Bioelectrochemically-enhanced *In Situ* Biodegradation of Benzene and Other Petroleum Contaminants in Groundwater

Song Jin, Ph.D., CHMM

Advanced Environmental Technologies, LLC
Fort Collins, Colorado

May 24, 2017

ACKNOWLEDGEMENT

Co-authors:

- Paul Fallgren, Advanced Environmental Technologies, LLC, Fort Collins, Colorado
- Matthew Larsen, CGRS Inc., Fort Collins, Colorado
- Jennifer Strauss, Division of Oil and Public Safety, Department of Labor and Employment, Denver, Colorado

OUTLINE

- Introduction to bioelectrochemical technologies (E-Redox^{TM})
- Technology applications
  - Bio-oxidation of petroleum hydrocarbons
  - E-Redox^{TM} (O) technology description
  - E-Redox^{TM} (O) case studies

E-Redox™

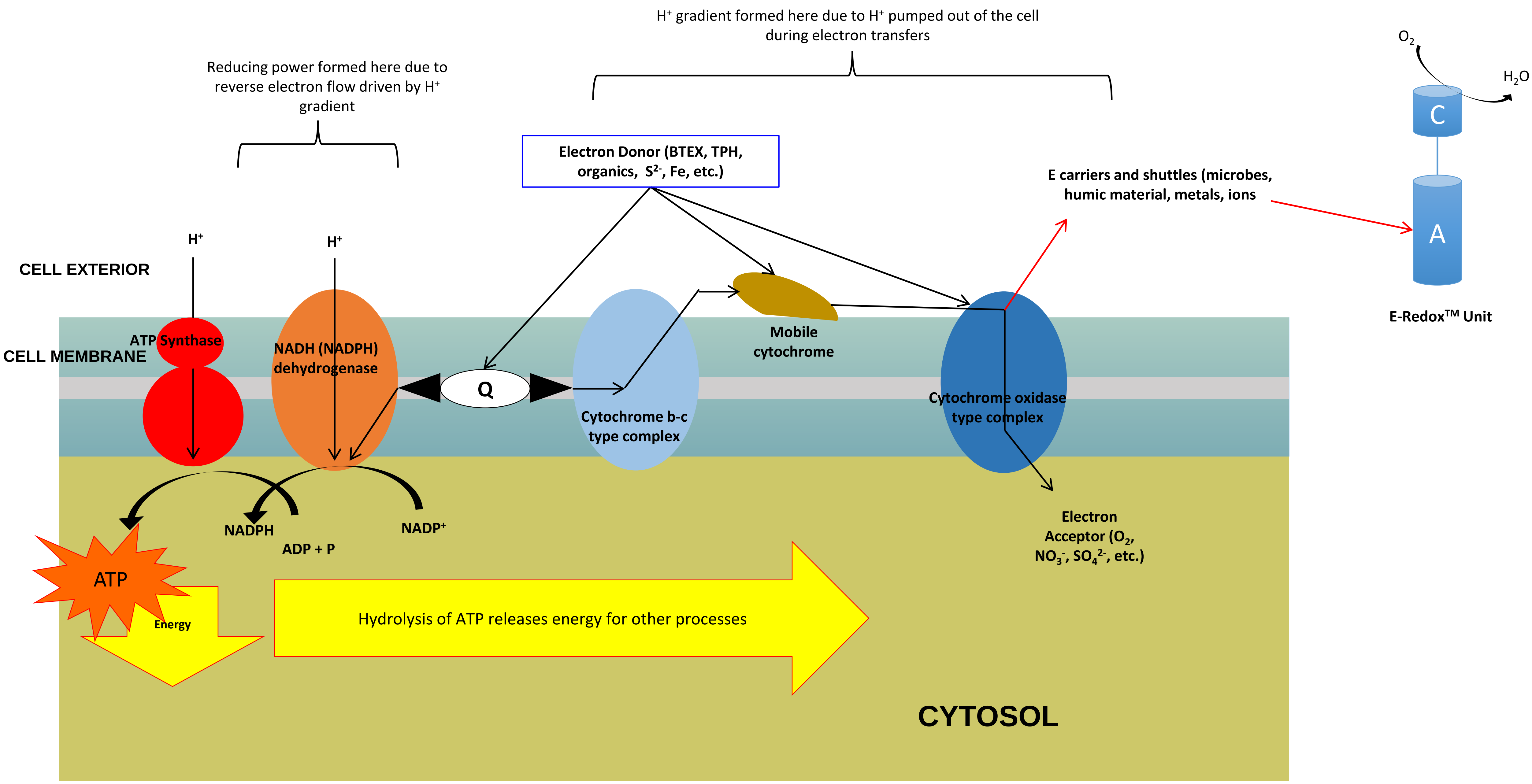
- E-Redox™ (O)-oxidation
  - Petroleum Hydrocarbons
  - BTEX
  - Other VOCs, SVOCs
- E-Redox™ (I)-reduction, desorption
  - PAHs?
  - Chlorinated Solvents
  - Nitrate/Nitrite, Perchlorate
  - PCBs
  - Nitro-aromatic compounds

E-Redox^{TM} (O)

Biodegradation of Petroleum Hydrocarbons

- Capable microorganisms (e.g., bacteria, species and populations)
- Organic compounds (e and c source) and bioavailability
- Nutrients
  - Macro-nutrients: nitrogen, phosphorus…
  - Micro-nutrients: trace metals…
- Electron Acceptors
  - O_2, NO_3^-, SO_4^{2-}, Fe^{3+}, organics, CO_2…
- Electron transfer – bio-oxidation

E-Redox™(O)



H+ gradient formed here due to H+ pumped out of the cell during electron transfers
Reducing power formed here due to reverse electron flow driven by H+ gradient
O2
H2O
C
A
E-RedoxTM Unit
Electron Donor (BTEX, TPH, organics, S2-, Fe, etc.)
E carriers and shuttles (microbes, humic material, metals, ions
H+
H+
CELL EXTERIOR
CELL MEMBRANE
ATP Synthase
NADH (NADPH) dehydrogenase
Q
Cytochrome b-c type complex
Mobile cytochrome
Cytochrome oxidase type complex
Electron Acceptor (O2, NO3-, SO42-, etc.)
NADPH
ADP + P
NADP+
ATP
Energy
Hydrolysis of ATP releases energy for other processes
CYTOSOL

Benzene Biodegradation Vs. Different TEAs

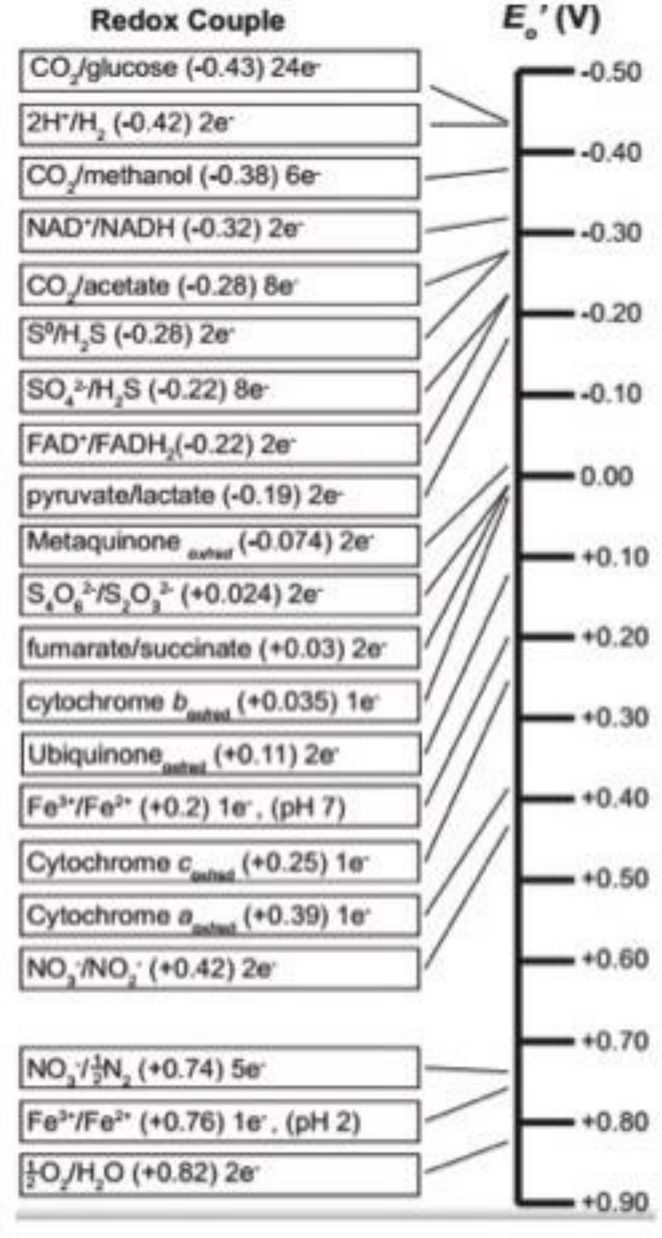
Aerobic: $C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$
$\Delta G = -3069$ kJ/mol

Denitrification: $C_6H_6 + 6NO_3^- + 6H^+ \rightarrow 6CO_2 + 3N_2 + 6H_2O$
$\Delta G = -2895$ kJ/mol

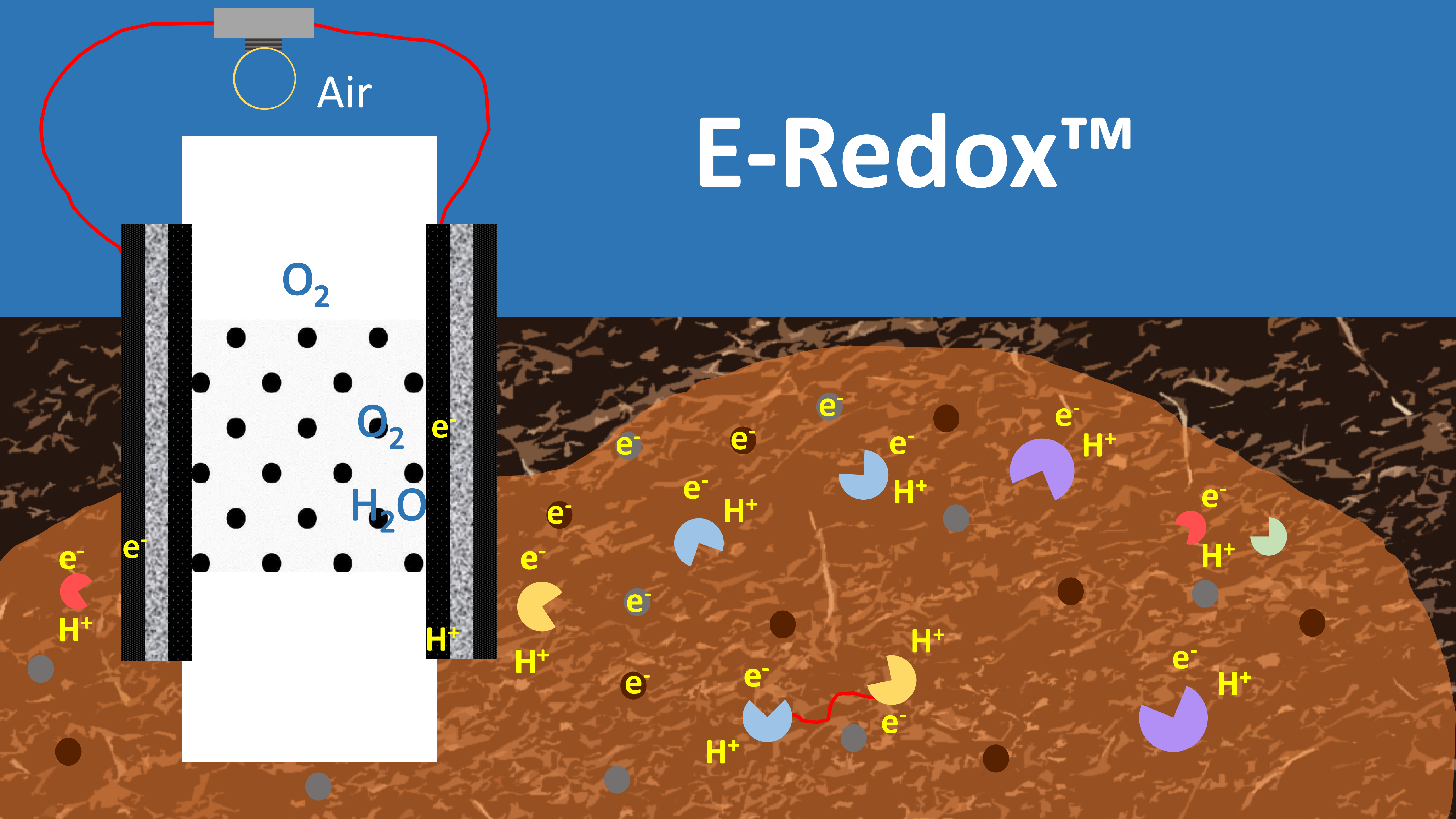
Iron-reduction: $C_6H_6 + 30Fe(OH)_3 + 60H^+ \rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$
$\Delta G = -492$ kJ/mol

Sulfate-reduction: $C_6H_6 + 3.75SO_4^{2-} + 7.5H^+ \rightarrow 6CO_2 + 3.75H_2S + 3H_2O$
$\Delta G = -116$ kJ/mol

Methanogenesis: $C_6H_6 + 4.5H_2O \rightarrow 3.75CH_4 + 2.25CO_2$
$\Delta G = -29$ kJ/mol

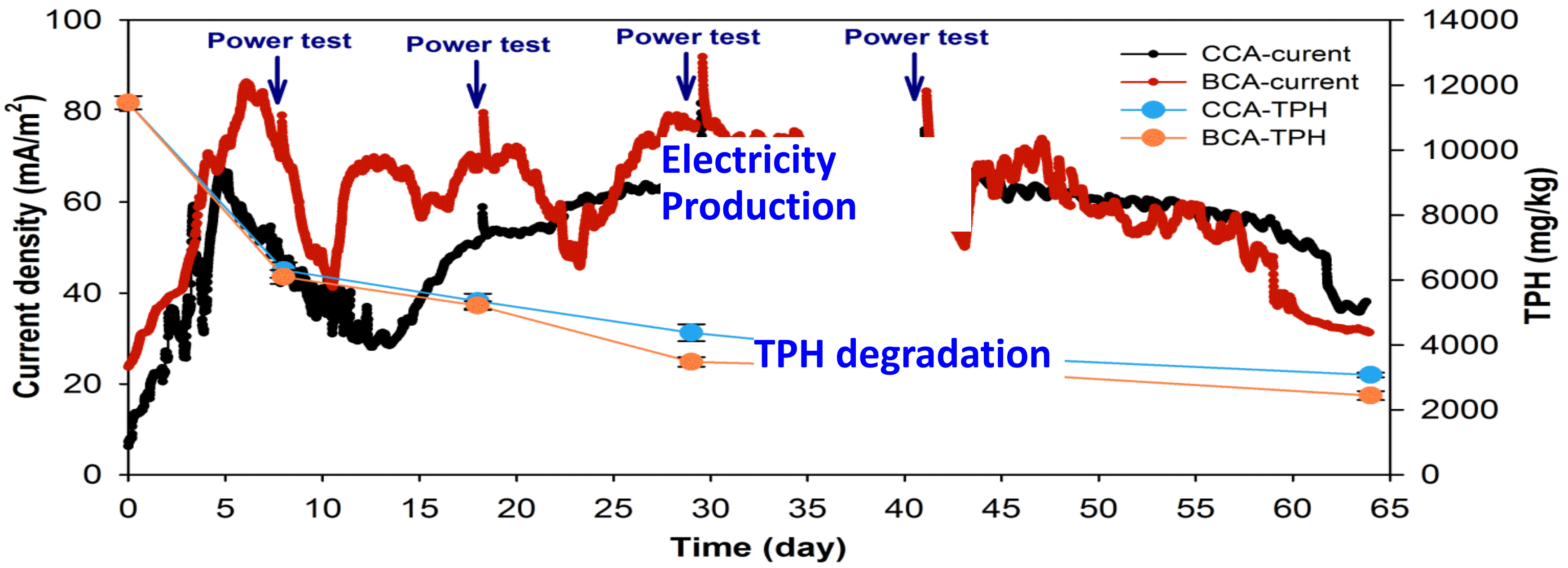


E-Redox™



Benzene Biodegradation Rates (with nutrient amendments)

E-Redox^{TM}: 585 ug/L/day
Aerobic: 400 ug/L/day
Denitrifying: 251 ug/L/day
Sulfidogenic: 189 ug/L/day
Methanogenic: lowest to negligible



Electricity generated in the E-Redox^{TM} system serves as an indicator for biodegradation and provides a weak power source (~mA/m^2)

(Lu et al. Environ. Sci. & Technol., 2014)

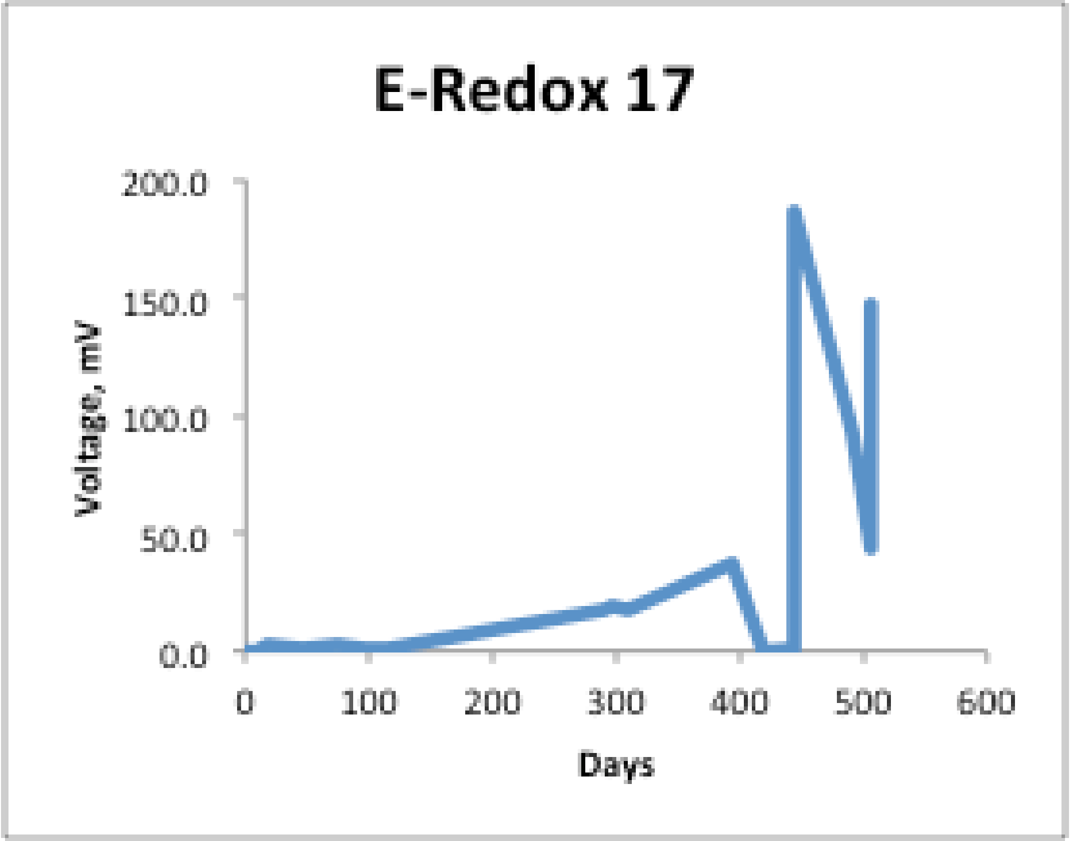
CASE STUDY 1

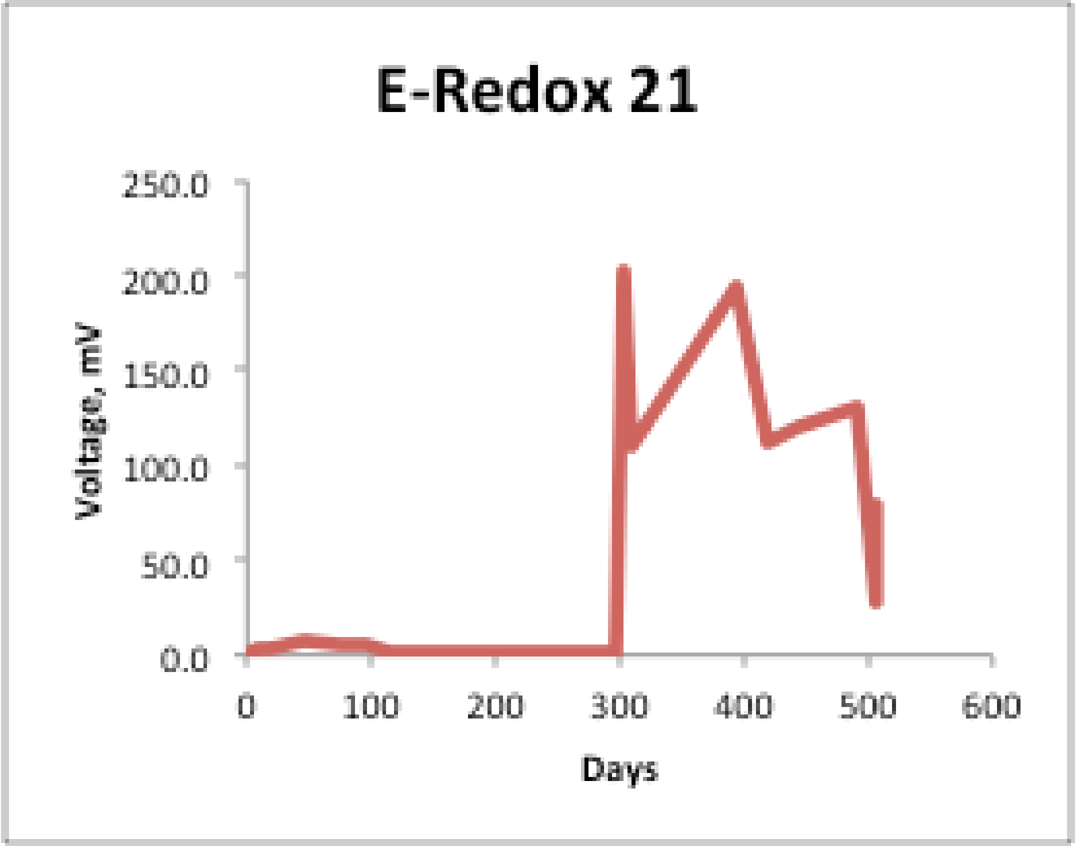
- Location: fuel station, ~2 street blocks area, Denver, CO
- Main COC: benzene in groundwater
- Lithology: silty to clayey sand in the vadose zone, clay in the saturated zone starting 15 ft bgs
- Other Site Notes
  - Groundwater flow rate estimated at 0.04 ft/day
  - Past remediation efforts involved injections of chemical oxidants and/or carbon-based materials
- Project Objectives

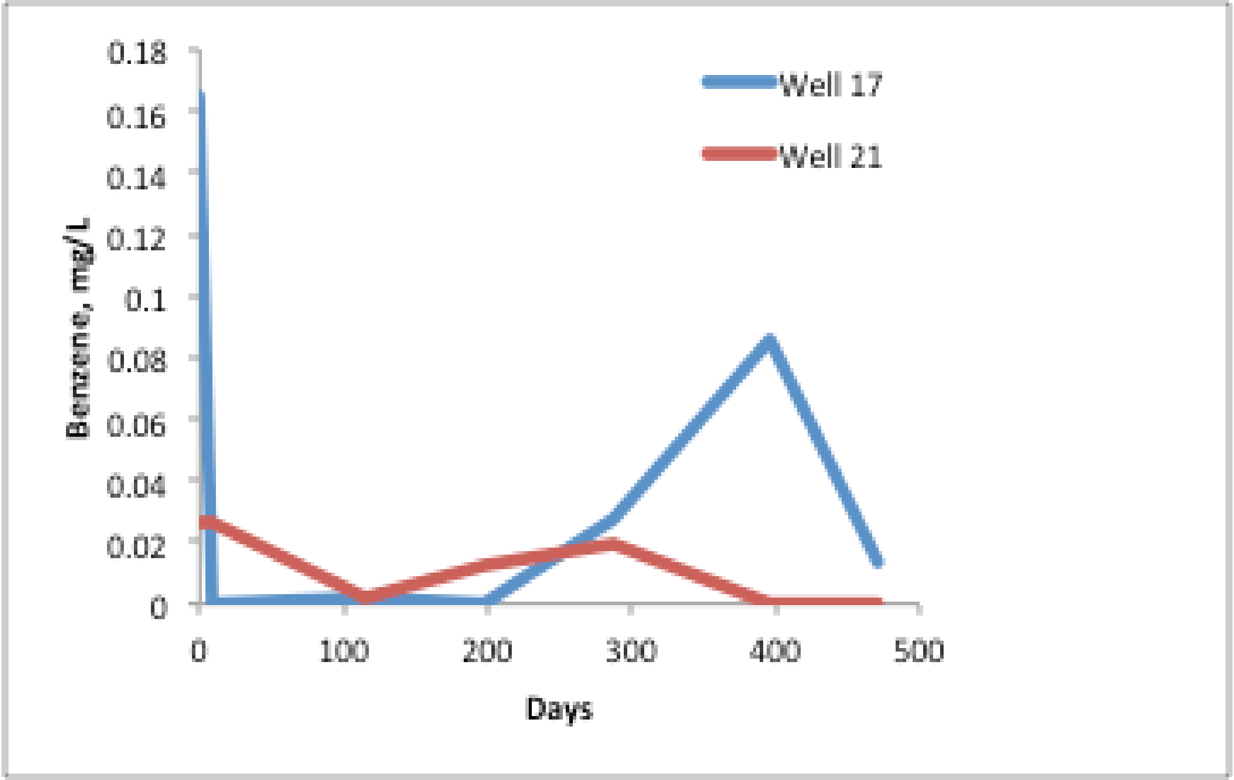
  Implementation of E-Redox^{TM} technology for *in situ* degradation of benzene and other hydrocarbon contaminants in the groundwater

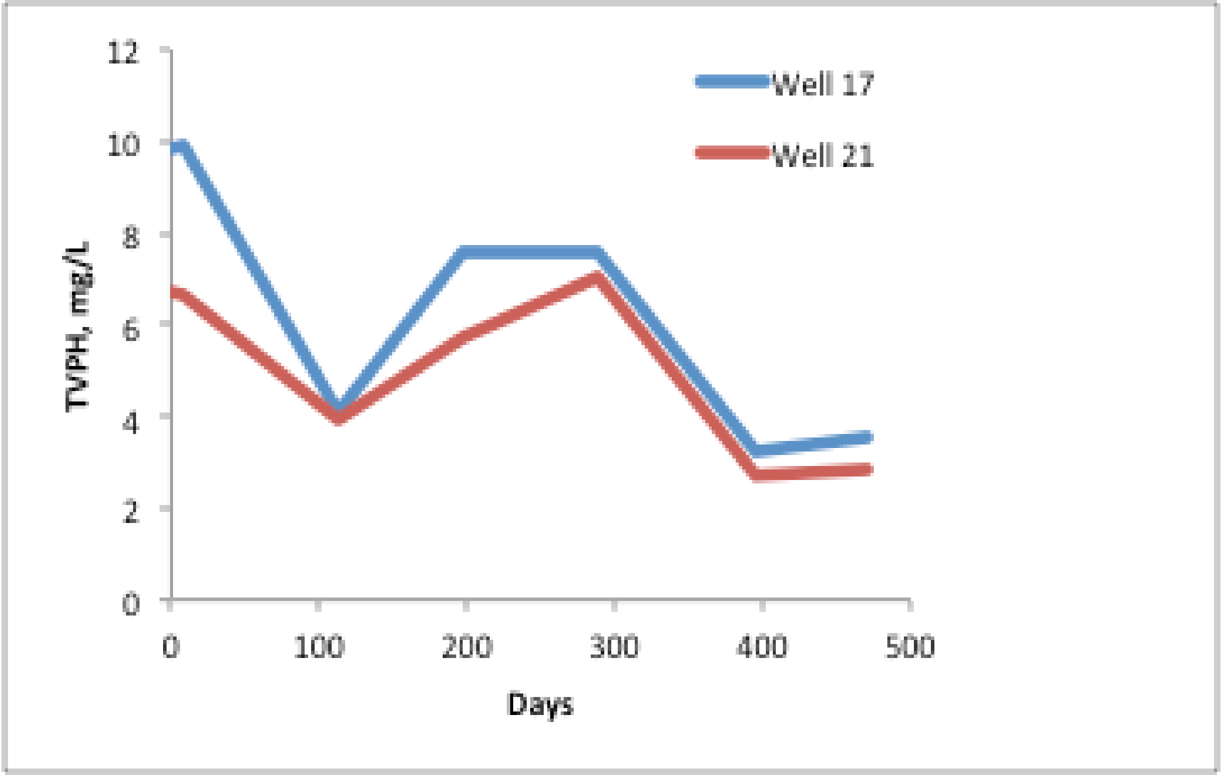
- Conducted field pilot test of two E-Redox™ units at the end of the 3rd Quarter 2015
- Expanded to full-scale implementation with eight additional E-Redox™ units (10 total units)
- E-Redox™ installations in four areas
  - 4 units in the fuel station source area
  - 2 units in a residential/commercial alley
  - 2 units along street in residential area (monitoring wells 7-11 ft from E-Redox™ wells)
  - 2 units by a restaurant parking lot
- Evaluated performance and operations
  - Maintenance and modifications required due to fluctuations in depth-to-water


TEST
WELL

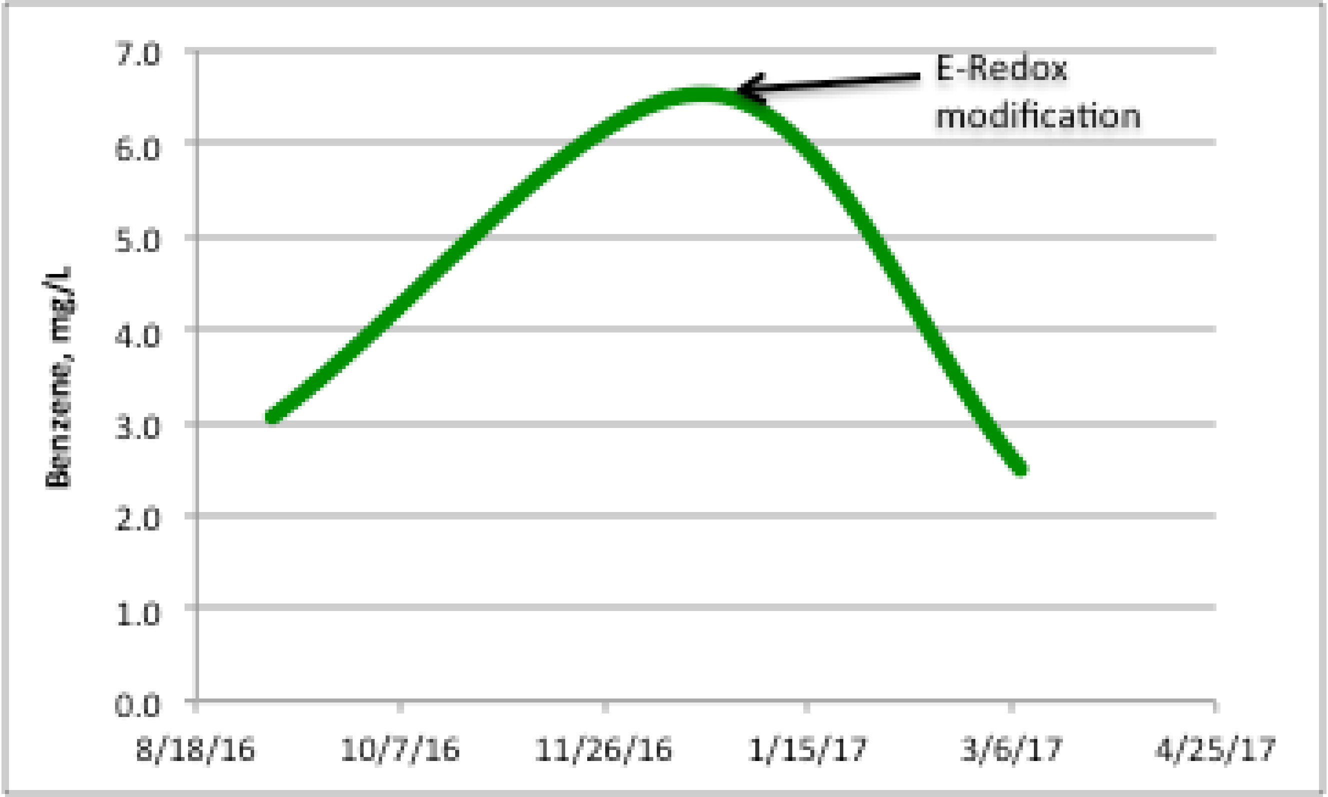

E-Redox 17
200.0
150.0
100.0
50.0
0.0
Voltage, mV
0
100
200
300
400
500
600
Days


E-Redox 21
250.0
200.0
150.0
100.0
50.0
0.0
Voltage, mV
0
100
200
300
400
500
600
Days


0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Benzene, mg/L
0
100
200
300
400
500
Days
Well 17
Well 21


12
10
8
6
4
2
0
TVPH, mg/L
0
100
200
300
400
500
Days
Well 17
Well 21

- Significant groundwater level shift during the 4th quarter 2016 caused blanket increase in benzene levels onsite
- E-Redox™ units modified at the site to accommodate groundwater level fluctuations
- Overall decrease in benzene level throughout the site since



Case Study 1 Summary

- Benzene biodegradation was substantially enhanced (5x of control NA)
- For the two wells started in 2015, benzene concentrations decreased to and maintained at lower concentrations when comparing 4th Quarter measurements for 2015 and 2016
- ROI measured > 11 ft
- Modifications to E-Redox^{TM} design minimize the influence from fluctuating groundwater levels

CASE STUDY 2

- Location: former petroleum plant facility, Lafayette, CO
- Main COC: benzene in groundwater
- Lithology: sandy clay to clay in the vadose zone, silty sand in the saturated zone underlain by sandstone 12-30 ft bgs
- Other Site Notes
  - 375 cubic yards of soil excavated in 2007
  - Implementation area surrounded by wells with ORC socks
- Project Objectives

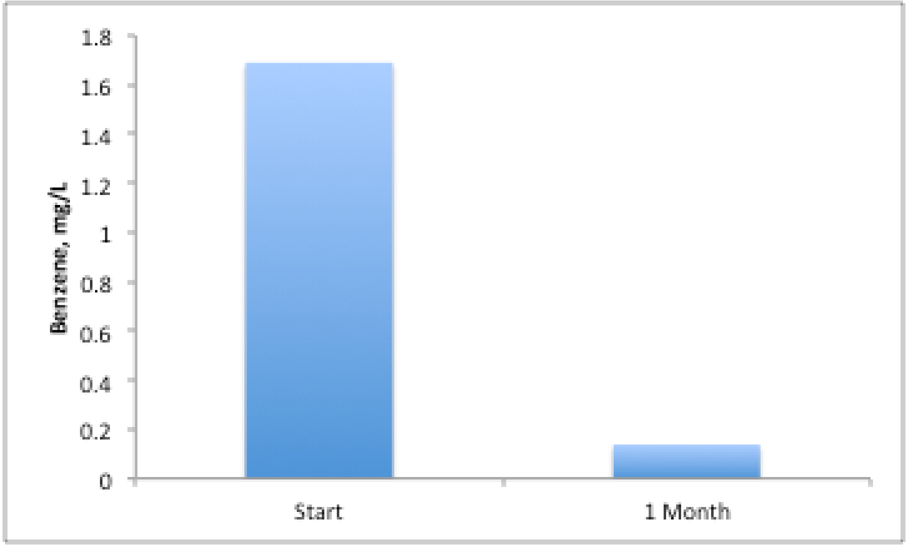
  Field implementation of the E-Redox^{TM} technology for *in situ* degradation of benzene and other hydrocarbon contaminants in the groundwater

- Field pilot of single E-Redox™ unit started first quarter 2017
- Other remedial methods include surface application of nutrients solid and ORC socks in various locations
  - DO and ORP measurements at monitoring wells near the E-Redox™ well indicate little influence of the ORC socks

Date	Voltage, mV
1/16/17	2.7
2/8/17	25.1
3/28/17	64.9
4/12/17	573

- Modification applied to the E-Redox™ unit to ensure continued performance even with changes to groundwater level
- Continue to monitor unit voltage and benzene of the surrounding monitoring wells
- Monitor DO and ORP of surrounding monitoring wells

92% decrease in benzene concentration after one month of operation



Date	Benzene, mg/L	Toluene, mg/L	Ethylbenzene, mg/L	Xylenes, mg/L	TVPH, mg/L
12/23/16	1.69	0.033	1.63	6.14	47.3
2/16/17	0.138	0.001	0.187	0.676	4.72

E-Redox^{TM} (O) Summaries

- ✓ E-Redox^{TM} technology significantly enhances biodegradation of BTEX, TPH-GRO, TPH-DRO and other petroleum hydrocarbons, e.g., >5x rate for benzene in GW, >10x for TPH-DRO in sediments
- ✓ Modular, sustainable, no energy input, almost no maintenance
- ✓ Voltage generation within the E-Redox^{TM} device correlates with active biodegradation activities and can serve as a remote monitoring parameter
- ✓ E-Redox^{TM} works best when matrix contains abundant water, conductivity is high, and electron acceptor is deficient
- ✓ E-Redox^{TM} can be a stand-alone tool or synergistically used with other remedial technologies (e.g., biostimulation, bioaugmentation, nutrients addition, carbon injection, chemOx, SVE, etc.)

Thank you

Song Jin
sjin@aetecs.com
sjin@uwyo.edu