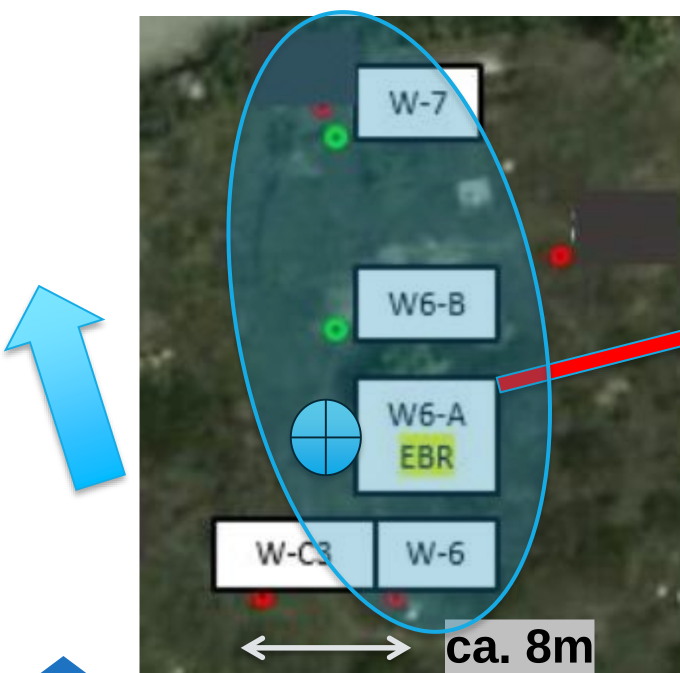
- In 2017 , Israel had 27 gas stations undergoing active remediation
- EBR technology was employed at 9 (33%) + 2 chlorinated solvent sites
- Today, 7 sites are in clean-closure monitoring after 1 year of operation
- EBR is ISO-certified and approved by the Israeli Water Authority
- No PRB Applications. No USA applications.

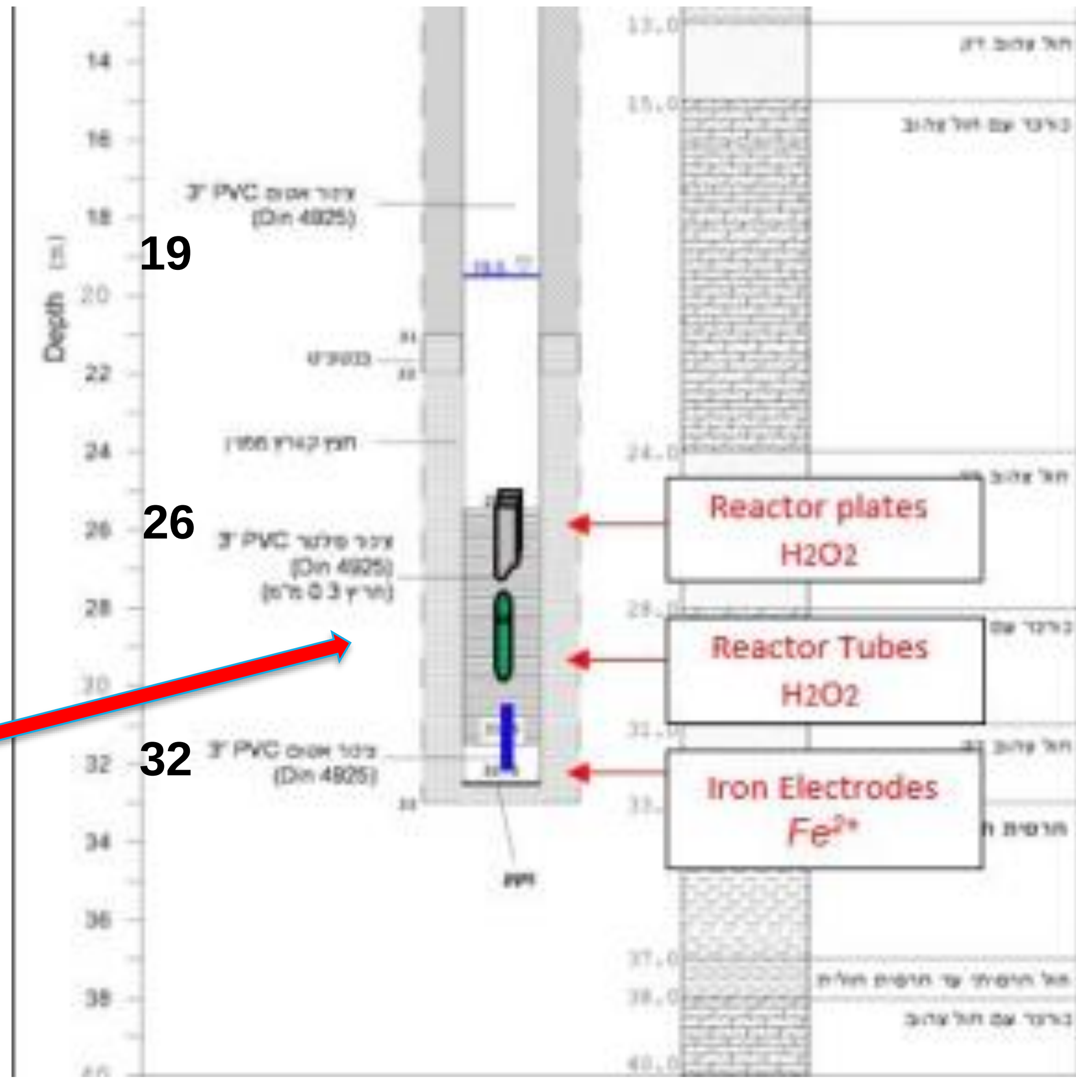




Case Study - Solvent Site

- DTW 19.5 m bgs
- Sandy aquifer impacts
  - PCE max. 257 ug/L
  - TCE max. 25,146 ug/L
  - DCE max. 47 ug/L





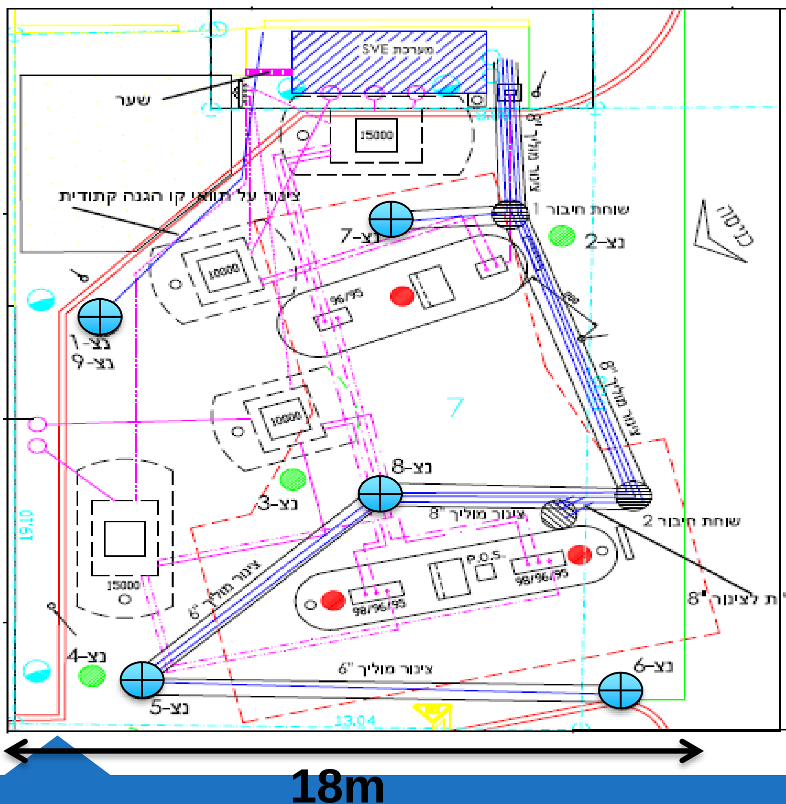
CVOC Removal (60 days; ppb)

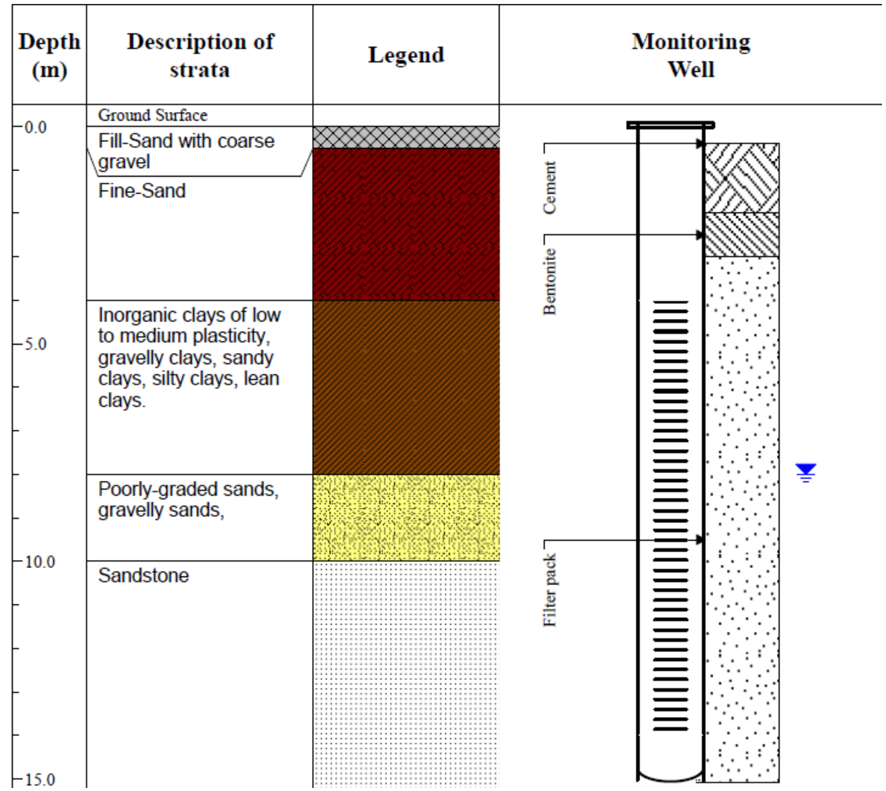
CVOC (ug/L)	Time (Days)	Well 6 (10 m up)	Well 6a EBR Well	Well 6b (5 m down)	Well 7 (20 m down)
PCE	0	8.7	257	<2	<2
	30	2.4	<2	<2	<2
	60	<2	5	<2	<2
TCE	0	752	25,146	74	24
	30	201	<2	6	14
	60	37	15	4	<2
DCE	0	14	47	<1	<1
	30	2.6	<1	<1	<1
	60	1.6	8	<1	<1

- Single EBR Well + Control Panel and remote monitoring < $45K installed
- ROI observed 20 m downgradient within 30 to 60 days.
- >99% CVOC removal within 30 days

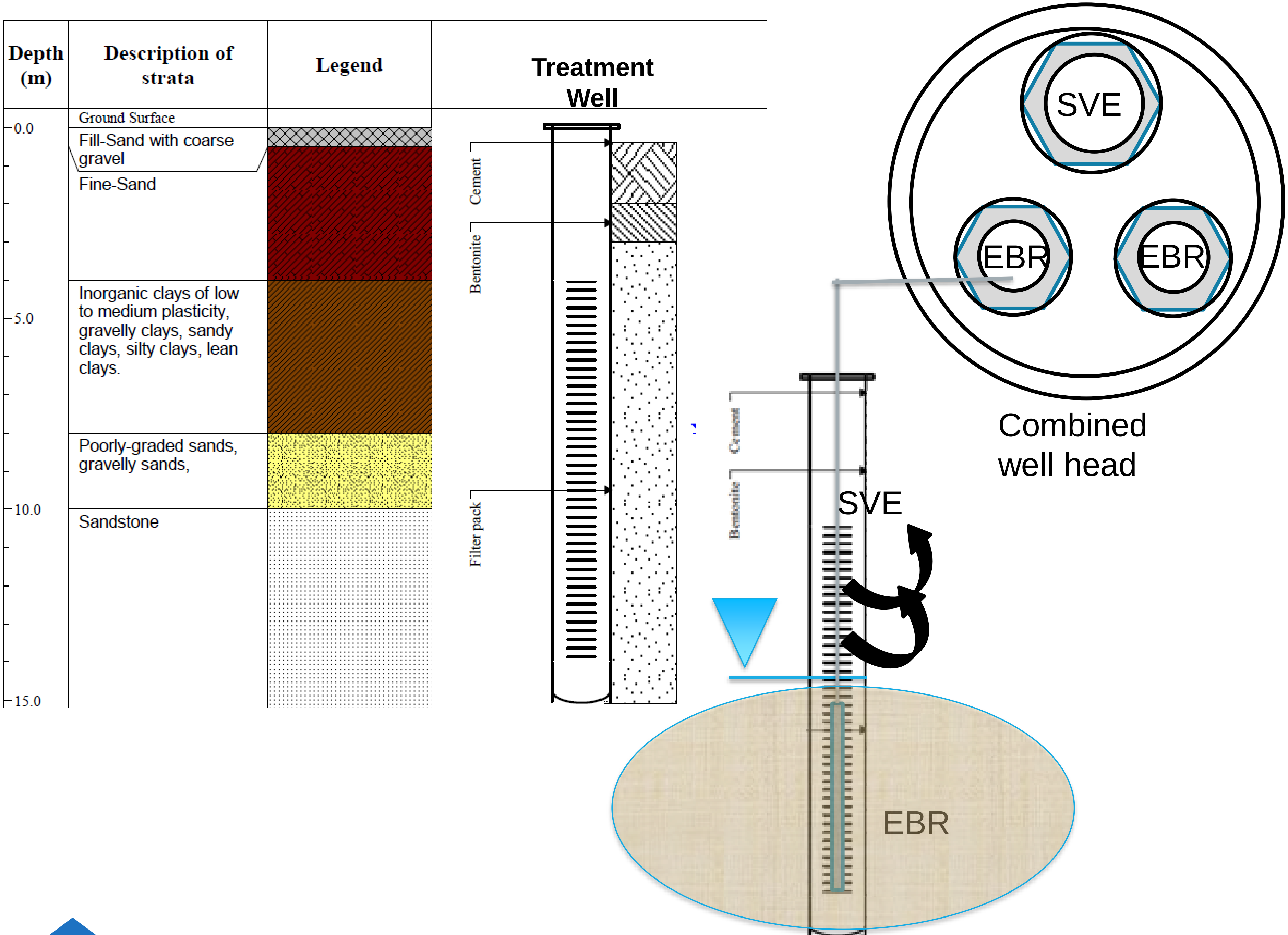
Case Study – Neve Tzedik Site

- Operating Gasoline Station
  - Groundwater at 7 to 8 m bgs
  - sandy aquifer with si cl lenses
  - MTBE >50 mg/L; TPH >100 mg/L
  - 242 m^2 impacted area

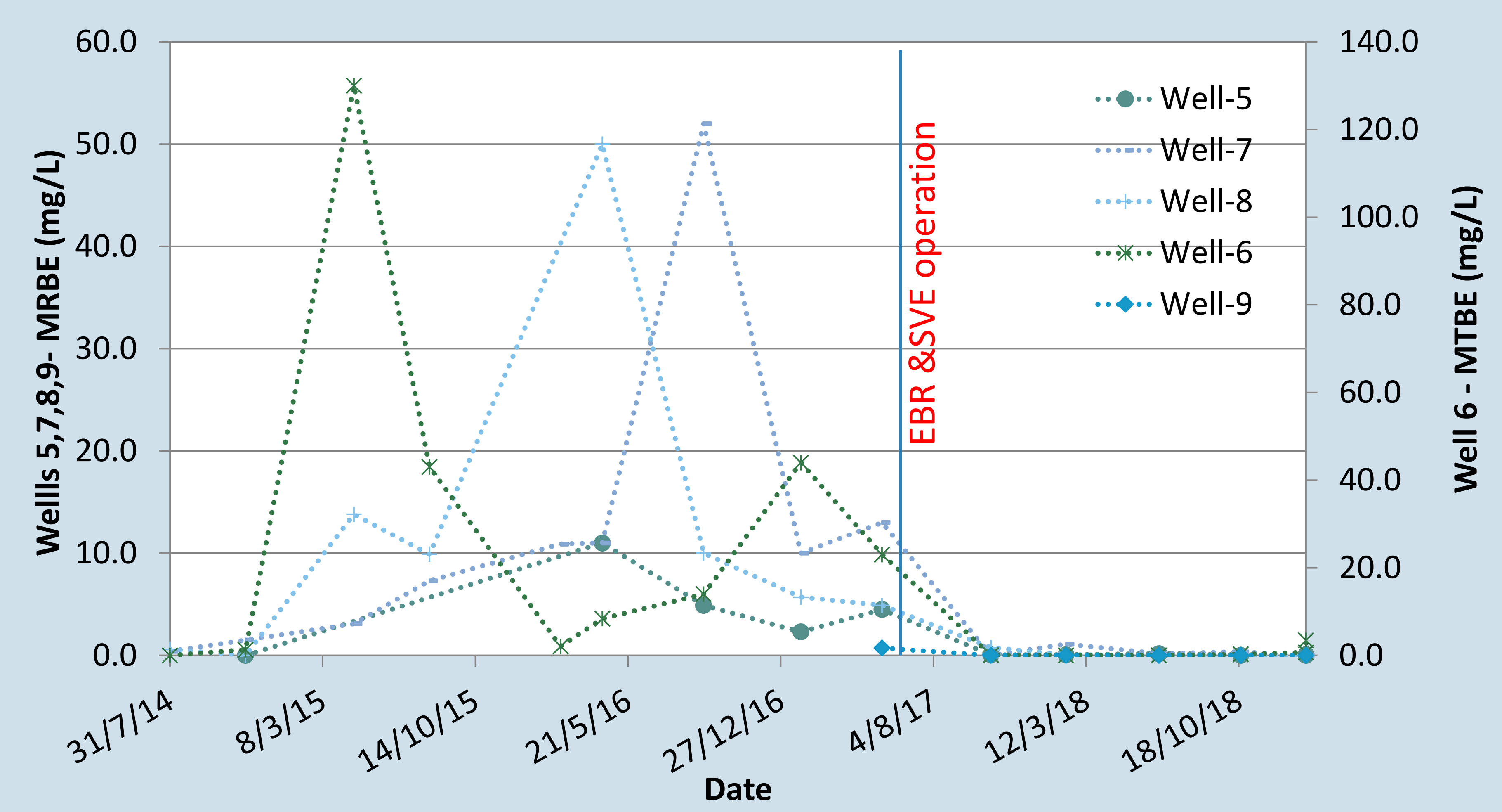




- 5 EBR/SVE Systems (2017)
- Monitoring wells

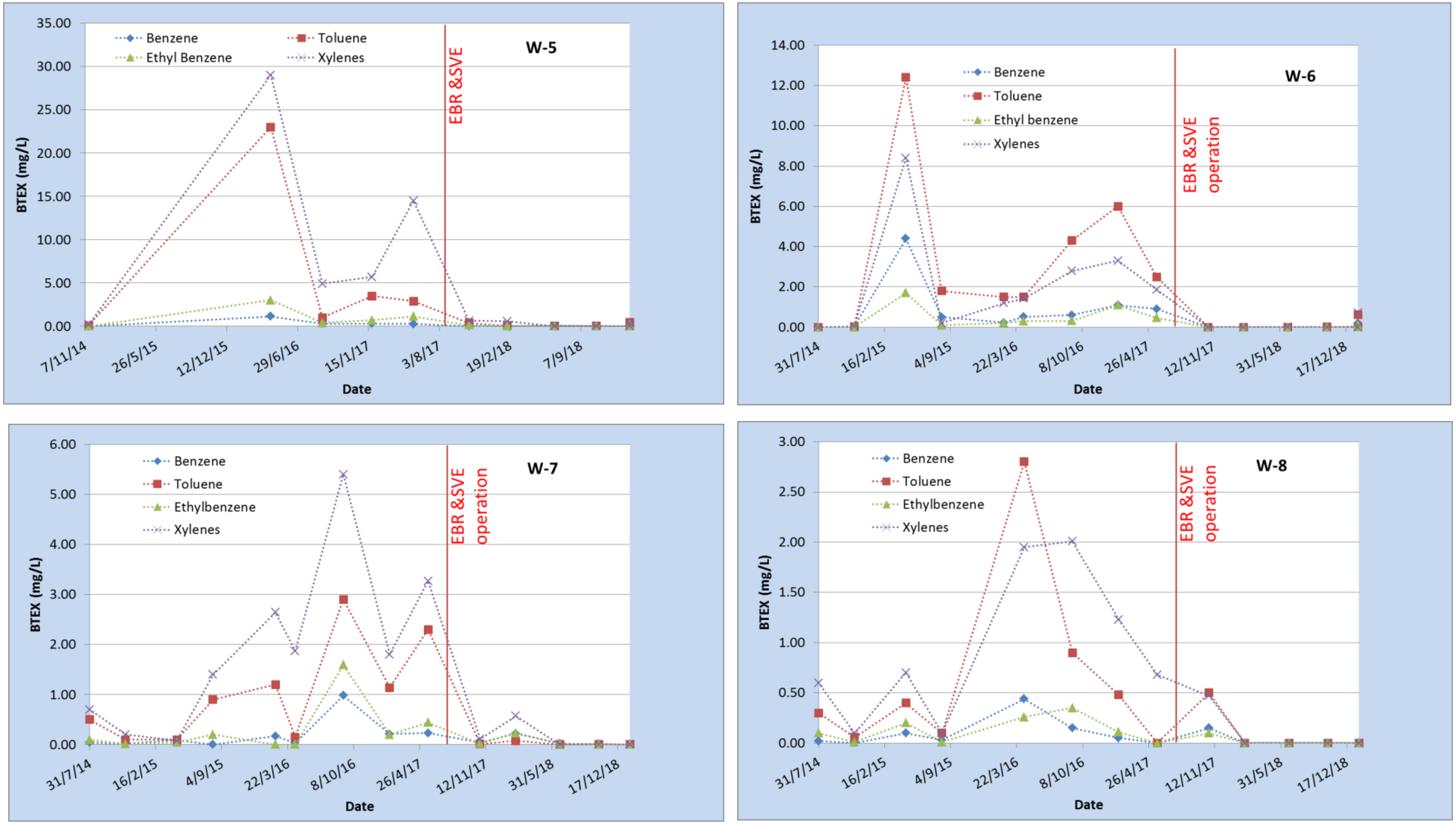

Depth (m)
Description of strata
Legend
Treatment Well
Ground Surface
0.0
5.0
10.0
15.0
Fill-Sand with coarse gravel
Fine-Sand
Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays.
Poorly-graded sands, gravelly sands,
Sandstone
Cement
Bentonite
Filter pack
SVE
EBR
EBR
Combined well head
Cement
Bentonite
SVE
EBR

MTBE Concentration (mg/L) in Water



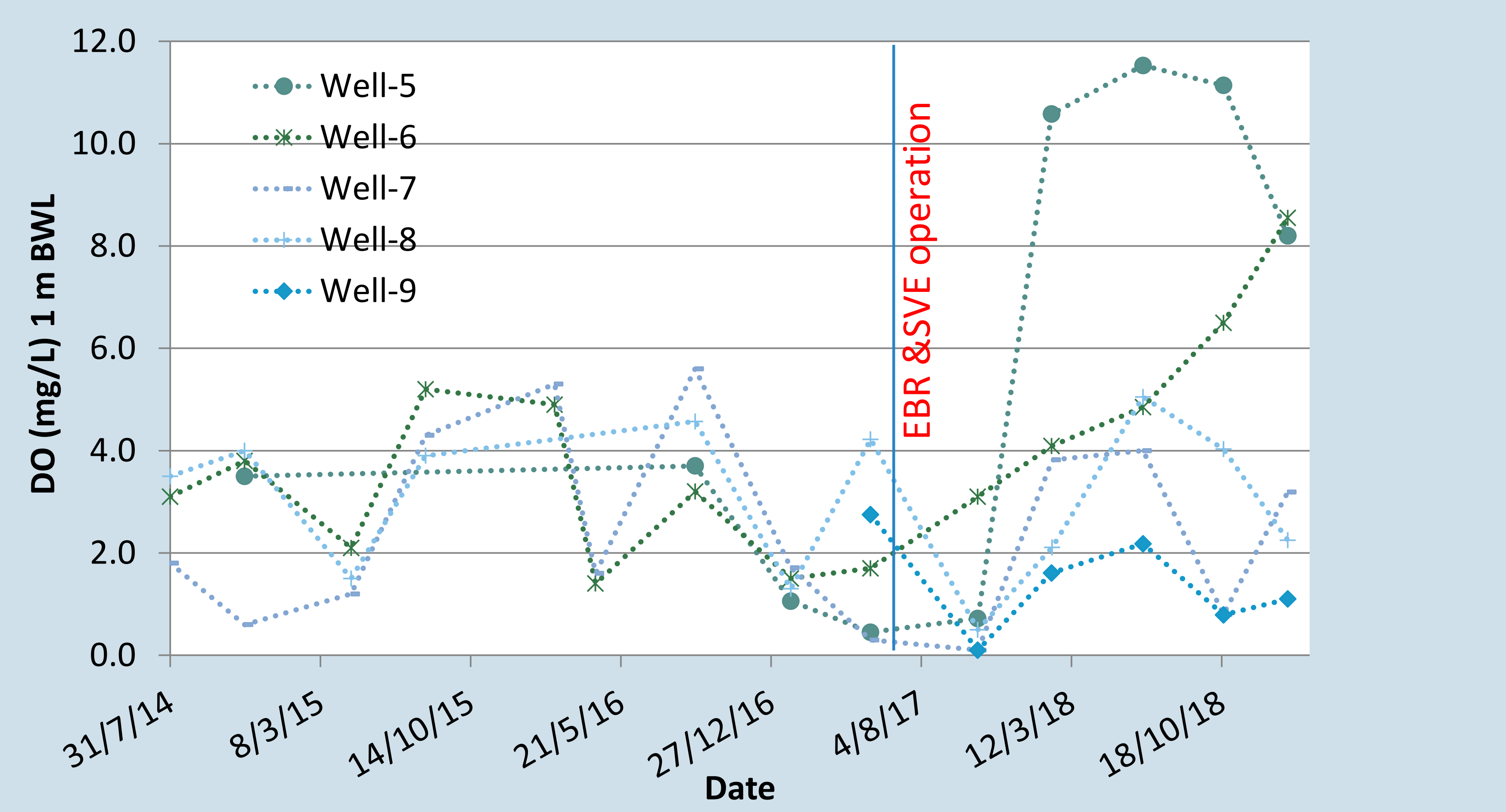
- MW-6 ca. 130 ppm to < 5 ppb within 12 months

BTEX Concentrations (mg/L) in Water

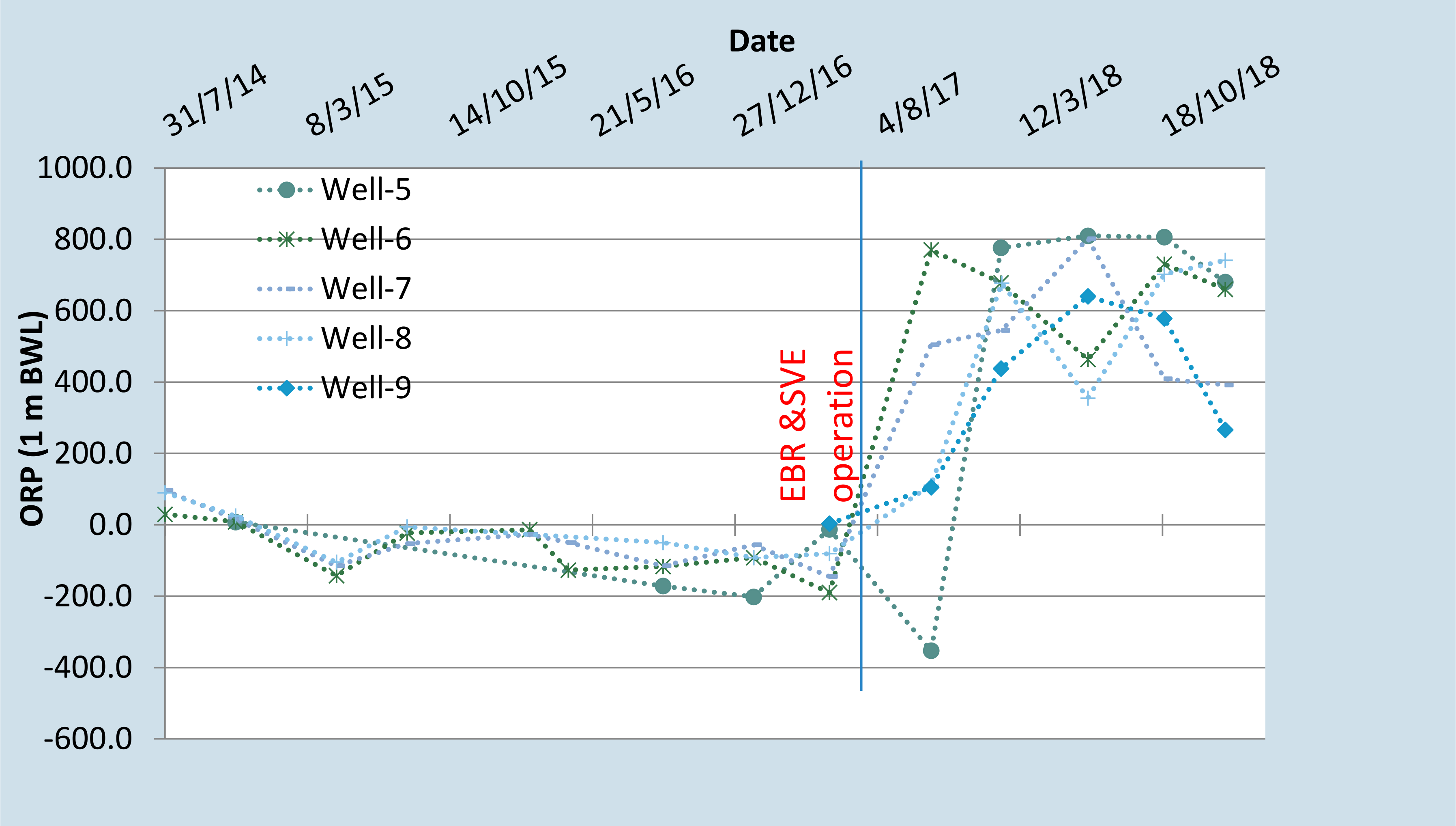


- MW-5 ca. 25 ppm to < 5 ppb within 12 months

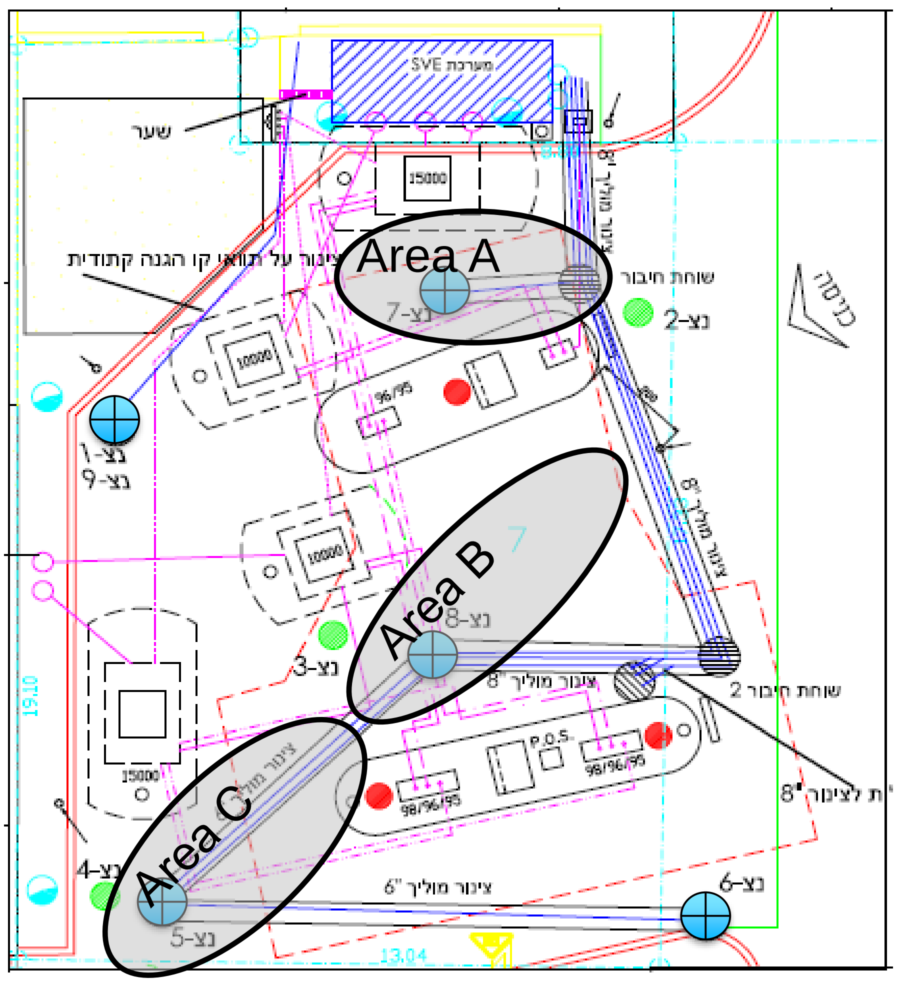
Dissolved Oxygen (DO)

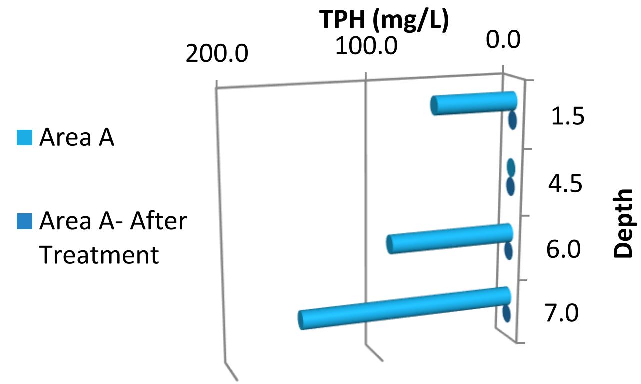


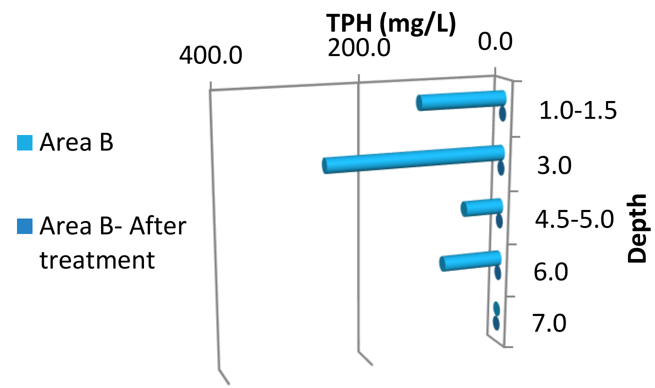
GW field parameters (ORP)

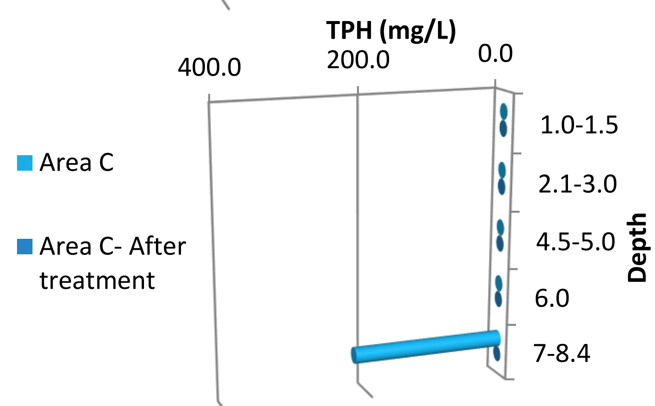


Soil / Groundwater BTEX (18 mo)





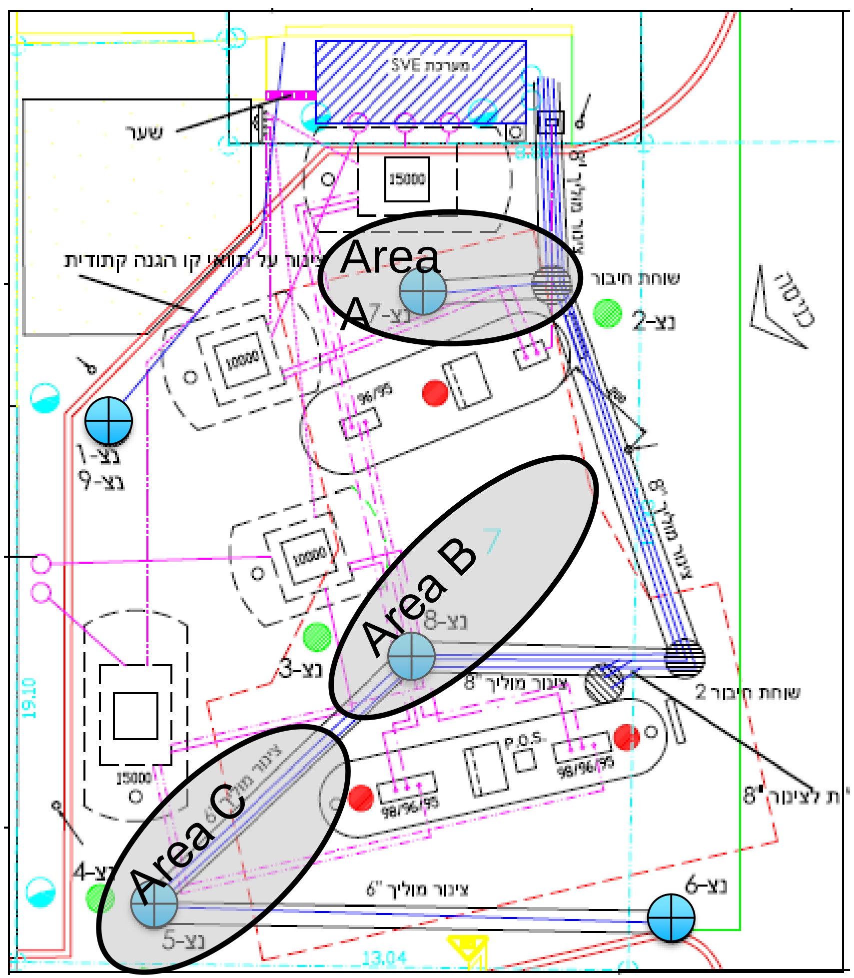


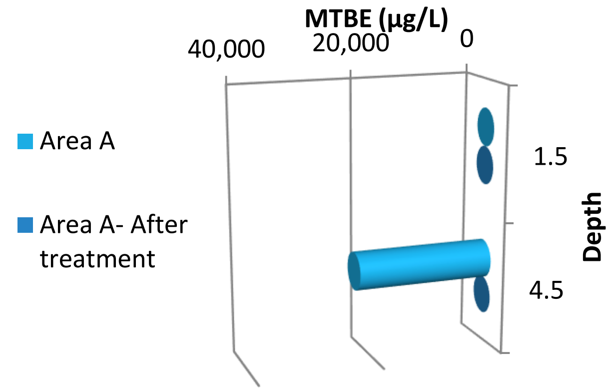


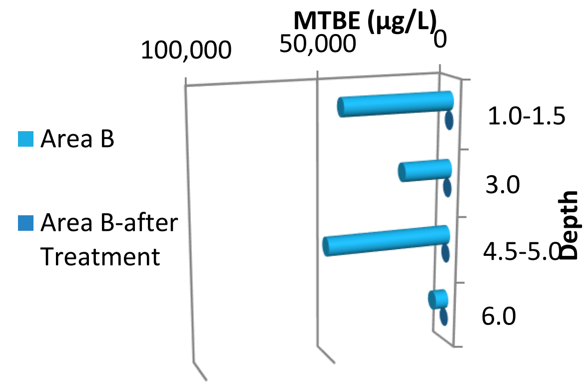
- From > 200 ppm to < 2 ppm

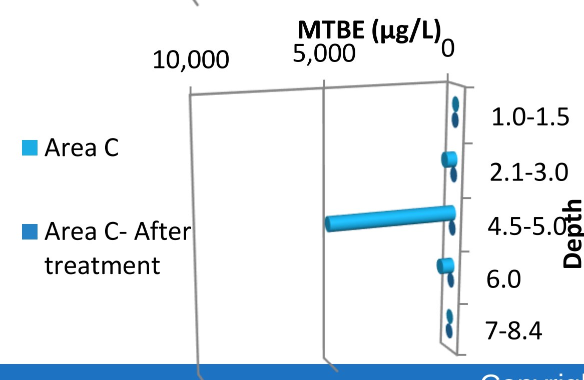
Soil / Groundwater MTBE (18 mo)

- From >50 ppm to < 0.05 ppm
- 5 EBR Wells, Control Panel, O&M < $150K



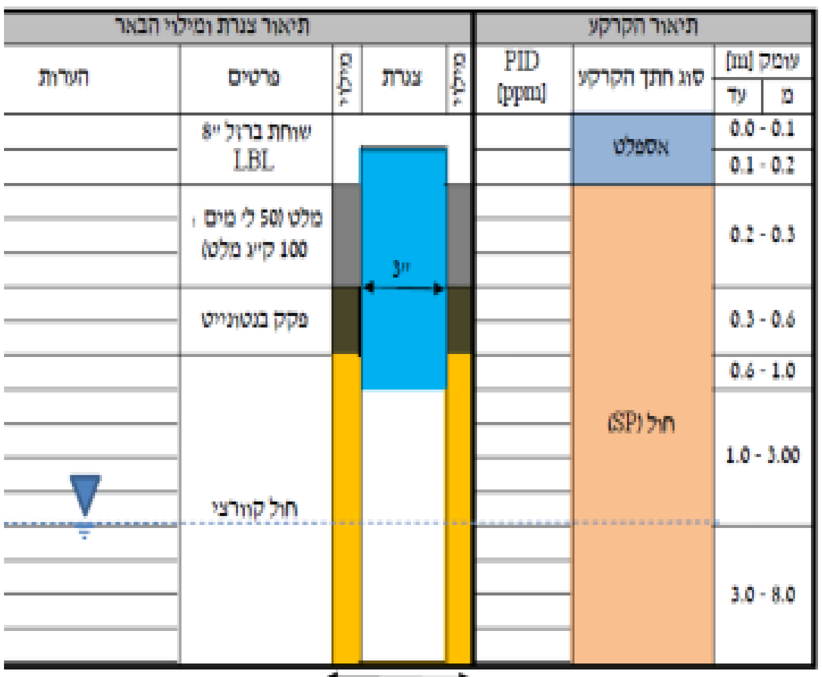






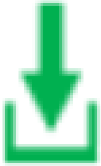
Case Study – Sonol Kiryon Site

- Operating Gasoline Station
  - Groundwater at 3 m bgs
  - sandy aquifer
  - MTBE >17 mg/L
  - ca. 300 m^2 impacted area

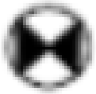


Case Study – Sonol Kiryon Site

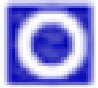
5 EBR (May 2018)



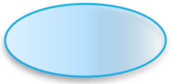
5 Monitoring Wells

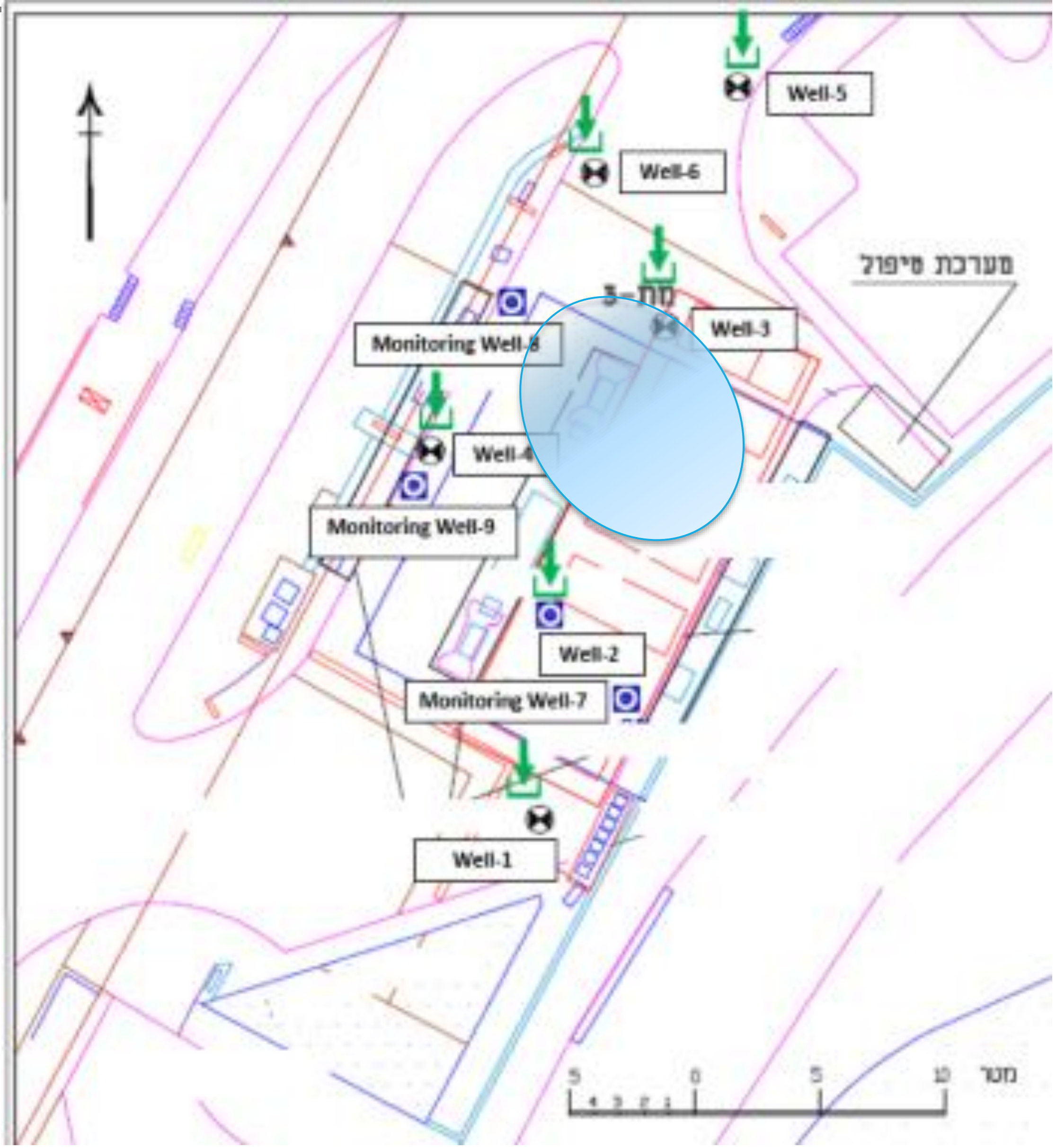


4 New Monitoring Wells



LNAPL Present





Groundwater MTBE (5 months)

GSI MANN-KENDALL TOOLKIT
for Constituent Trend Analysis

Evaluation Date:	12/2018	Job ID:	07-2018 Sonol Hakirion
Facility Name:	SONOL HAKIRION	Constituent:	MTBE
Conducted By:	E.Elgressy ltd	Concentration Units:	mg/L

Sampling Event	Sampling Date	Well 1	Well 2	Well 3	Well 4	Well 5	Well-6
		MTBE CONCENTRATION (mg/L)					
1	10/2/2014	7.9	26	188	62		
2	18/6/2014	5.4	30	94	50		
3	17/11/2014	5.8	8.6		LNAPL Lens	70	24.5
4	19/10/2015	0.98	60		20	10	39
5	28/2/2016	1	15	LNAPL Lens	21	0.4	15
6	6/7/2016	1.9	6.4		8.9	1.3	6.1
7	10/10/2016	1.19	2.1		6.6	0.82	5.5
8	22/2/2017	2.2	2.2		12	7.7	0.59
9	14/6/2017	1.08	10.1		22	14	1.66
10	23/10/2017	0.45	12		17	0.25	1.46
11	21/5/2018		7				
12	25/10/2018	0	0	LNAPL Lens	1.5	0.05	0.09
13							
14							
15							
16							
17							
18							
19							
20							
Coefficient of Variation:		1.03	1.13	0.47	0.87	1.94	1.29
Mann-Kendall Statistic (S):		-31	-30	-1	-23	-16	-30
Confidence Factor:		99.2%	97.8%		97.7%	94.0%	100.0%
Concentration Trend:		Decreasing	Decreasing		Decreasing	Prob. Decreasing	Decreasing

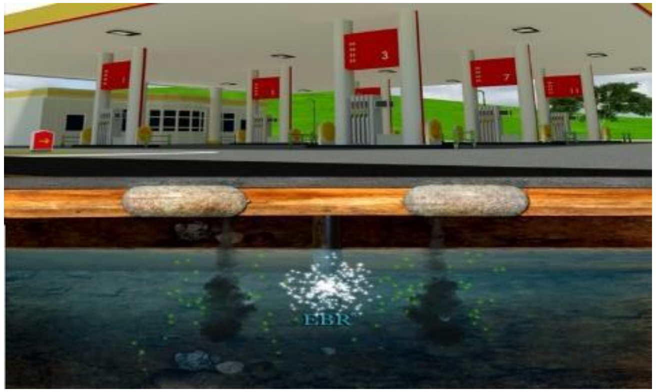
Activation of EBR 15/07/2018

5 months EBR operation (as of December, 2018)

Groundwater COIs ug/L (7 months)

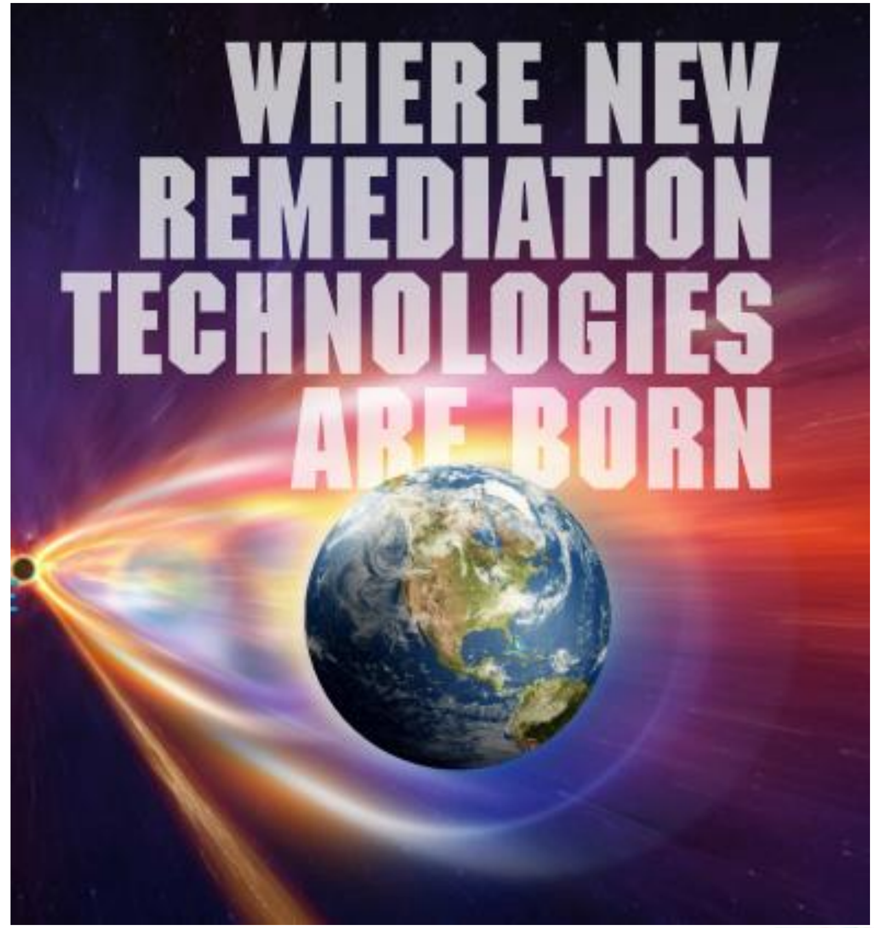
Well	Date	MTBE	Benzene	Xylenes	TBA	CFUs/ml
MW-7	5/2018	11,000	0.21	60	--	--
	12/2018	50	<5	<5	7,100	24,000
MW-8	5/2018	5,000	<5	<5	--	--
	12/2018	2,800	<5	40	114,000	7,700
MW-9	5/2018	7,000	<5	<5	--	--
	12/2018	120	<5	<5	5,600	100,000

- Toluene, Ethylbenzene <5 ppb
- 6 EBR Wells, Control Panel, O&M < $180K



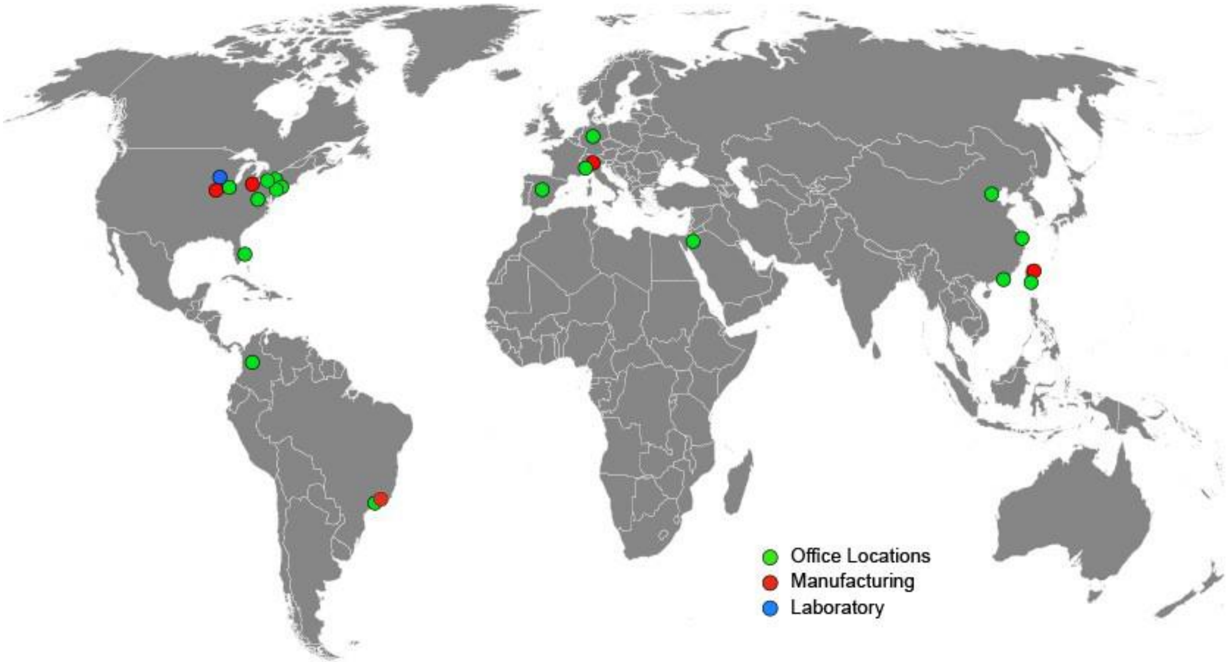
Learn More About EBR MOA

provect "EBR"®
ISCO GENERATOR



Provectus Environmental Products

- Complimentary Site Evaluation
- Complimentary review of quarterly field performance data with every project
- Laboratory Treatability Studies
- Turn-Key, Pay-for-Performance Contracting Options
- Project Specific Guarantees and Warranties



- USA (Florida, Illinois, New Jersey, Ohio, Pennsylvania, Wisconsin)
- Australia, Brazil, Canada, China, Colombia, Germany, Israel, Italy, Spain and Taiwan

Future R&D / Continued Studies

Validate ROI and Effective Propagation Time, Vertically and Horizontally
(ESTCP submittal Mueller, Shi, Ginn, and Tratnyek 2019)

- ORP / Measurements (indirect)
- COI Reductions (indirect)
- Fe2+/Fe3+ measurements: Particle size (BEM) and mineralogy (XRD patterns, TEM micrographs, XPS spectra and high-resolution scan); possible using variations of Bradley and Tratnyek (2019).
- Self-Potential Method (direct): passive geophysical analysis based on the natural occurrence of electrical fields resulting from the existence of source currents in the conductive subsurface (Fachin *et al*., 2012)
- Electrical Resistivity Tomography (direct): measures variations in electrical conductivity associated with changes in pore water ionic strength or water phase saturation.
- Lab-fabricated oxygen microprobes/sensors (direct): validate the distribution of ROS.
- Simple and Predictive Models: facilitate PRB design and implementation