E-Redox (Electrons and Chemicals), Bugs, and Other Remedies

Song Jin, PhD., CHMM (sjin@aetecs.com)
Joseph Aiken, REP

Advanced Environmental Technologies;
JA Environmental Consulting, LLC
Fort Collins, Colorado

June 12, 2023

Presenters

- **Song Jin, Ph.D., CHMM**
  - Ph.D. Environmental Microbiology and Biogeochemistry
  - 25+ Years of Experience
    - Applied R&D in remediation and engineering at MWH, Western Research Institute, TriHydro
    - Adjunct prof at U of Wyoming since 2008; Founder of AET 2009
  - 38 patents including E-Redox and Ginate technologies
  - 98 peer-review and 150+ professional conference publications
  - 60+ full scale applications of E-Redox technology
- **Joseph W. Aiken**
  - BS Natural Resource Management
  - 40+ years of experience
    - 35 years environmental consulting – Woodward Clyde, ENSR, Mactec, IRG
    - JA Environmental Consulting, LLC and AET
      - REP No. 61
      - Real estate license
  - 1990 patent for chlorinated solvent remediation technology
  - Numerous environmental assessments and remediation projects; for example:
    - Lowry AFB remediation
    - Dry cleaners, gas Stations, landfills, refineries, brownfields, and impaired properties transaction…..

Advanced Environmental Technologies (AET)

- Minority-owned small business in Fort Collins, Colorado
- Technology innovator and implementer
- Leading Technologies
  - E-Redox for remediation (patents 11447429B2, 10647581, 10406572, 9045354B2, 7858243B2, 9545652B2)
    - E-redox-I for reductive degradation (e.g., USACE RFP for Fort Carlson and Offutt AFB
    - E-Redox-O for remediation (e.g, CO OPS remedial tool list)
  - Ginate soil enhancer/plant food/organic amendment
    - Raises soil quality and enhances “soil microbiome”
    - OMRI listed organic product/fertilizer (e.g., golf courses in Denver, Fort Collins, and park in Timnath)
- Team approach to provide comprehensive service
- 60+ field applications of E-Redox since 2014

ACKNOWLEDGEMENTS

- Mr. Paul Fallgren – AET
- Mr. Kylan Jin – AET (intern), UCLA
- Mr. Nick Santiago – AET
- Professor Jason Ren – Princeton University

I. Case studies of E-Redox®-I for reductive remediation (e.g., chlorinated solvents, perchlorate, and PFAS in GW)

II. Case studies of E-Redox®-O for oxidative remediation (e.g., petroleum hydrocarbons)

III. Mechanisms of E-Redox®-I and E-Redox®-O technologies

IV. BioRemeter™ for real-time in-situ monitoring of biodegradation/NSZD/MNA

E-Redox®

Boosts bio(oxidative)degradation

Abiotic redox reactions for COC destruction and desorption

E-Redox® ($O_{\text{-oxidation}}$)

Typical Petroleum Hydrocarbons (e.g., BTEX)

Some PAHs

Other VOCs, SVOCs

Desorption of mass into water phase

E-Redox® ($I_{\text{-Reduction}}$)

Certain Oxyanionic Metals (e.g., CrVI)

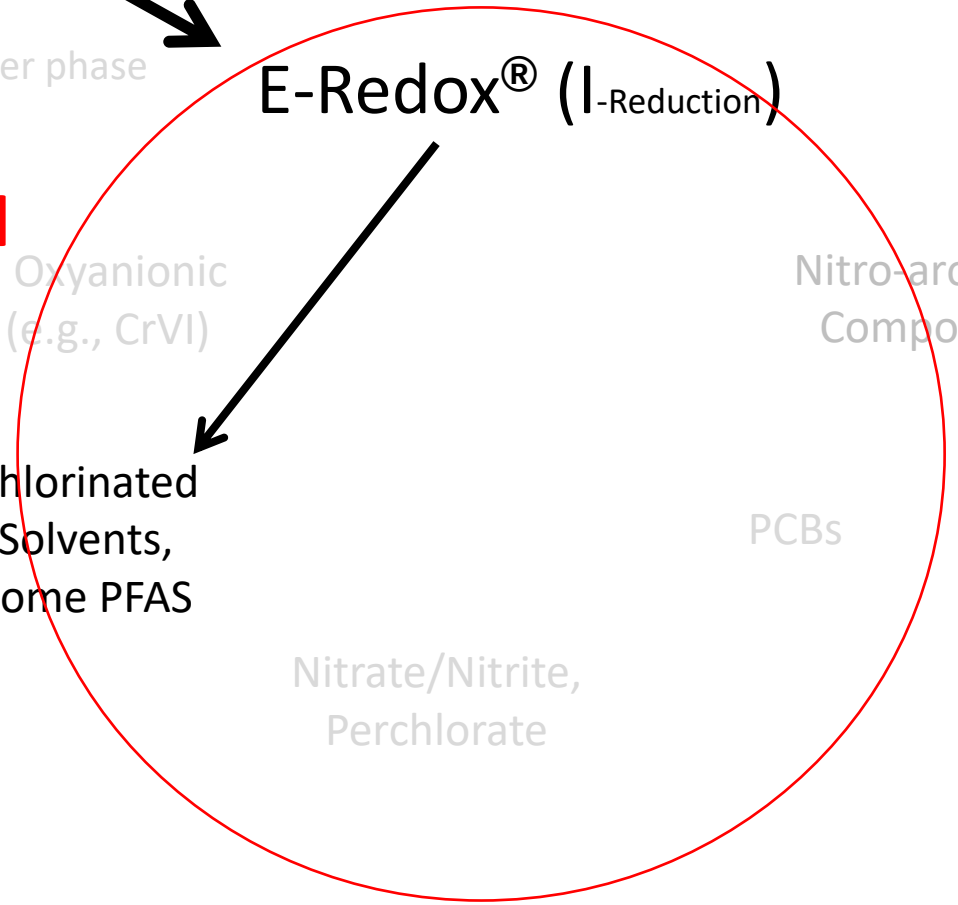
Chlorinated Solvents, Some PFAS

Nitrate/Nitrite, Perchlorate

PCBs

Nitro-aromatic Compounds

E-Redox®



A “static” electrical field in the matrix (including tight formations) and a perpetual source of electrons for abiotic reductive degradation

Desorption of contaminants that also benefits biological dechlorination

Sets and maintains low redox conditions

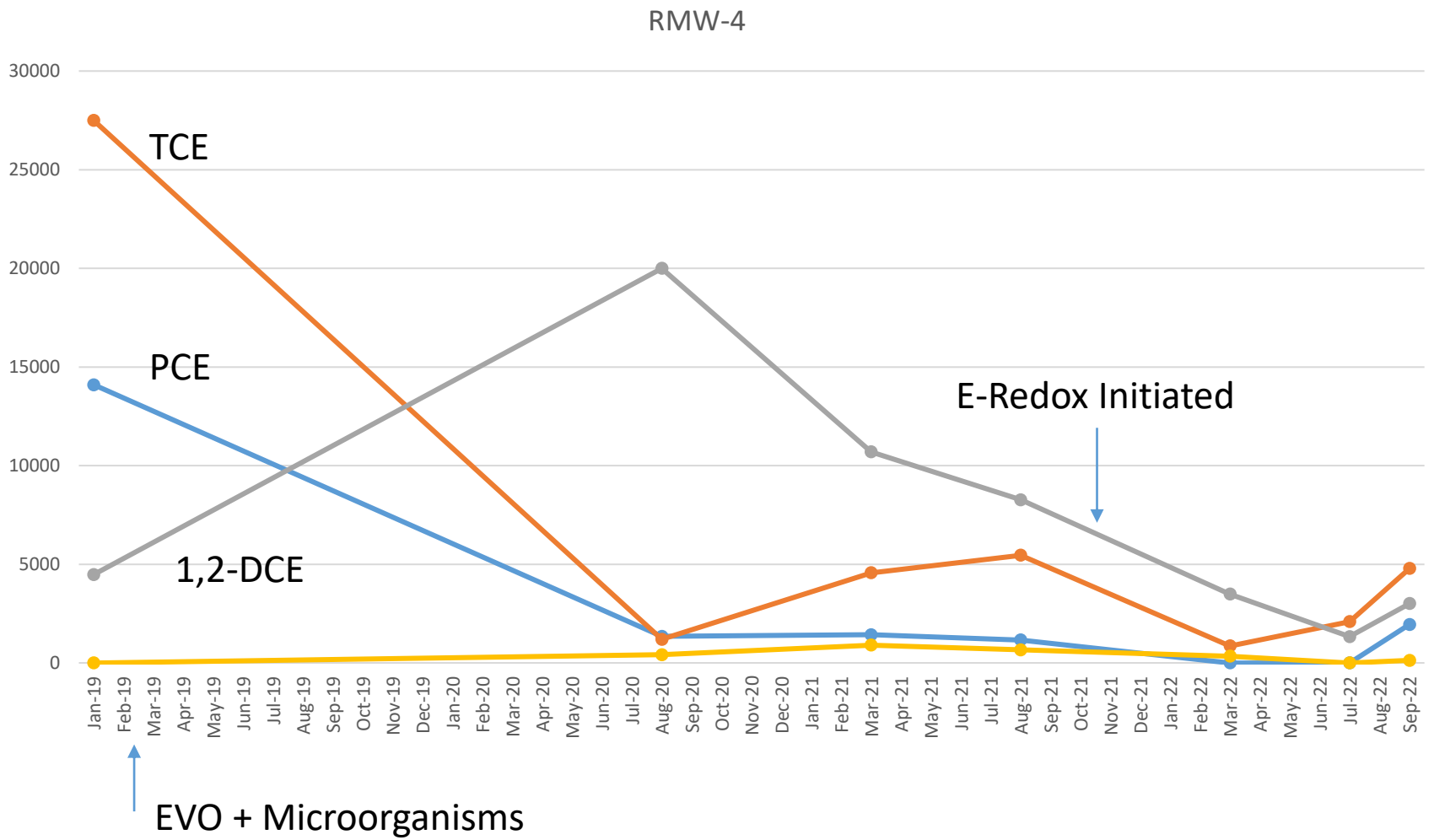
FORMER DRY CLEANER SITE ON EAST COLFAX AVENUE, DENVER, CO

Location: Redeveloped retail site/former dry cleaner (Denver, CO)

Contaminated Matrix: Groundwater

Primary Contaminants of Concern: Tetrachloroethene (PCE), trichloroethene (TCE) and 1,2-dichloroethenes (DCEs)

Remedial Solution: *In situ* degradation of PCE, TCE, and DCEs in groundwater by using E-Redox®-I technology


RMW-4
30000
25000
20000
15000
10000
5000
0
TCE
PCE
1,2-DCE
E-Redox Initiated
EVO + Microorganisms
Jan-19
Feb-19
Mar-19
Apr-19
May-19
Jun-19
Jul-19
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Sep-22

FORMER SHOPPING CENTER, NORTHGLENN, CO

Location: Northglenn, CO

Site History: Former shopping center with dry cleaners

Site Owner: Northglenn Urban Renewal Authority (NURA)

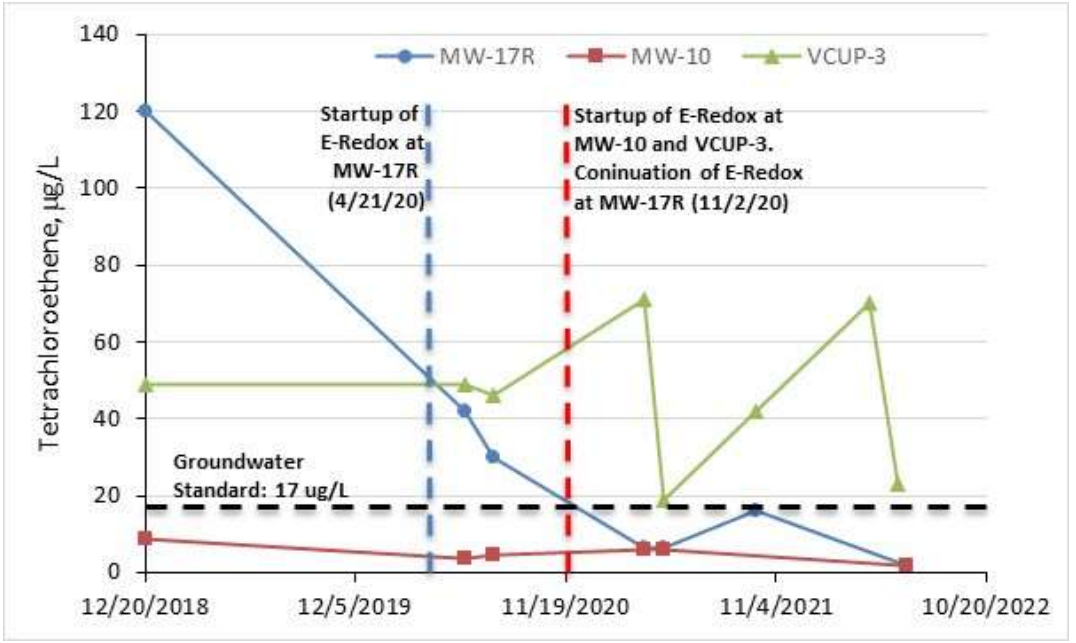
Main Contaminant: Tetrachloroethene (PCE)

Contaminated Matrix: Groundwater (alluvial, clay)

Remediation History: ISCO injections

Remedial Issues: Bedrock channels and DNAPL settling in bedrock depressions in residential area

Remedial Solution: E-Redox®-I technology



E-Redox®-I units were decommissioned after <1-yr operation. The site was closed with a No Action Determination (NAD) granted by the Colorado Department of Public Health and Environment in September 2022

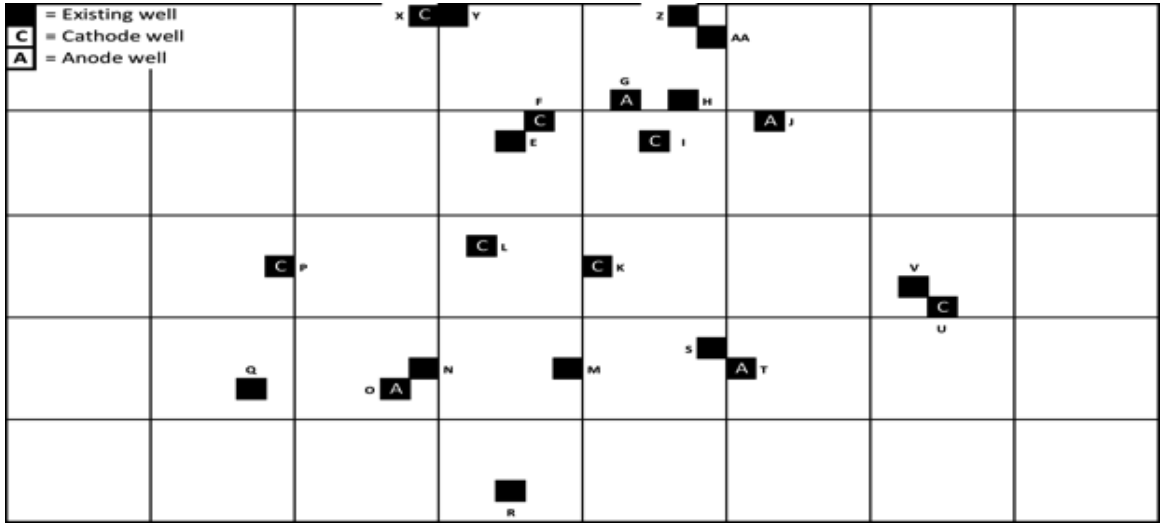
FORMER AHESIVES PRODUCTION PLANT
(under post-remedial monitoring)

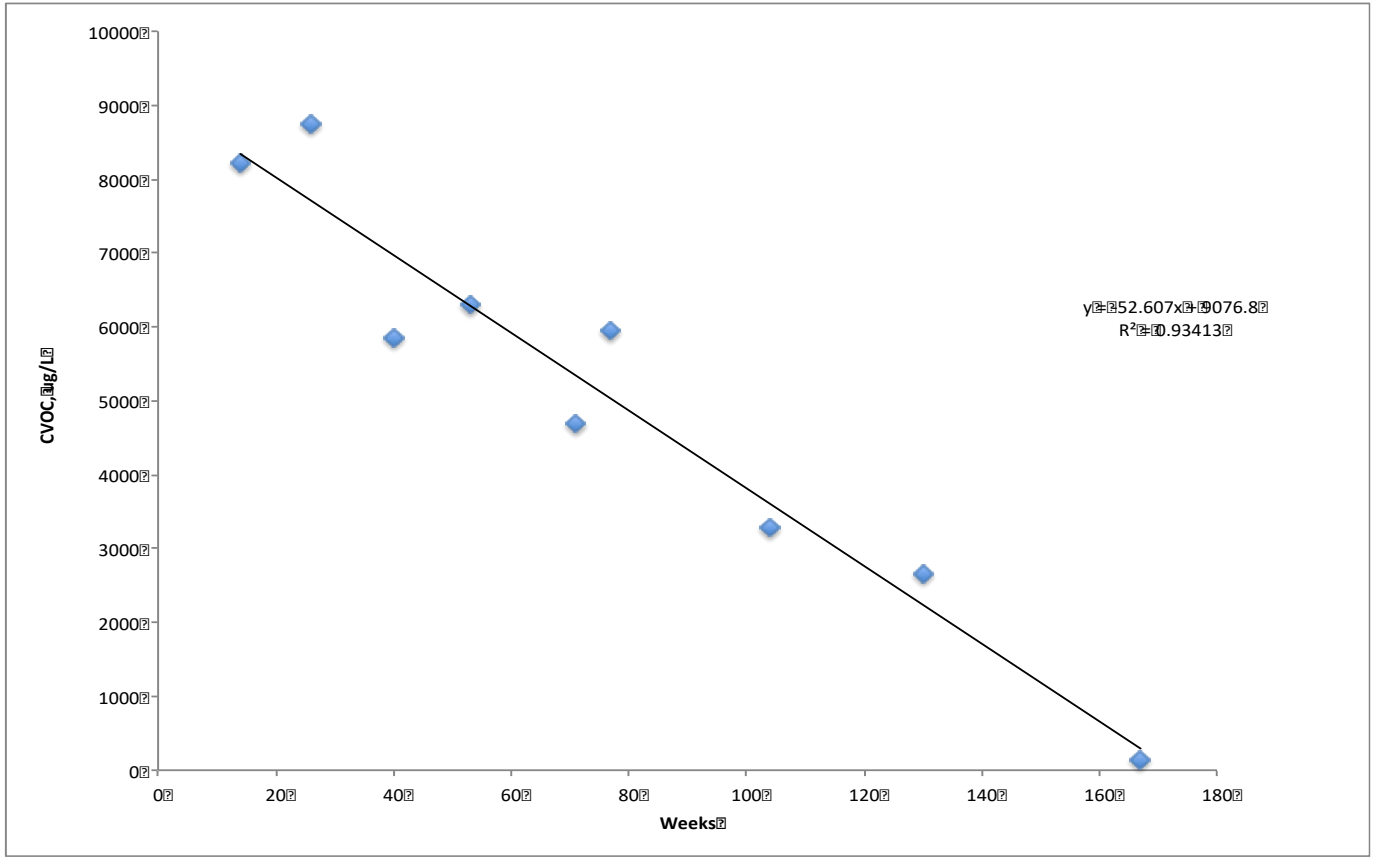
Location: Former adhesives production plant near Charleston, SC

Contaminated Matrix: Groundwater and saturated soil

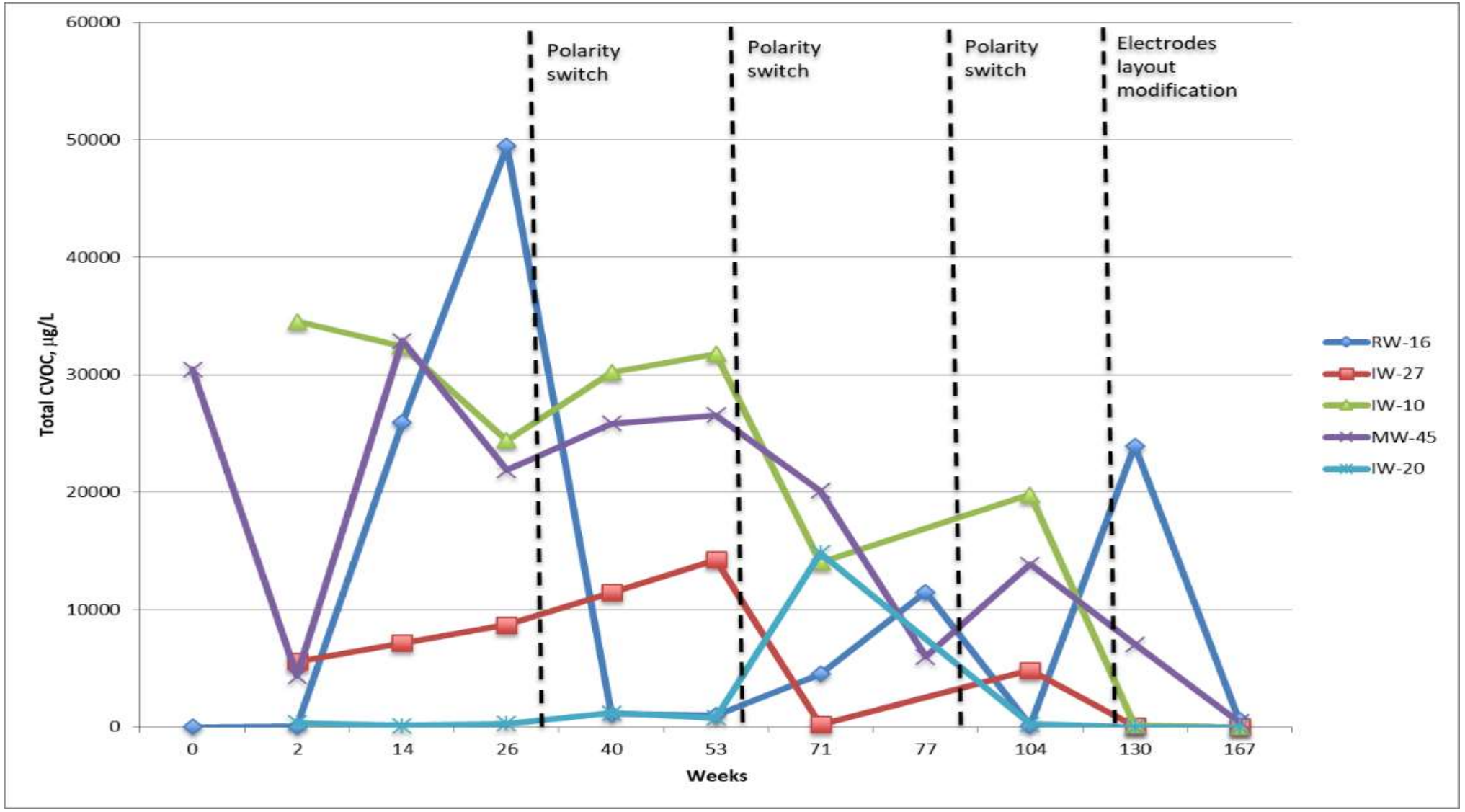
Primary Contaminants of Concern: Chlorinated VOCs (TCE, DCEs, vinyl chloride)

Remedial Solution: E-Redox®-I technology for *in situ* destruction and desorption/removal of chlorinated VOCs





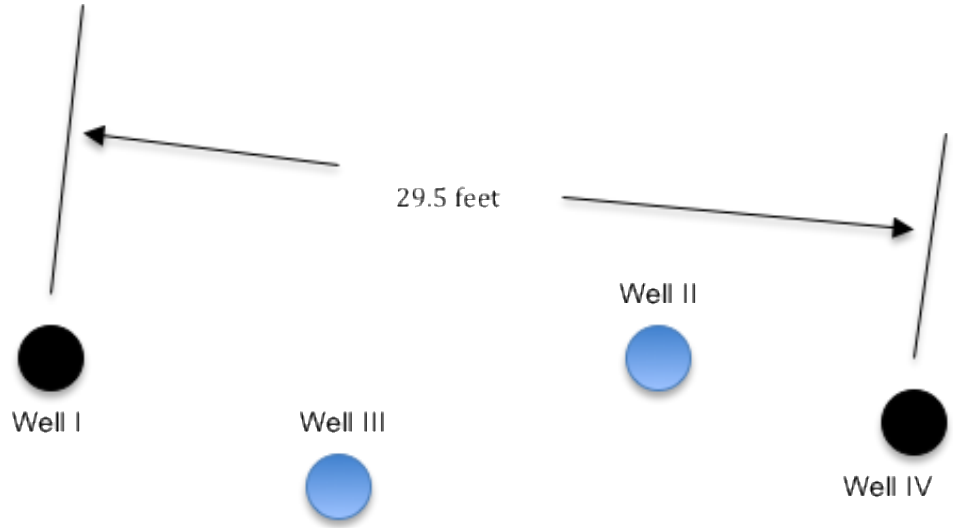
Total site-wide chlorinated volatile organic compounds (CVOC) concentrations



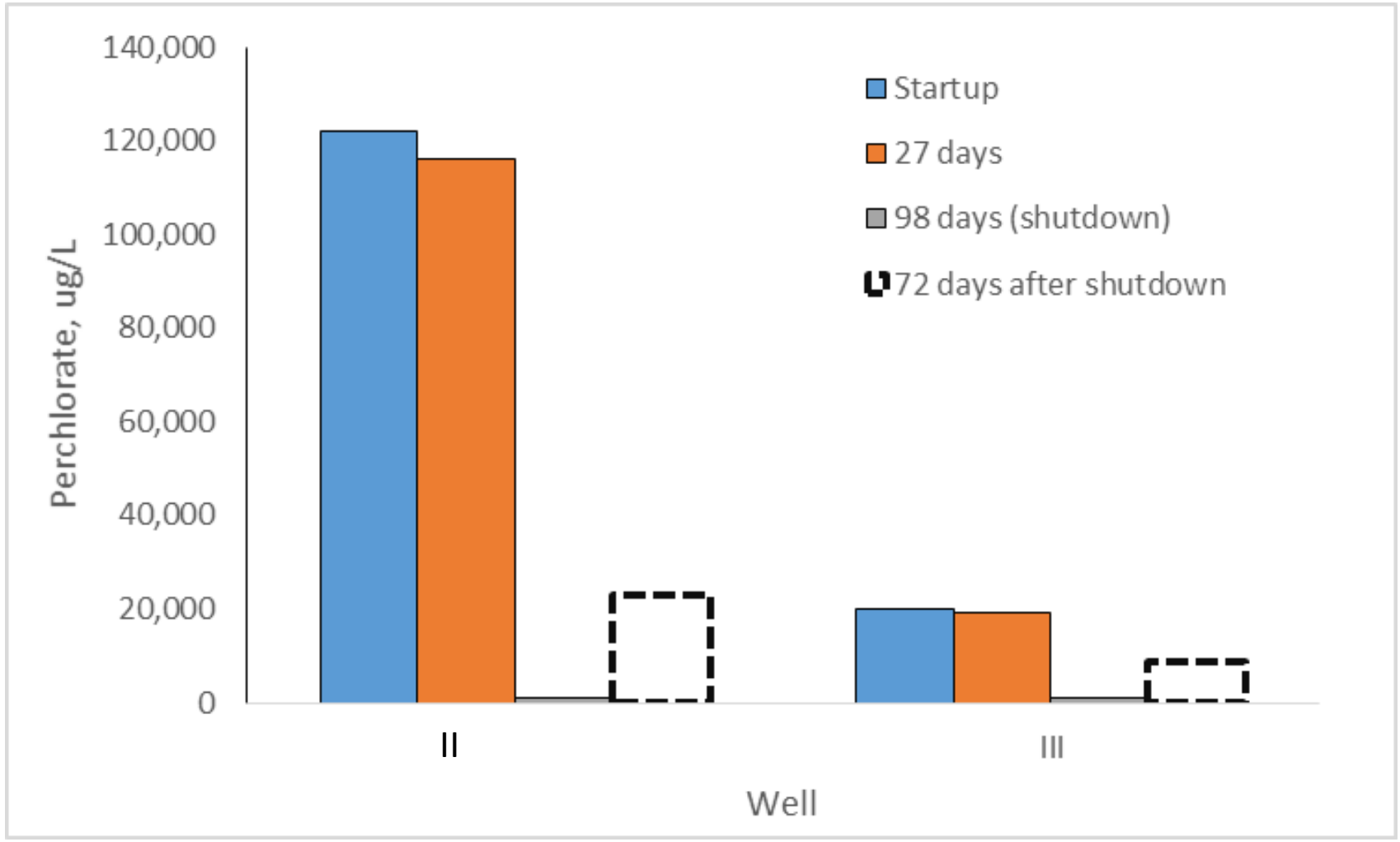
E-Redox®-I facilitated desorption-reduction for faster mass removal and degradation

Former Explosives Testing Site, San Bernardino, CA

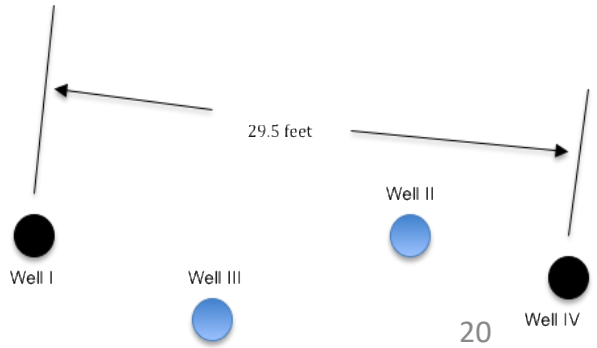
- Former explosives testing site
- Groundwater contaminants: primarily perchlorate
- Past remediation efforts not effective due to low-permeability of aquifer material (clay and shale)
- No municipal power access; solar cells were used for establishing a low-intensity electric field



E-Redox® field test site layout

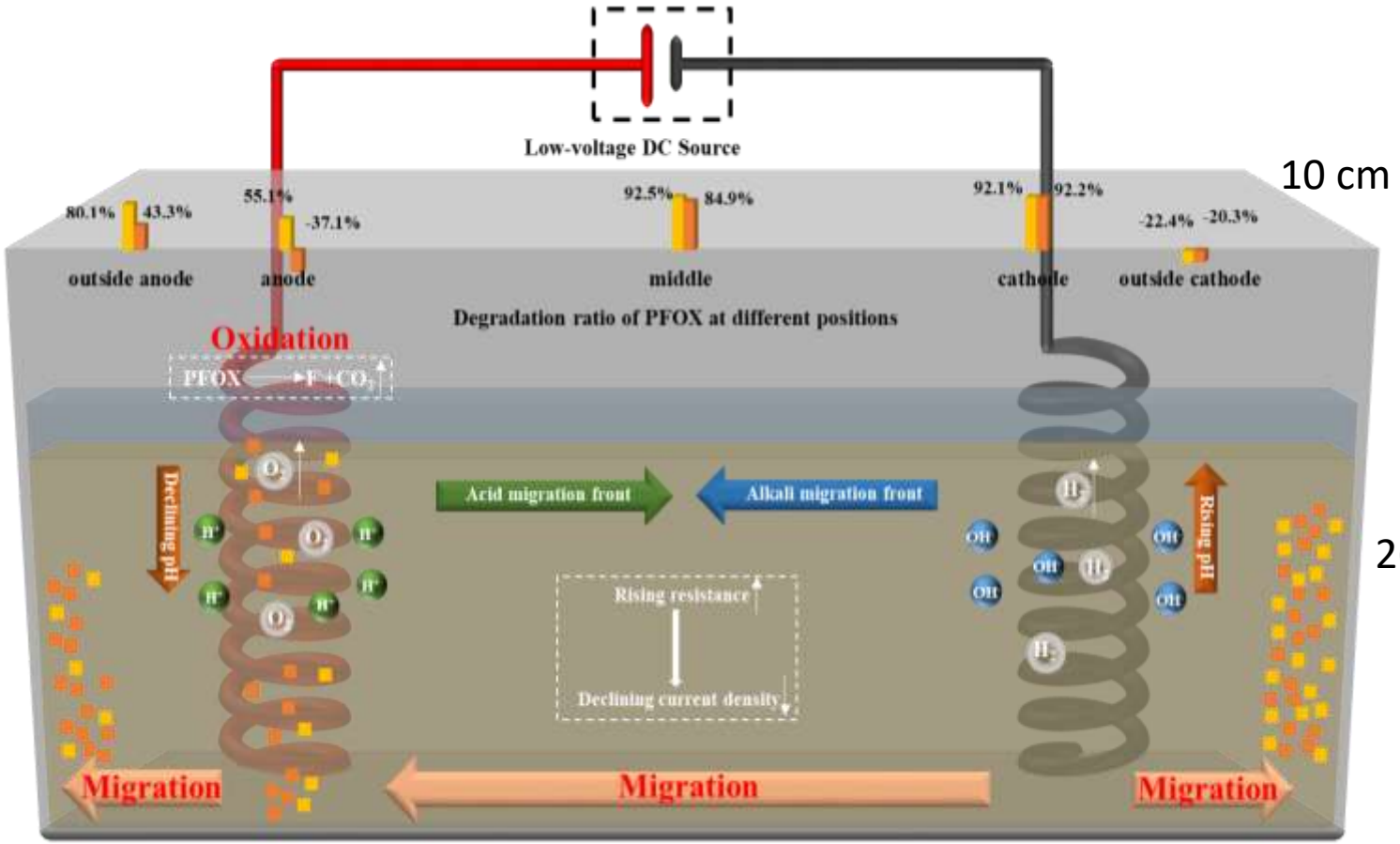


Perchlorate concentrations (98 days of field demonstration)



Bench Test:

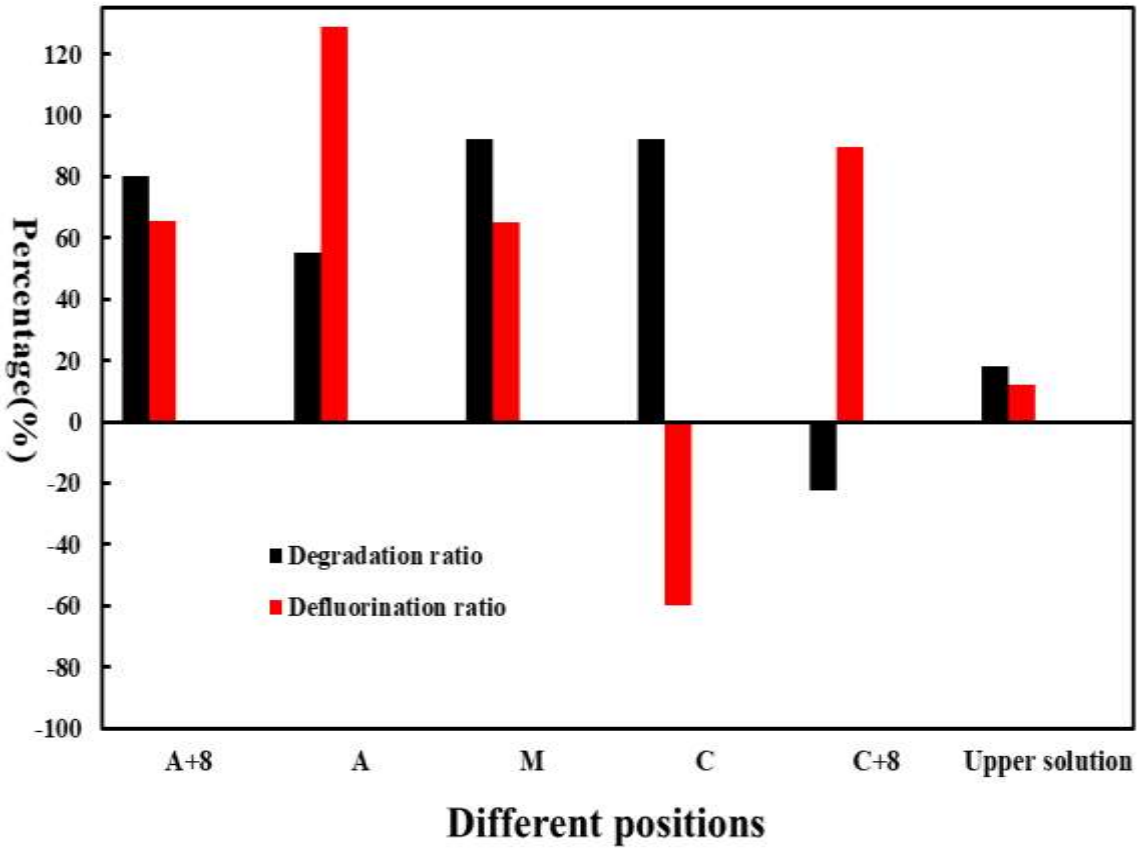
E-Redox for per- and polyfluorinated substances (PFAS, "forever compounds") destruction and desorption/mobilization



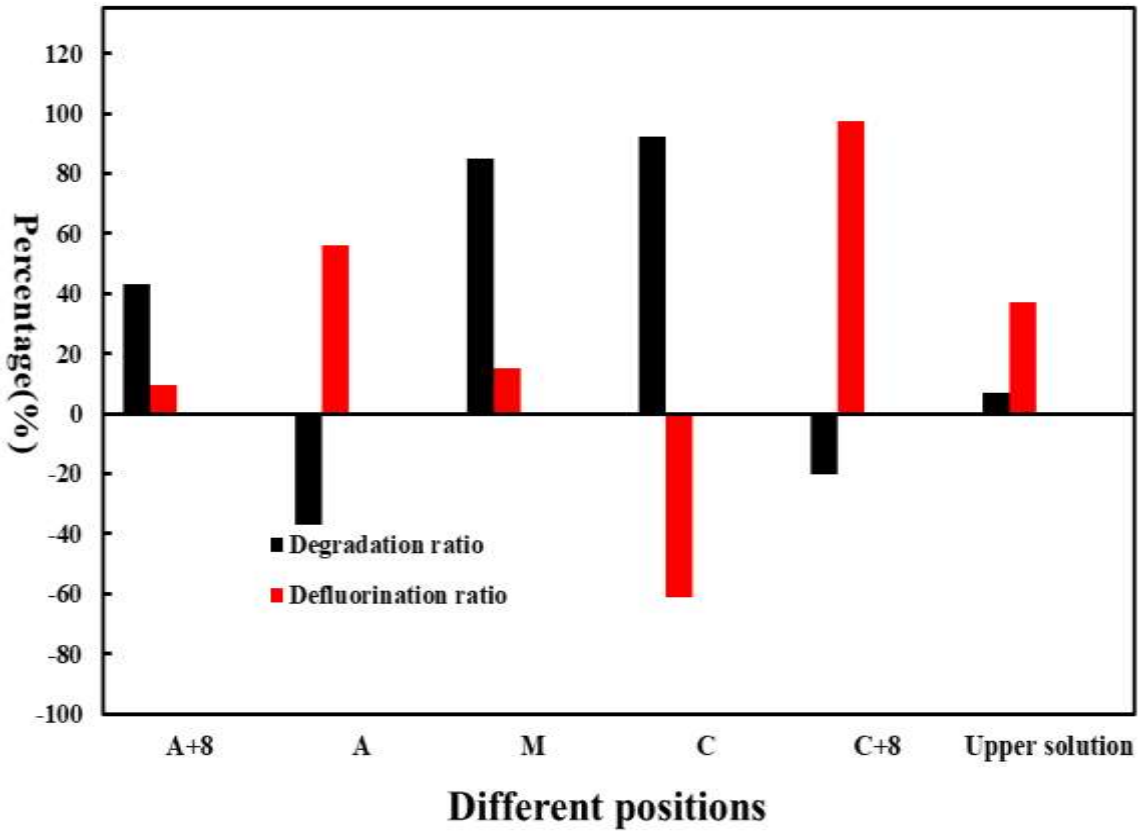
E-Redox-initiated destruction and migration of Perfluorooctanoic acid POFA (■) and perfluorooctane sulfonate PFOS (■) compounds in bench reactors

(Hou et al., 2022, *Chemosphere* 287) (perfluorinated butyric acid [PFBA], perfluoropentanoic acid [PFPeA], perfluorohexanoic acid [PFGxA], perfluoroheptanoic acid [PFHpA], perfluorooctanoic acid [PFOA, 98%]), perfluorohexane sulfonate [PFHxS] and internal standards (perfluorooctanoic acid internal standard [13C-PFOA, 98%] and perfluorooctane sulfonate internal standard [13C-PFOS, 98%])

PFOA



PFOS



A = Anode
C = Cathode
M = Middle
+8 = distance (8 cm)

Positive bar: PFAS degradation/defluorination%; negative bar: PFAS desorption/migration in%.

Total mass (10d): 51.7% of PFOA and 33% of PFOS destructed

44.7% and 23% defluorination mass balance, intermediates TBD

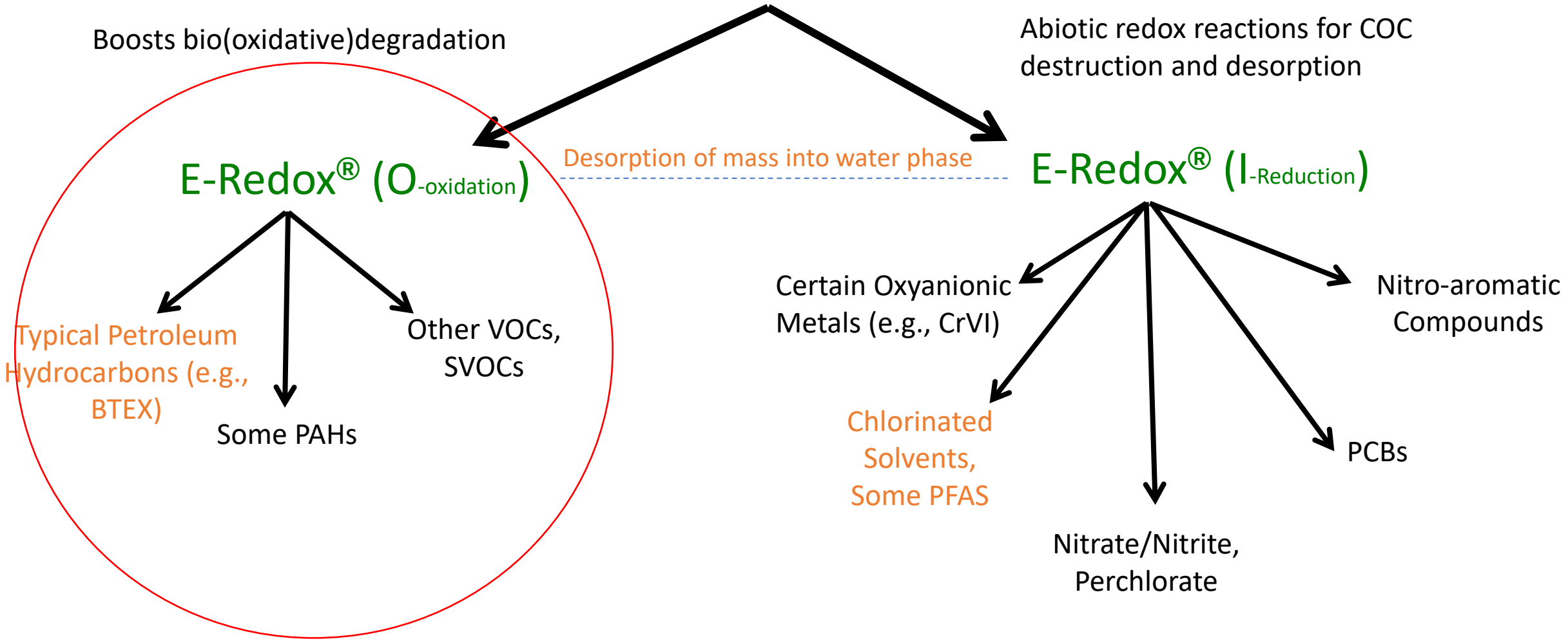
Desorption of PFAS observed

(Hou et al., 2022, *Chemosphere* 287)

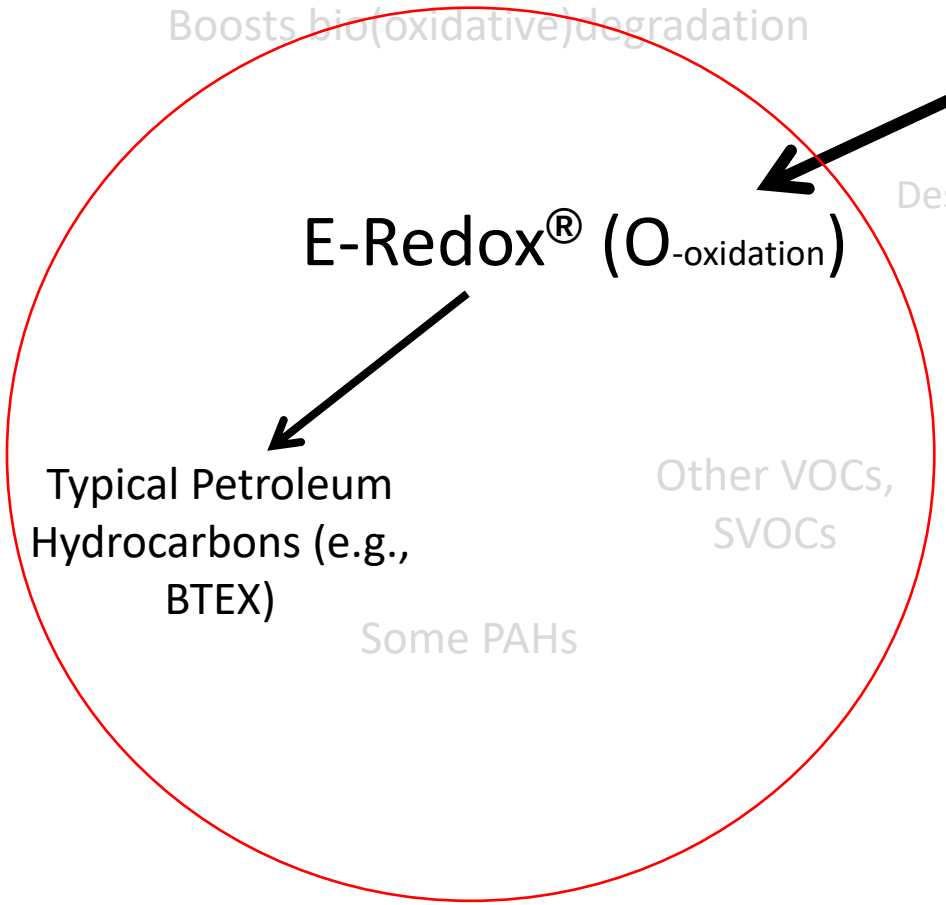
E-Redox® -I (Reduction) Highlights

- **IT WORKS IN CLAY as well**
- Initiates and sustains both **abiotic and biological degradations (dichlorination of CVOC and defluorination of PFAS)**
- **Desorption** of COCs (CVOC and PFAS) into the water for enhanced mass removal and destruction
- **ROI of 25-50 ft** (500-2,000 sf/unit); consumes minimum energy, convenient O&M, fits remote sites
- Integrates with other remediation technologies:
  - ZVI rejuvenation
  - Extends electron donor longevity
  - Rapidly establishes **low redox potential** condition for reductive remedies

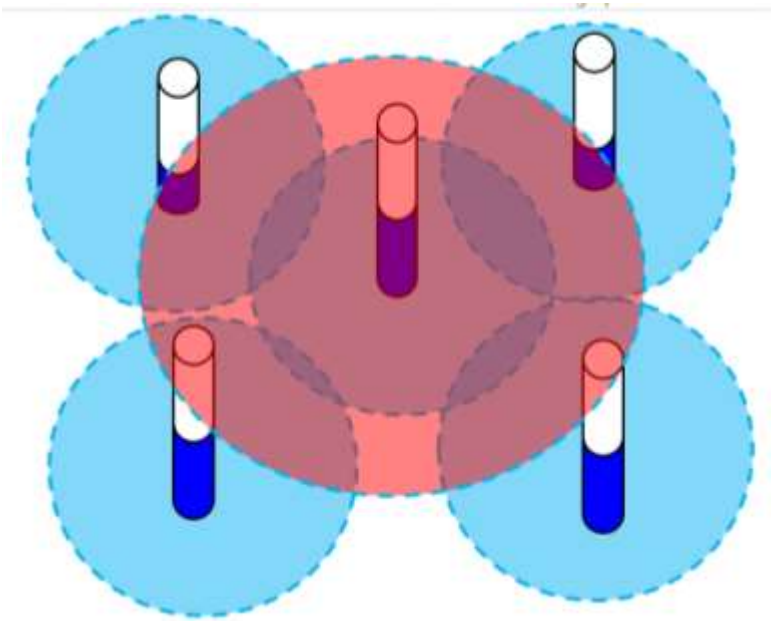
E-Redox®


Boosts bio(oxidative)degradation
Abiotic redox reactions for COC destruction and desorption
E-Redox® (O-oxidation)
Desorption of mass into water phase
E-Redox® (I-Reduction)
Typical Petroleum Hydrocarbons (e.g., BTEX)
Some PAHs
Other VOCs, SVOCs
Certain Oxyanionic Metals (e.g., CrVI)
Nitro-aromatic Compounds
Chlorinated Solvents, Some PFAS
PCBs
Nitrate/Nitrite, Perchlorate

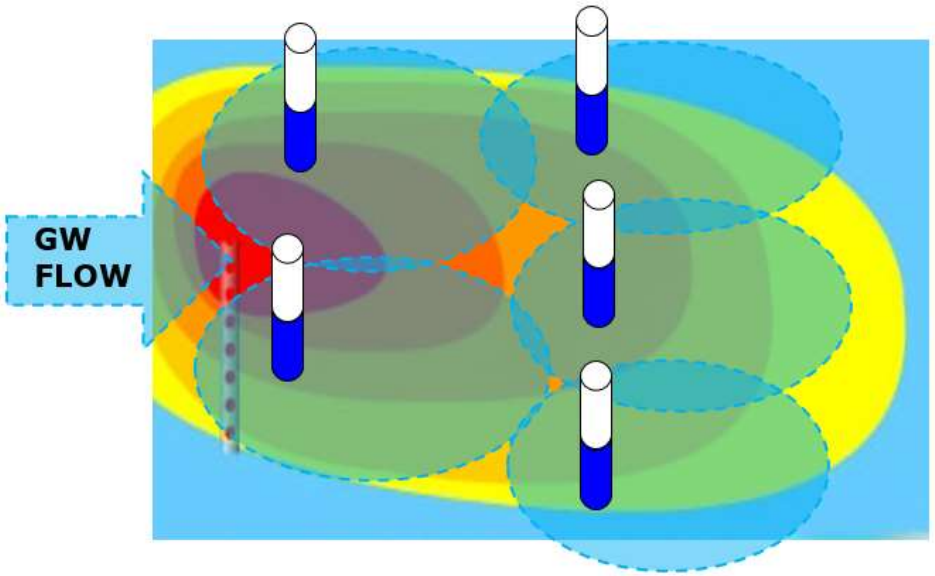
E-Redox®



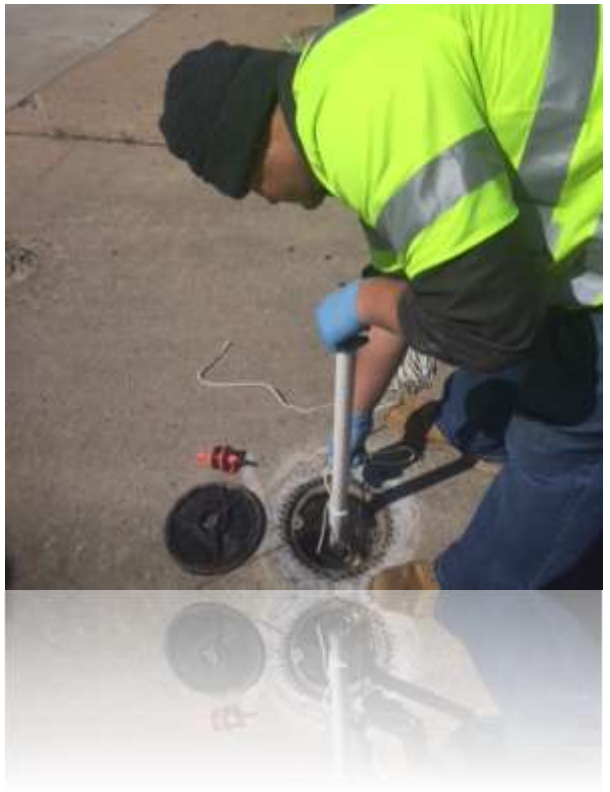
A respiratory "Snorkel" for microbes to support and expedite biodegradation in a matrix (including tight formations) depleted of electron acceptors, without any physical injection of any e-acceptors (air/oxygen/nitrate/sulfate)



E-Redox®-O for source and small plume treatment



E-Redox®-O as reactive barrier for areal plume and edge treatment



E-Redox®-O for Petroleum Degradation

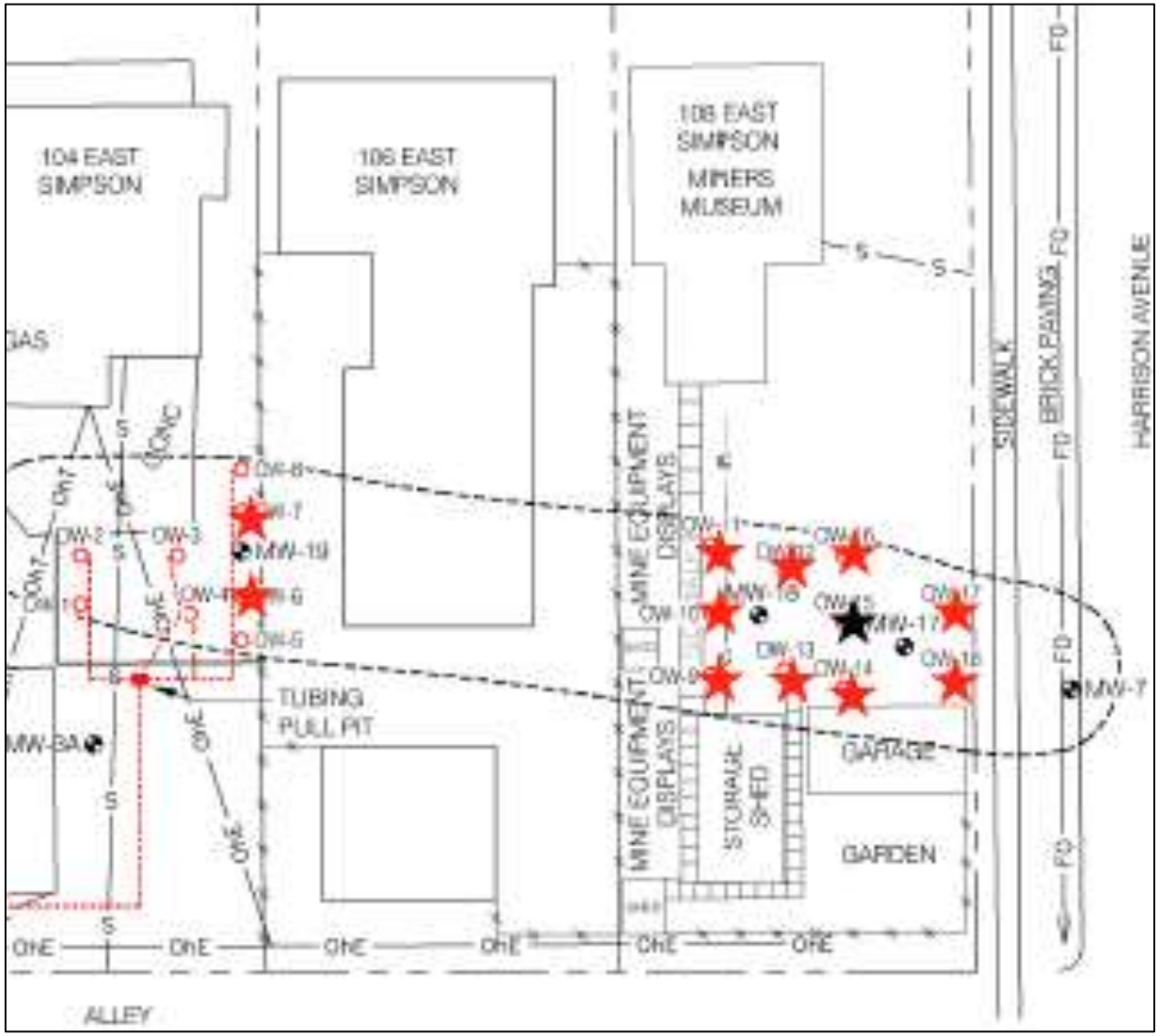
CASE STUDY 1: FORMER PETROLEUM BULK PANT (CLOSED)

Location: Former petroleum bulk plant (contaminant area in residential area) in Lafayette, CO

Contaminated Matrix: Groundwater and saturated soil

Primary Contaminants of Concern: Benzene, TPH

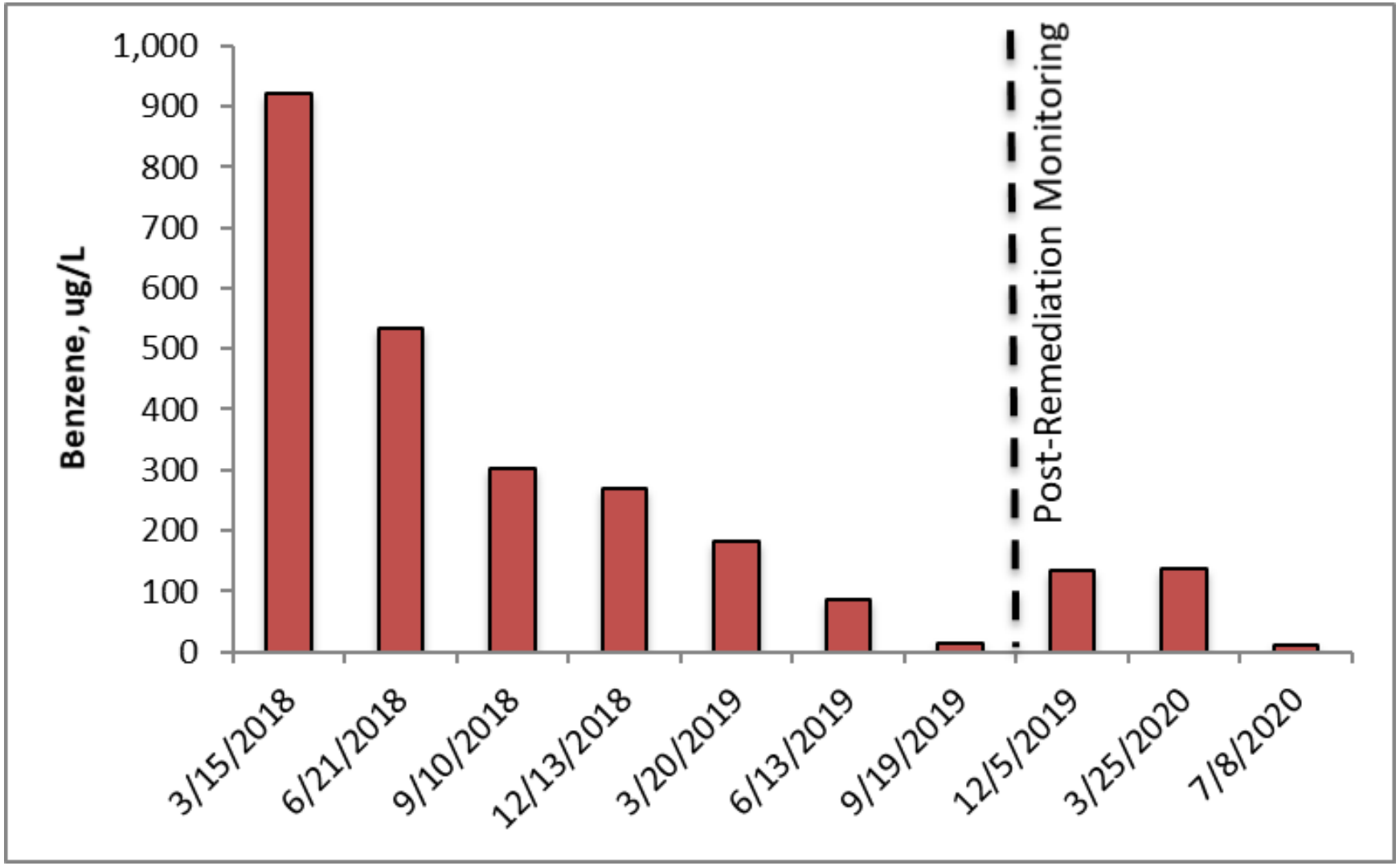
Remedial Solution: E-Redox®-O technology for *in situ* biodegradation of benzene and other petroleum hydrocarbons




COLORADO'S NORTHERN COAL FIELD
LEST WE FORGET


CGRS

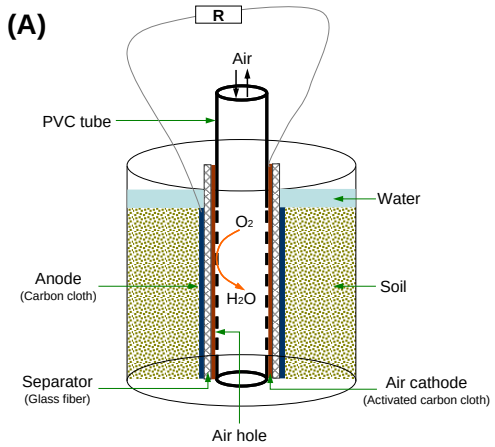
Overall site benzene concentrations

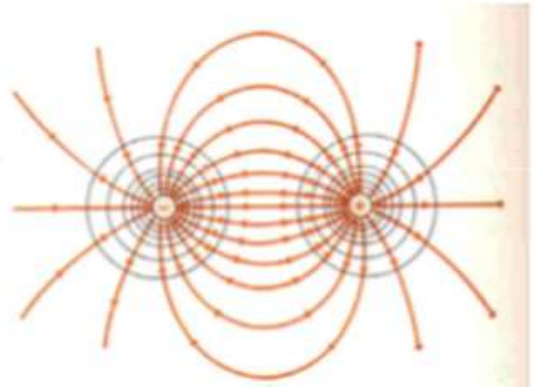


129 ug/ml/month degradation of benzene site-wide

E-Redox®-O (oxidation) Highlights

- ✓ **E-Redox®**-O technology is a **"passive" active** treatment for petroleum hydrocarbons by providing a perpetual terminal electron acceptor and expediting electron transfer for microbes
- ✓ E-Redox® favors sites with good matrix electrical conductivity (most sites). **IT WORKS IN CLAY as well**
- ✓ Voltage profiles in the E-Redox® device as a tool for **in-situ real-time monitoring** of biodegradation and potential deficiencies – **BioRemeter ™**
- ✓ Modular, sustainable, **zero energy input**, minimum maintenance
- ✓ E-Redox® can be a stand-alone remedy or synergistically used with other remedial technologies (e.g., nutrients addition, bioaugmentation, carbon-based trapping materials, chemOx, SVE, etc.)





Microbial-Electro-Chemistry Redox Technology

1

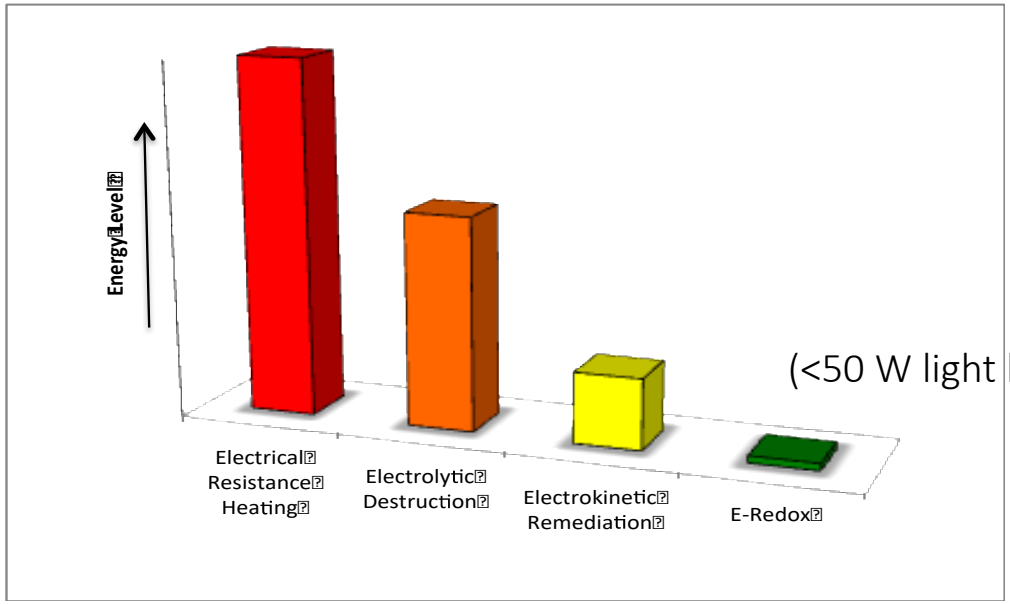
Reactions via electron transport and shifts of matrix particle/water interface charges and configurations

2

Friendly for fine-grained lithology with higher electrical conductivities: silts & clays

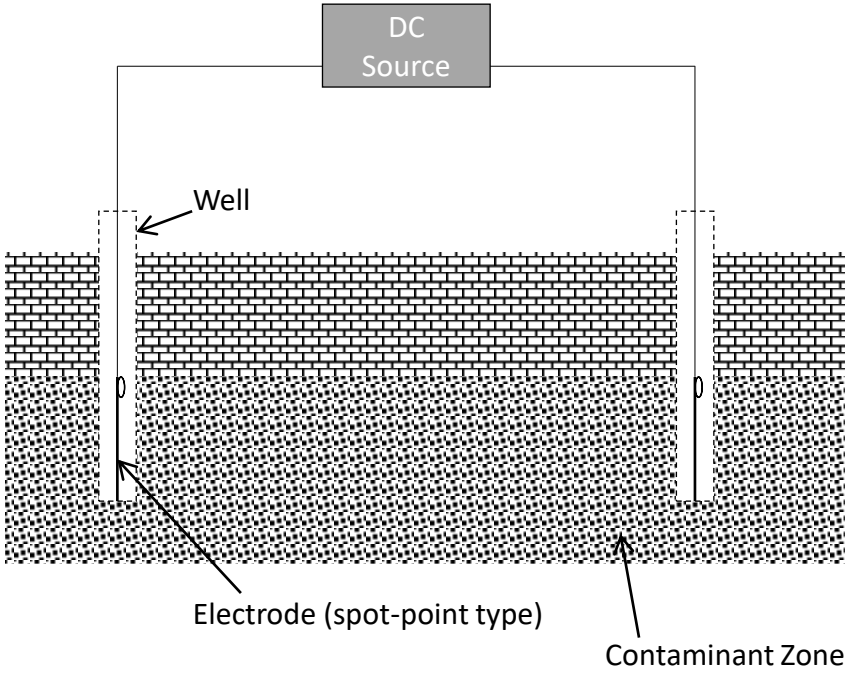
E-Redox®-I (reduction and localized oxidation)

- Establishes a low-voltage/low-amperage static electric field in the contaminated matrix.
- Promotes reductive destruction and desorption of source compounds from soil into water



Relative Electrical Energy Requirement

(<50 W light bulb/module)



Patented by AET, 1st Field Application 2014
Jin et al., 2008. Chem Eng J, 140:642
Jin and Fallgren 2009, J Haz Mat, 153:127
Luo et al., 2010. Chem Eng J, 160:185

E- Tools

	Typical Linear Current Density	Typical Linear Voltage Density	Current Loading	Main Reactions
Electrolytic Destruction (ER)	50 mA/cm	5000 mV/cm		Electrode surface/interface reactions, reactive barrier applications
Electrokinetic Migration (Remediation)		500 mV/cm	0.123-0.615 mA/cm^2	Movements of soluble constituents in the matrix
E-Redox®-I	2 mA/cm	<50 mV/cm	0.002-0.006 mA/cm^2	Static electrical field by turning soil particles into “micro-capacitors” and disturbing solid-water interface charges and configurations

E-Redox®-I: “micro-conductor”, “micro-capacitor” mechanism for redox reactions and mass desorption

- Soil particles in the influenced matrix act as micro-conductors, become polarized, and act as “micro-capacitors”* with constant charging and discharging cycles:
  - Abiotic reductive destruction of chlorinated solvents and oxyanions
  - Beneficial to biological dechlorination
  - Localized redox reactions destruct PFAS compounds

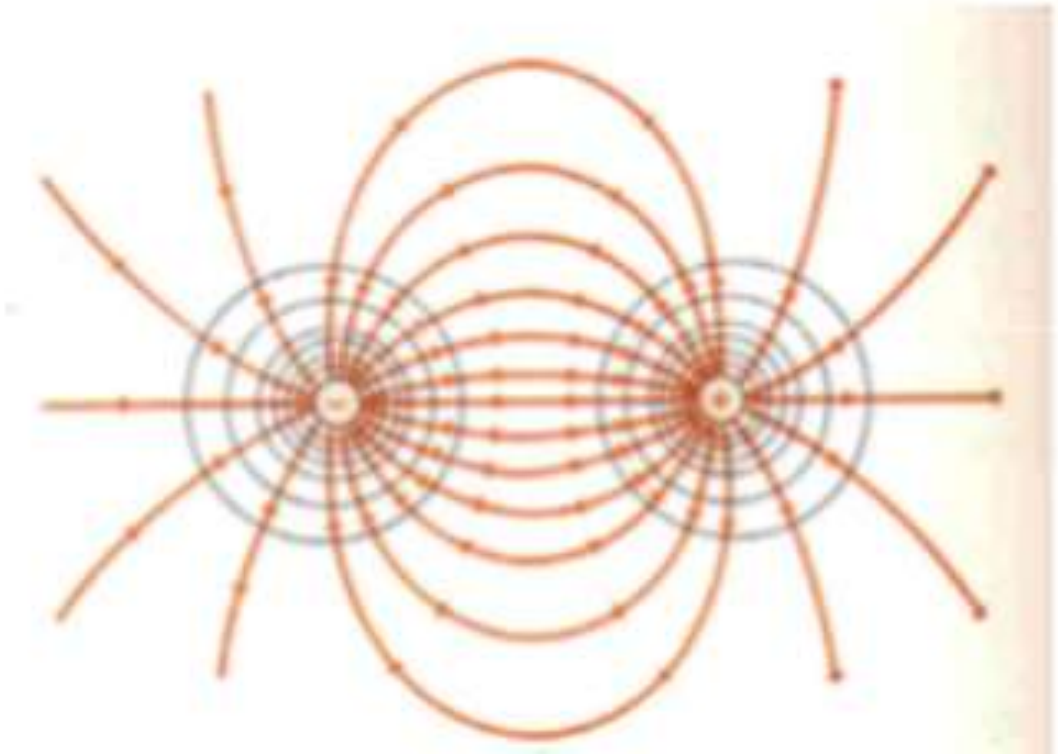
- Constant shifts of surface charge causes electrostatic and hydration repulsion, disturbs the “water cage” configuration and results in:
  - Desorption of contaminants from soil/solids into water
  - Elimination of “rebounds”

** Dietmar Rahner, Dresden U of Technology, 2002*

Static Electric Field

- Field data indicate a radius of influence (ROI) of ~25-30 ft in clay and silts; >50 ft for matrices with injection history of carbon, ZVI, or other conductive compounds

- Electrodes spacing: ~25 ft for mixed saturated and unsaturated matrices



E-Redox®-O (oxidation)

Environmental Science & Technology
Article
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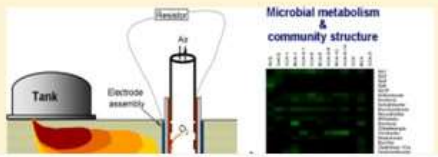
Microbial Metabolism and Community Structure in Response to Bioelectrochemically Enhanced Remediation of Petroleum Hydrocarbon-Contaminated Soil

Lu Lu,[†] Tyler Huggins,[†] Song Jin,[‡] Yi Zuo,[§] and Zhiyong Jason Ren*[,†]

[†]Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, Colorado 80309, United States
[‡]Department of Civil and Architectural Engineering, University of Wyoming, Laramie, Wyoming 82071, United States
[§]Chevron Energy Technology Company, San Ramon, California 94583, United States

Supporting Information

ABSTRACT: This study demonstrates that electrodes in a bioelectrochemical system (BES) can potentially serve as a nonexhaustible electron acceptor for *in situ* bioremediation of hydrocarbon contaminated soil. The deployment of BES not only eliminates aeration or supplement of electron acceptors as in contemporary bioremediation but also significantly shortens the remediation period and produces sustainable electricity. More in... and ce... bioelect... with ca...



Environmental Science & Technology
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Article

Molecular Transformation of Crude Oil Contaminated Soil after Bioelectrochemical Degradation Revealed by FT-ICR Mass Spectrometry

Huan Wang, Lu Lu, Huan Chen, Amy M. McKenna, Jie Lu, Song Jin, Yi Zuo, Fernando L. Rosario-Ortiz, and Zhiyong Jason Ren*

Cite This: *Environ. Sci. Technol.* 2020, 54, 2500−2509

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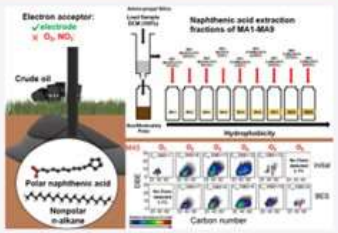
ABSTRACT: Bioremediation is a low-cost approach for crude oil spill remediation, but it is often limited by electron acceptor availability. In addition, the biodegradation products of crude oil contaminants are complex, and transformation pathways are difficult to decipher. This study demonstrates that bioelectrochemical systems (BESs) can be effective in crude oil degradation by integrating biological and electrochemical pathways, and more importantly, it provides the first understanding on the daughter products of bioelectrochemical hydrocarbon degradation. Using electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and two-dimensional gas chromatography (GC × GC), the results showed that the active BES reactor improved the total petroleum hydrocarbon (TPH) degradation by ~70% than open circuit control reactors. After separating the daughter products into nine fractions (MA1−MA9)



ELSEVIER
Journal of Hazardous Materials
Volume 274, 15 June 2014, Pages 8-15

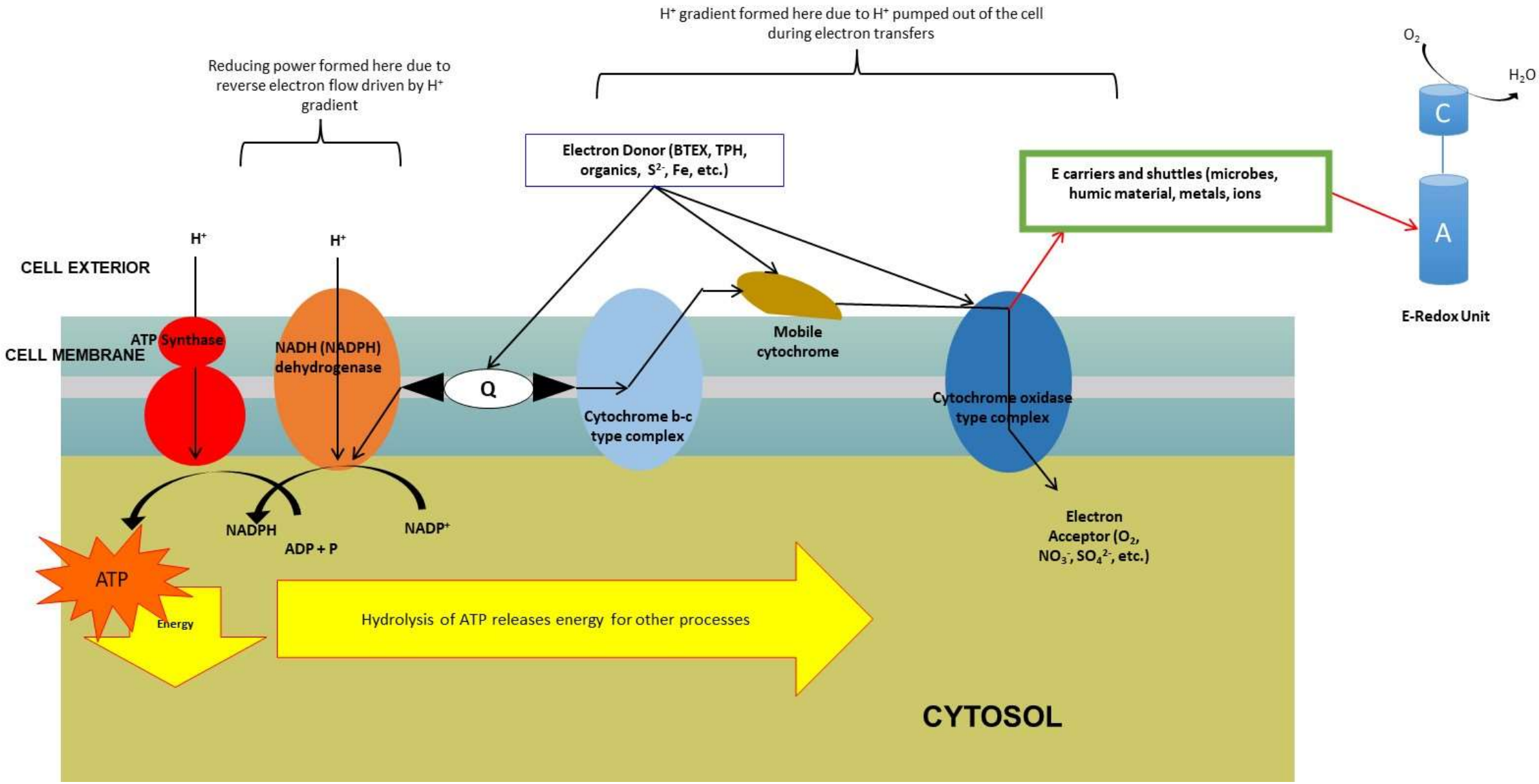
Enhanced bioremediation of hydrocarbon-contaminated soil using pilot-scale bioelectrochemical systems

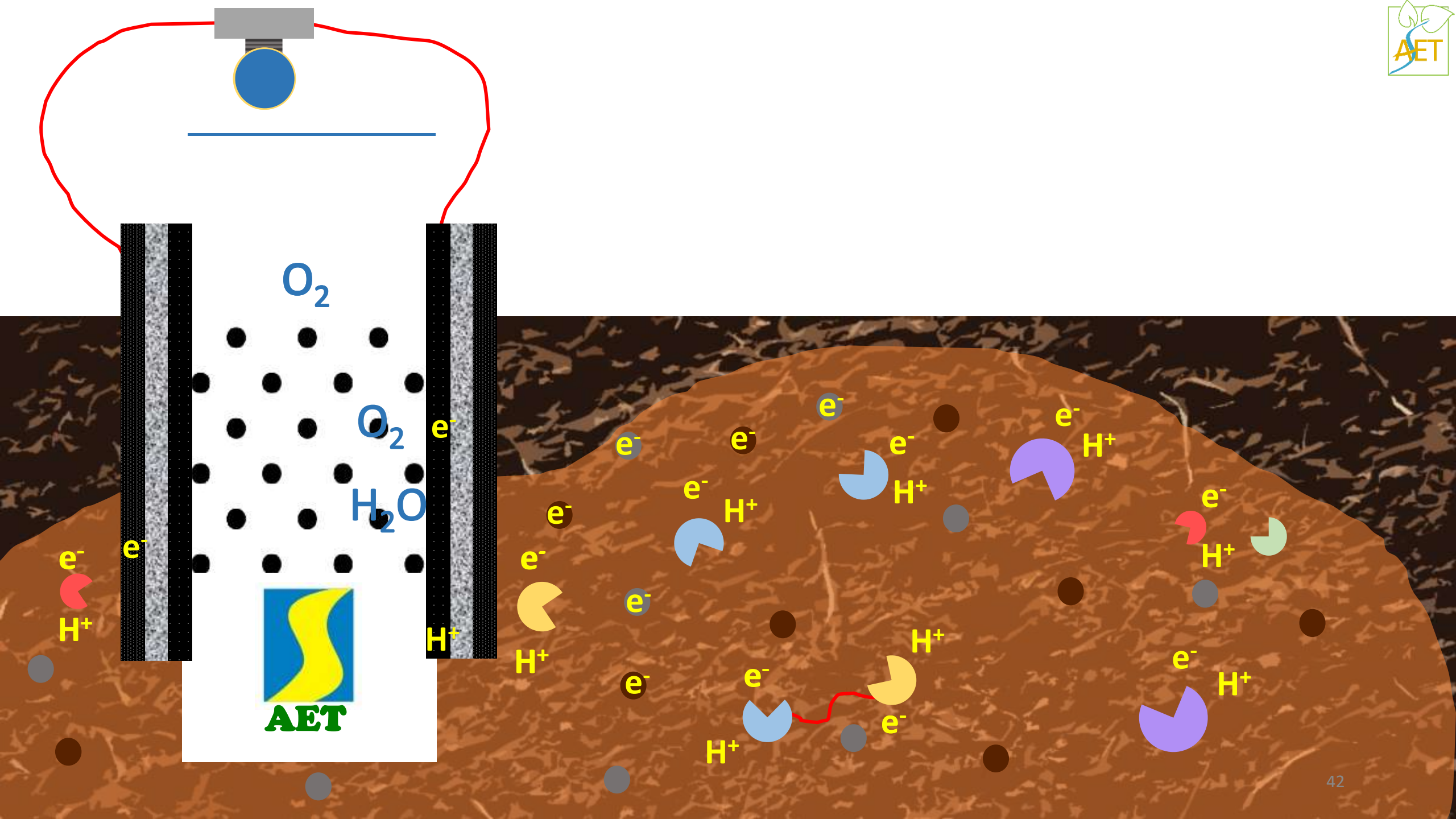
Lu Lu [a], Hadi Yazdi [a], Song Jin [b], Yi Zuo [c], Paul H. Fallgren [d], Zhiyong Jason Ren [a, d]

ELSEVIER
Chemosphere
Volume 235, November 2019, Pages 776-784

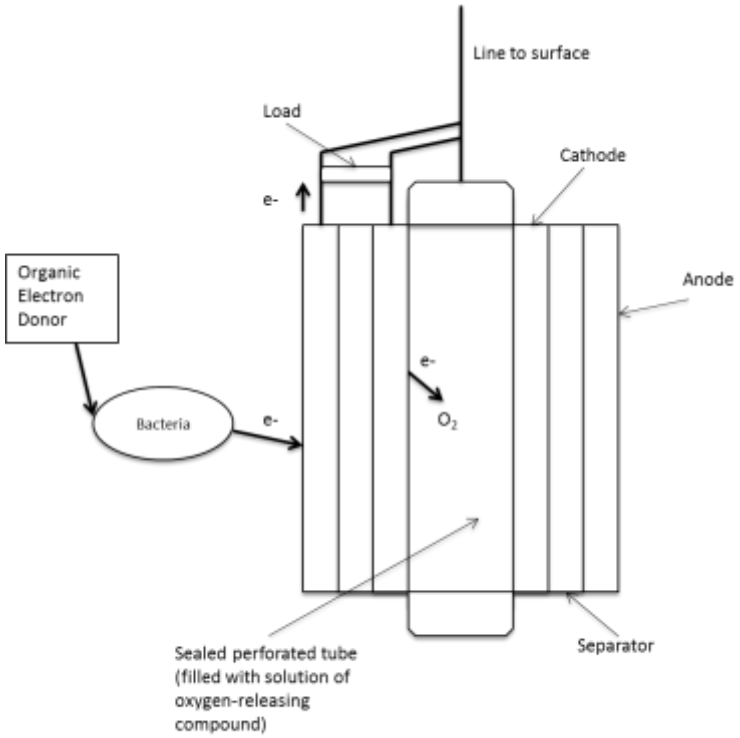
Dominance of electroactive microbiomes in bioelectrochemical remediation of hydrocarbon-contaminated soils with different textures

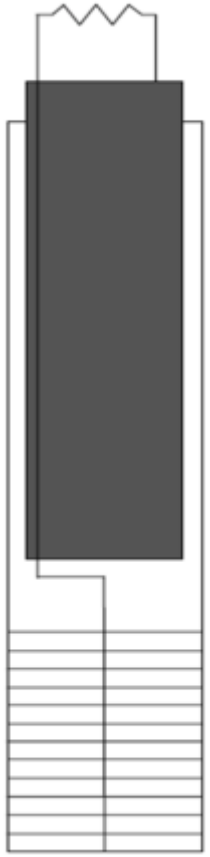
Huan Wang [a, b], Lu Lu [a, b], Deqiang Mao [c], Zhe Huang [b], Yixiao Cui [b], Song Jin [d], Yi Zuo [e], Zhiyong Jason Ren [a, b]


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
Electron Donor (BTEX, TPH, organics, S²⁻, Fe, etc.)
E carriers and shuttles (microbes, humic material, metals, ions
O₂
H₂O
C
A
E-Redox Unit
H⁺
H⁺
CELL EXTERIOR
CELL MEMBRANE
ATP Synthase
NADH (NADPH) dehydrogenase
Q
Cytochrome b-c type complex
Mobile cytochrome
Cytochrome oxidase type complex
NADPH
ADP + P
NADP⁺
ATP
Energy
Hydrolysis of ATP releases energy for other processes
Electron Acceptor (O₂, NO₃⁻, SO₄²⁻, etc.)
CYTOSOL


O_2
O_2
H_2O
e⁻
H⁺
AET

BioRemeter™





Project student intern won 2018 President's Environmental Youth Award


RadioShack
T-RMS DIGITAL MULTIMETER
AUTO
0.044
HOLD
REL Δ
RANGE
SELECT
Duty
Hz
EF
OFF
mA/A
μA/A
V
OFF
10A MAX
UNFUSED
500V MAX

BioRemeter™ Survey Vs. CO2 Measurements for Biodegradation

CO_2% by gas tube	Microbial activity scale	BioRemeter	Improved microbial activity scale
0%	None	12.9 mV	Lower
0.1%	None to very low	16.9 mV	Low
0.3%	Very low	19.2 mV	Low to Moderate
1.0%	Very low	20.5 mV	Low to Moderate
5%	Low	21.4 mV	Low to Moderate
9%	Moderate	51.8 mV	Moderate to High

If we assume 10% of TPH is 10% of TOC:

Upper limit: y = 0.0253V (g/d)
Lower limit: y = 0.0077V (g/d)

y = TPH degradation rate (g/day)
x = E-Redox voltage (mV)

SUMMARY

- E-Redox® (I and O) technology works on electron transfer and redox reactions (oxidation and reduction), applicable to CLAY and other tight matrices
- E-Redox®-I is mainly an abiotic pathway; E-Redox®-O is mainly a biodegradation pathway
- E-Redox® facilitates desorption of COCs (CVOC, petroleum compounds, and PFAS) into the water for faster mass removal and destruction
- E-Redox® is compatible and synergistic to other remediation tools
- BioRemeter™ is a novel tool for real-time in-situ monitoring of biodegradation activities and TPH levels in saturated soil and groundwater

E-Redox®

Song Jin PhD., CHMM
E: songjin@aetecs.com
T: 970.889.8410