E-Redox®

A Novel Bioelectrochemical Tool for Effective Treatment of Petroleum Contaminants with Zero Energy Input

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Acknowledgement

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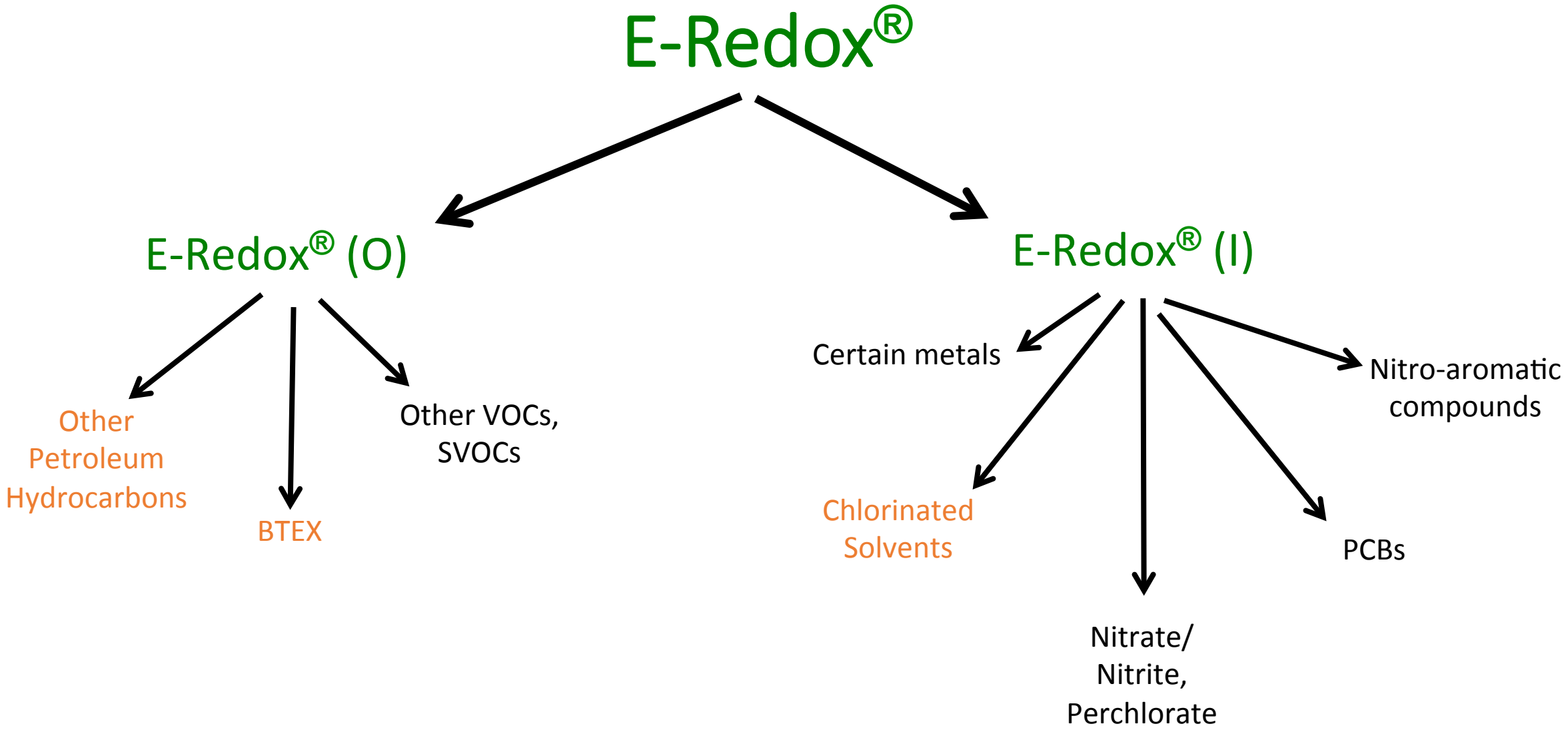
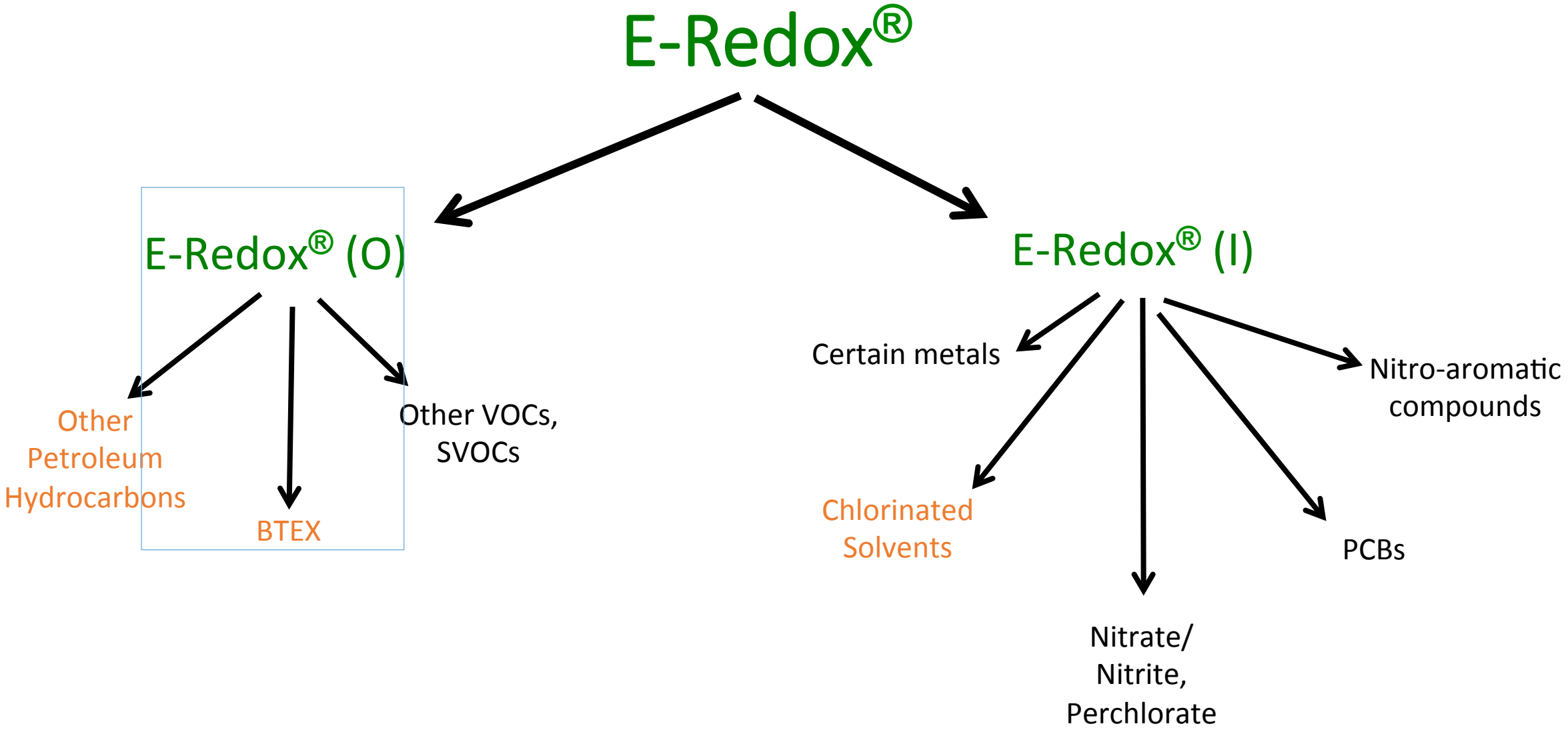
Jennifer Strauss, Office of Public Safety, State of Colorado, Denver, CO

Challenges in treating subsurface contaminants?

- Matrix permeability - delivery − ROI
- rate − time
- $ - $ - $
- Sustainability


E-Redox®
E-Redox® (O)
E-Redox® (I)
Other Petroleum Hydrocarbons
BTEX
Other VOCs, SVOCs
Certain metals
Chlorinated Solvents
Nitrate/ Nitrite, Perchlorate
PCBs
Nitro-aromatic compounds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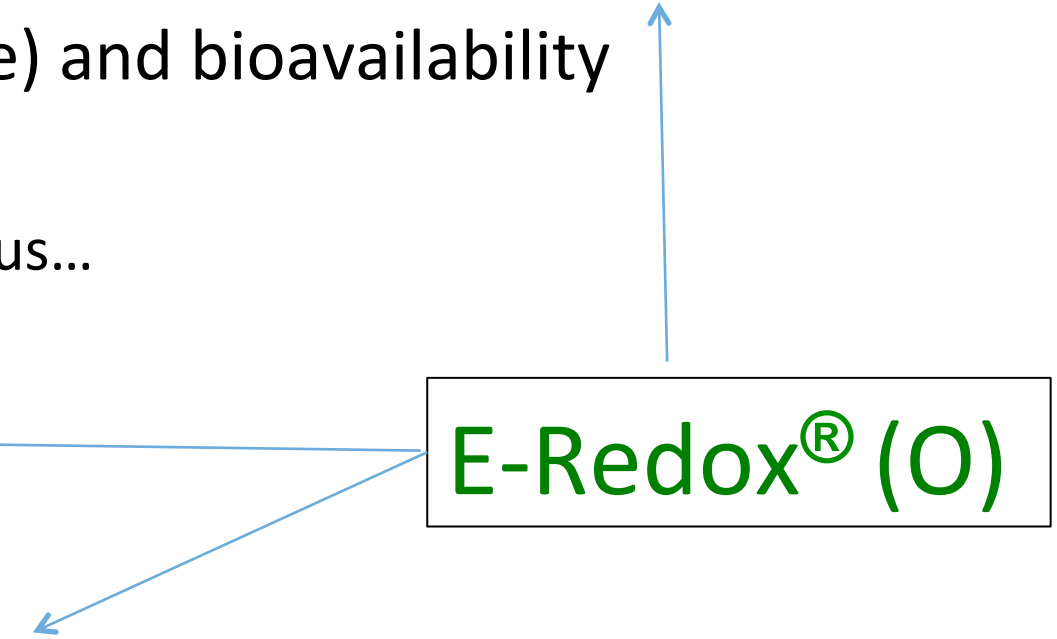
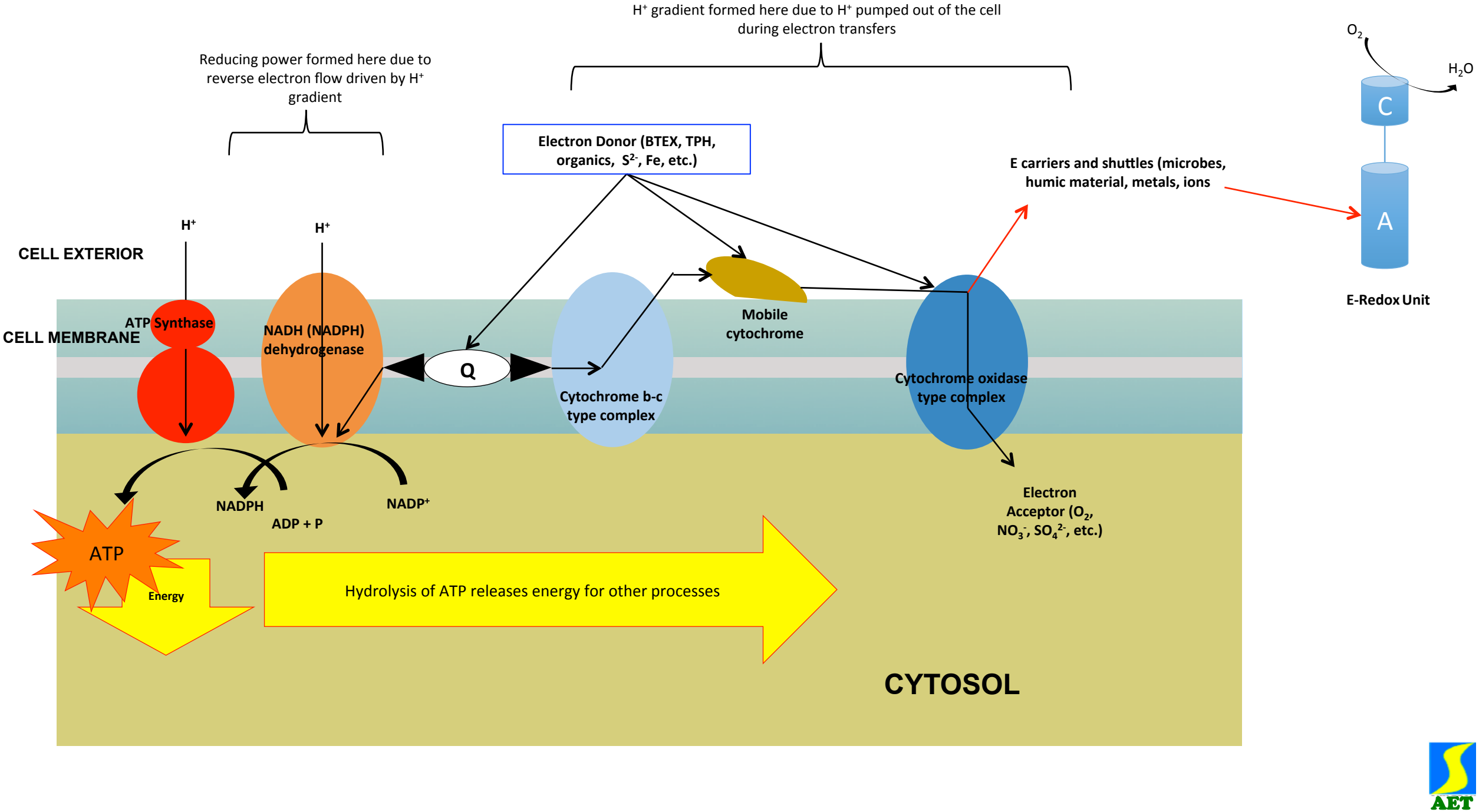
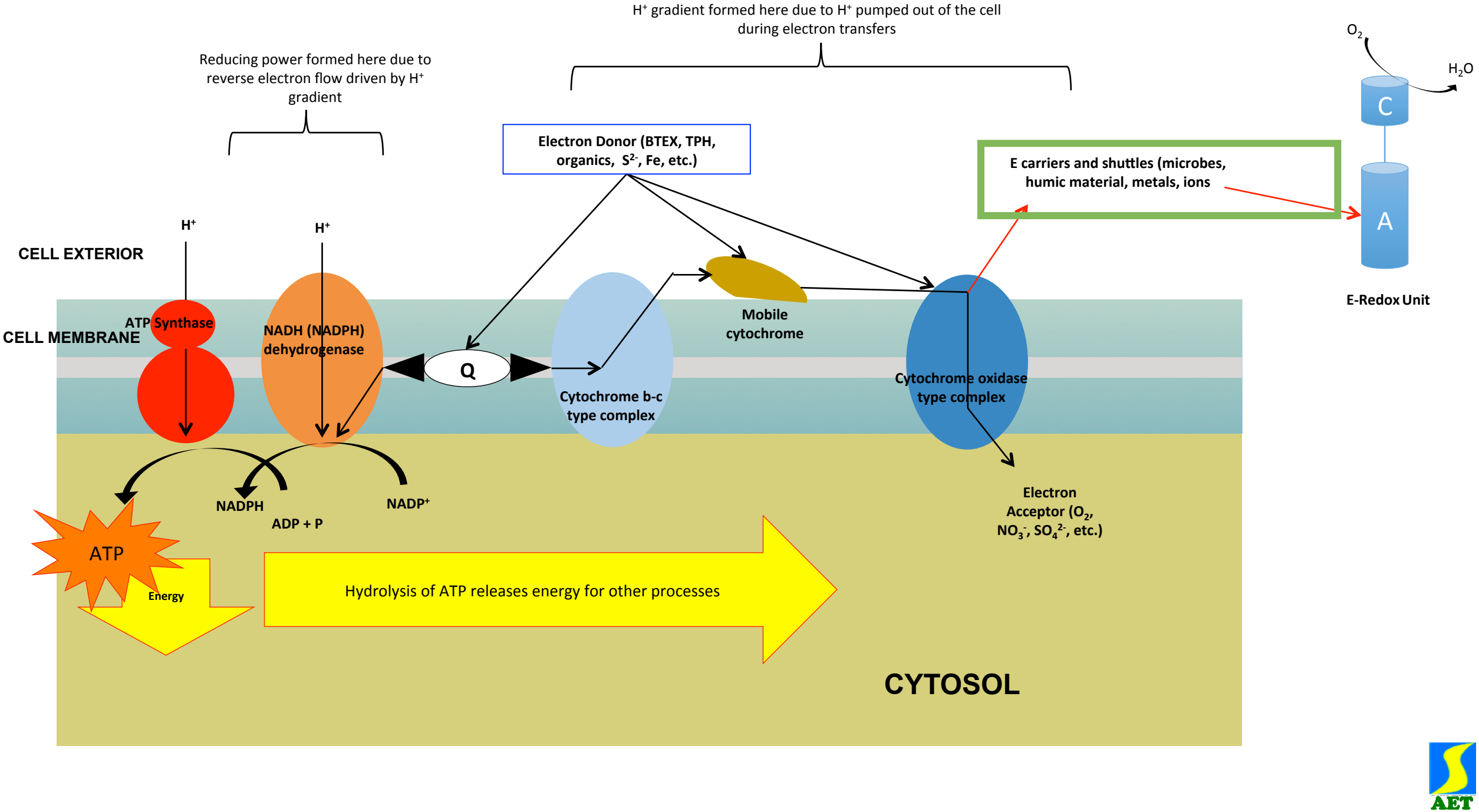
Oxidative Biodegradation

- 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




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
Electron Acceptor (O2, NO3-, SO42-, etc.)
NADPH
NADP+
ADP + P
ATP
Energy
Hydrolysis of ATP releases energy for other processes
CYTOSOL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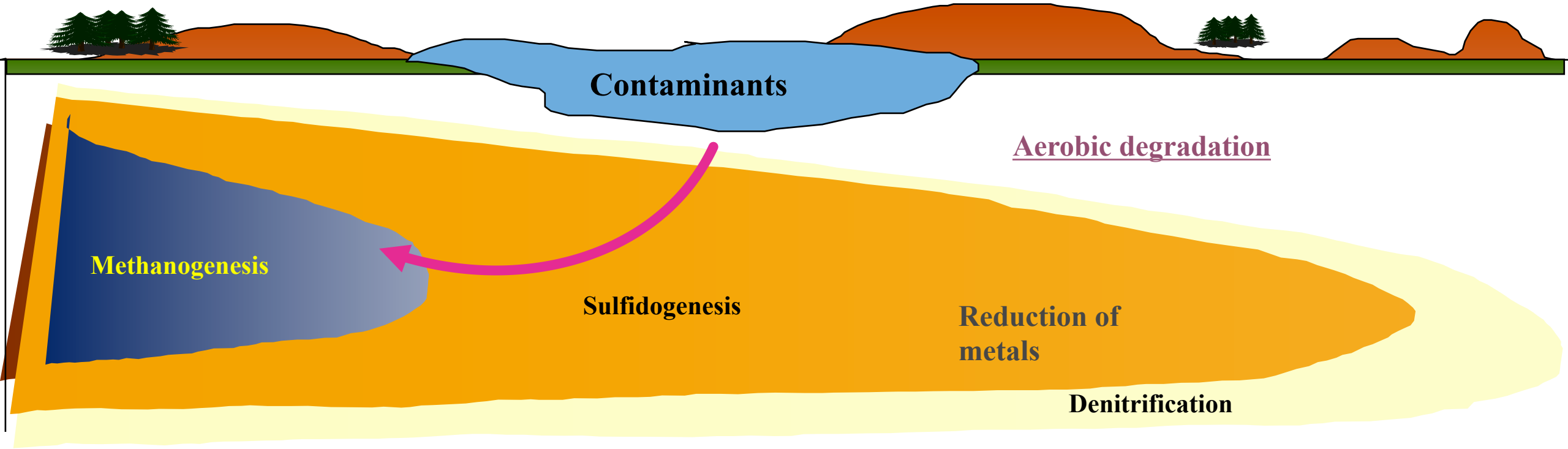
Electron Acceptor Gradient and Biodegradation



Benzene Biodegradation Vs. Different TEAs

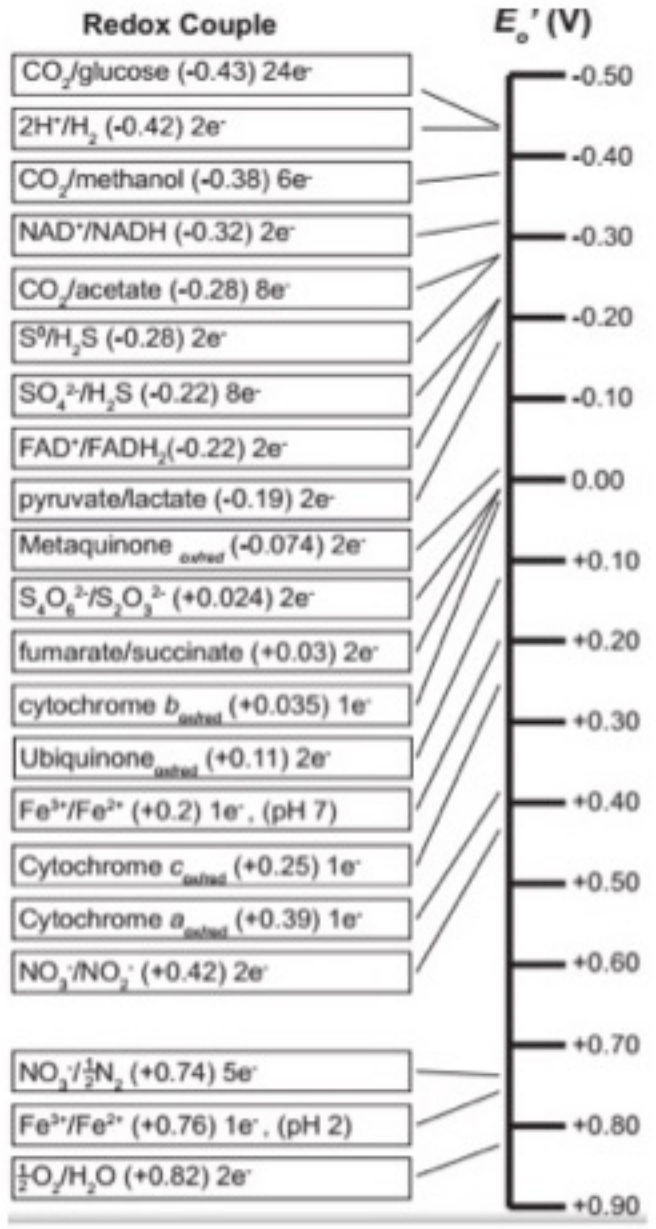
Aerobic: $C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$
$\Delta G = -3069$ kJ/mol

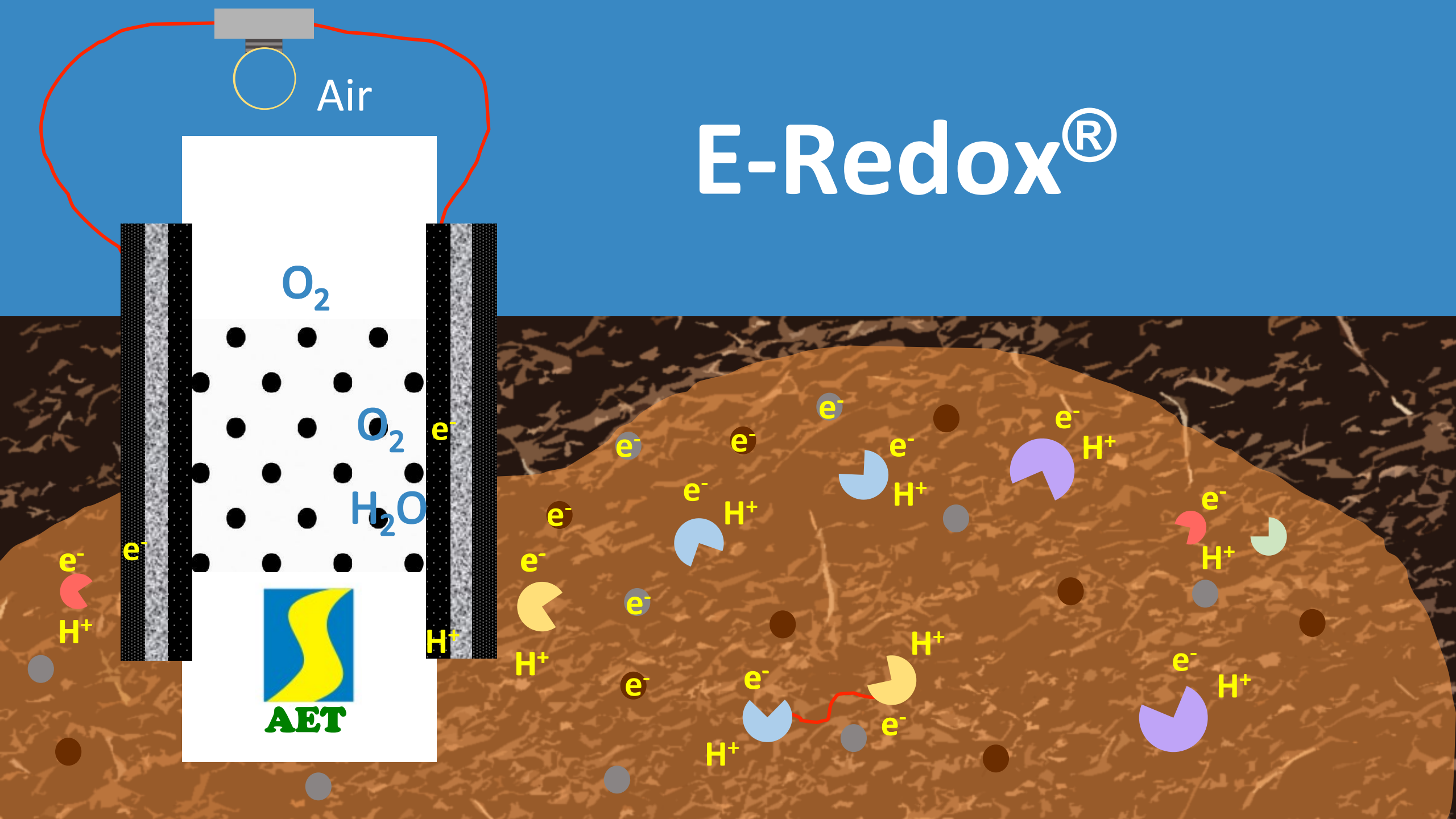
Denitrification: $C_6H_6 + 6NO_3^- + 6H^+ \rightarrow 6CO_2 + 3N_2 + 6H_2O$
$\Delta G = -2895$ kJ/mol

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

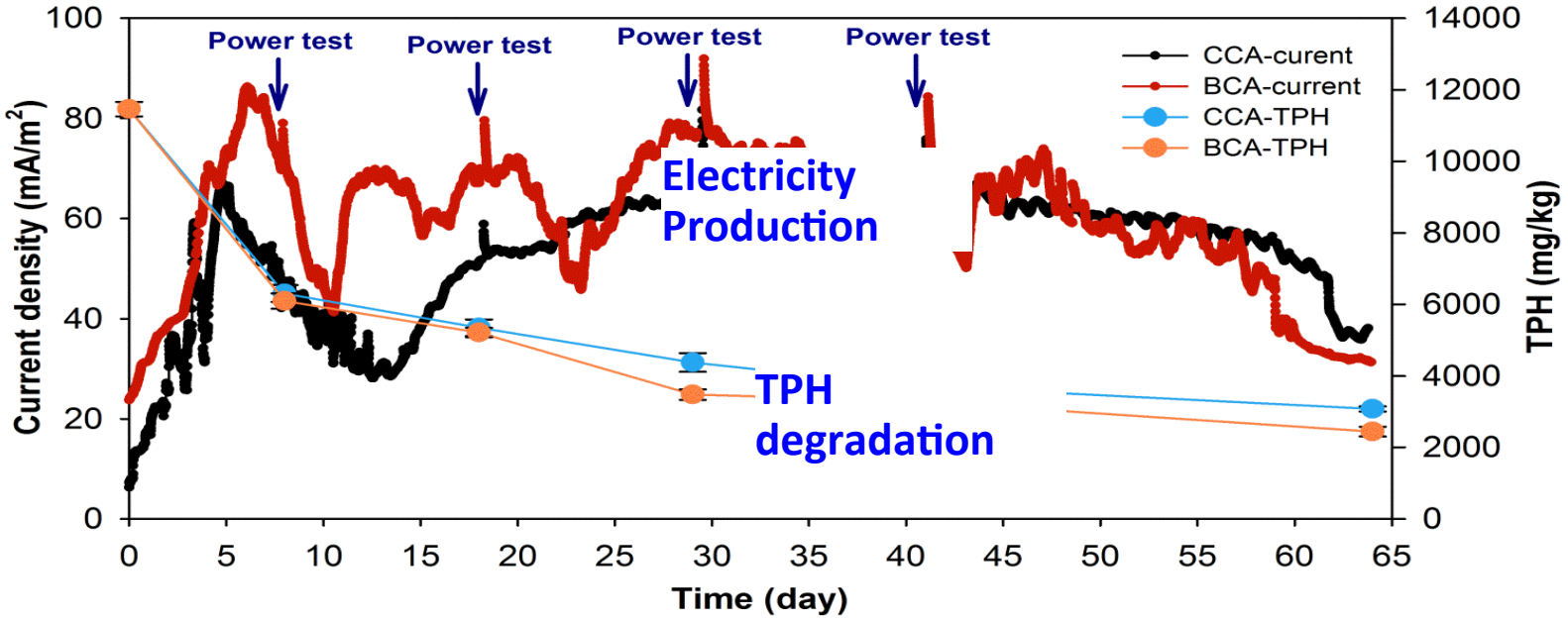



Air
E-Redox®
O_2
O_2
H_2O
e⁻
H⁺
AET

Benzene Biodegradation Rates (with nutrient amendments)

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

Bioremeter ™



Electricity generated in the E-Redox® system serves as an indicator for biodegradation and provides a weak power source (~mA/m²)

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

E-Redox® Field Implementations

E-Redox® Field Implementations In Colorado

Locations: a number of fuel stations, ~2 street blocks area, Denver area, Colorado

Main COC: BTEX and other petroleum hydrocarbons in groundwater and saturated zones, sporadic sources in smear and vadose zones

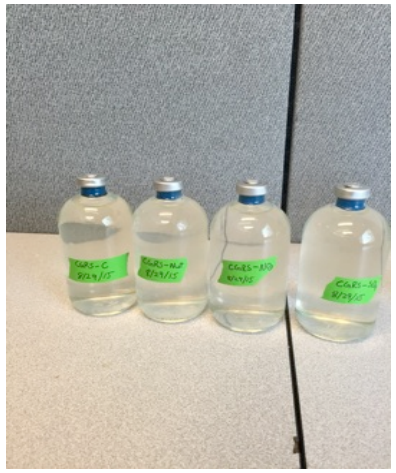
Lithology: silty to clayey sand in the vadose zone, clay in the saturated zone starting 10-15 ft bgs

Other Site Notes:

- Groundwater flow velocity estimated at 0.04 ft/day
- Past remediation efforts involved nutrient amendments, air sparging, injection of carbon-based materials, and chemical oxidants

Bench Tests (2-3-wk)

Field samples



Microbial assays

Bench-scale E-Redox®

E-Redox® System Field Installation (2-3 days for a typical UST site)

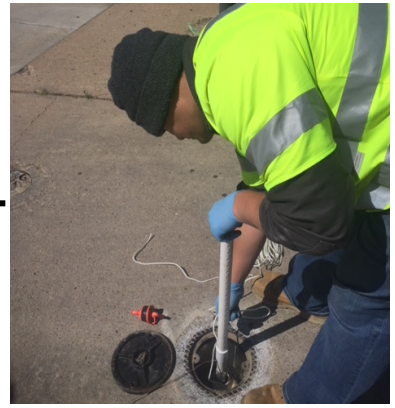
Site

Health & Safety Meeting

Pre-installation monitoring

E-Redox® unit prep

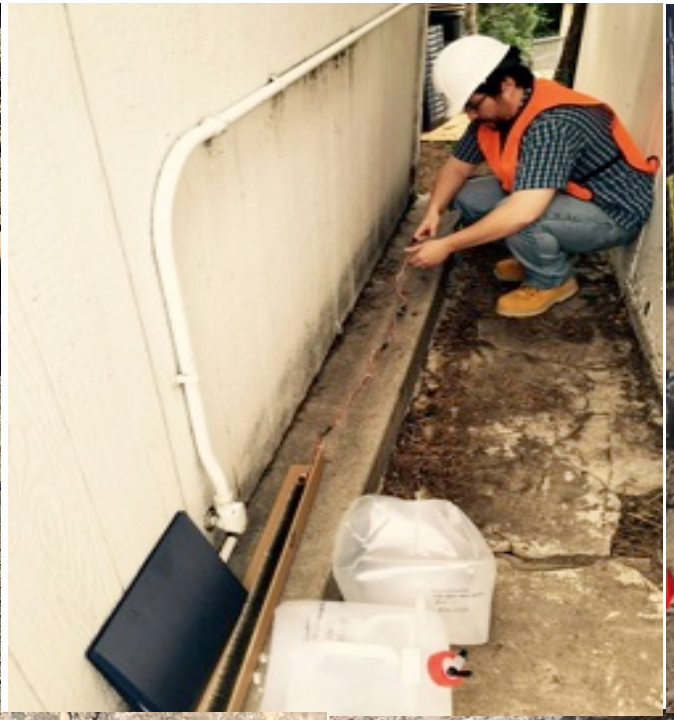
E-Redox® unit installation



Securing E-Redox® unit

Voltage monitoring

Closing well cover

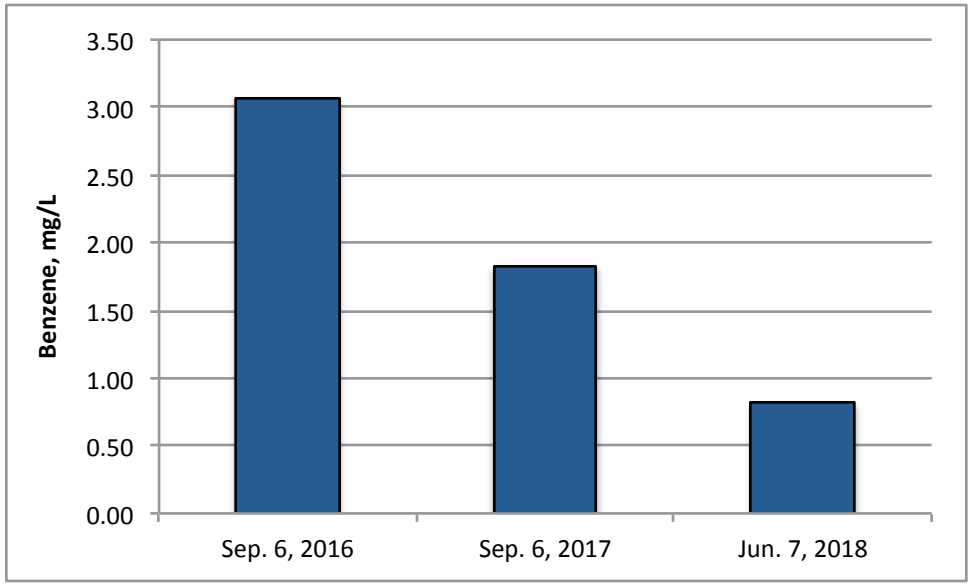



TEST
WELL

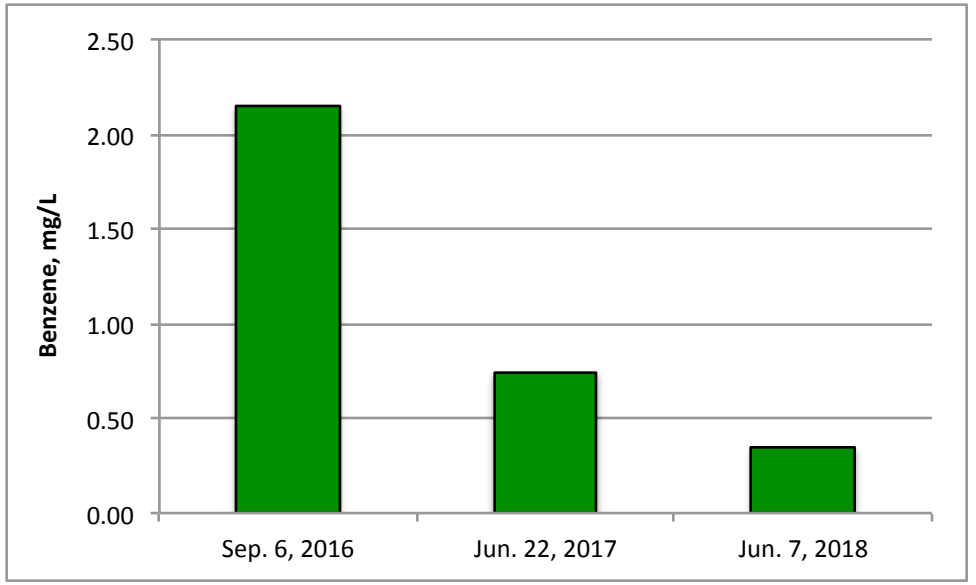

CGRS

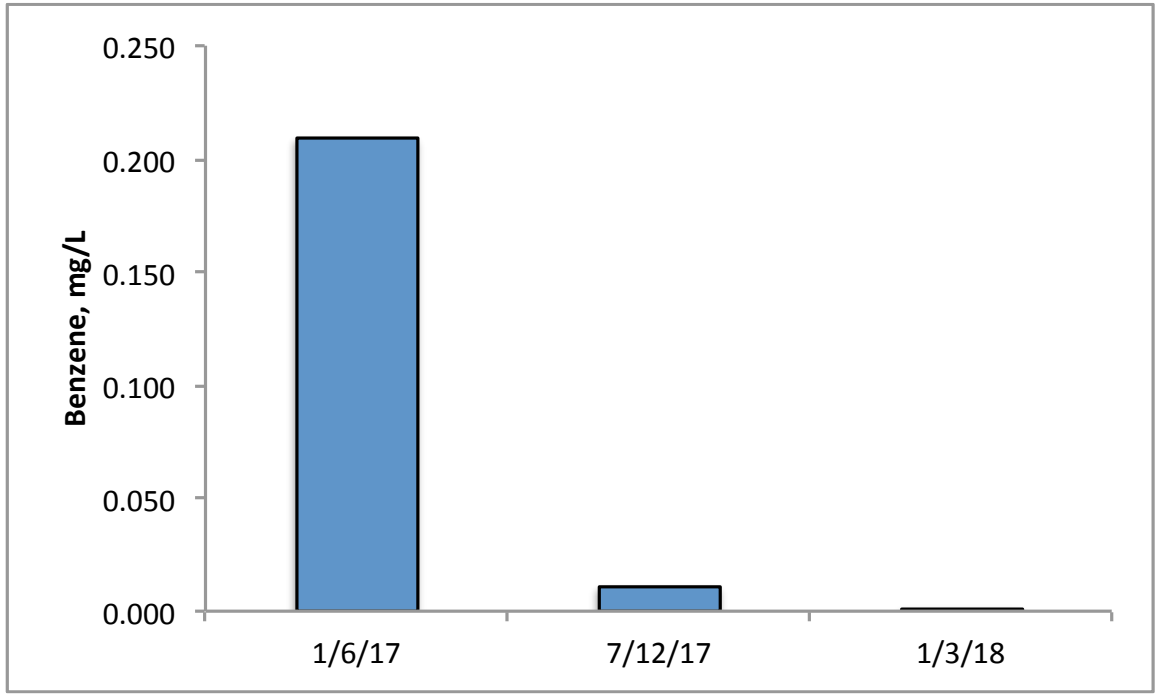
Operating fueling station in Denver, CO

Benzene concentrations -- whole site

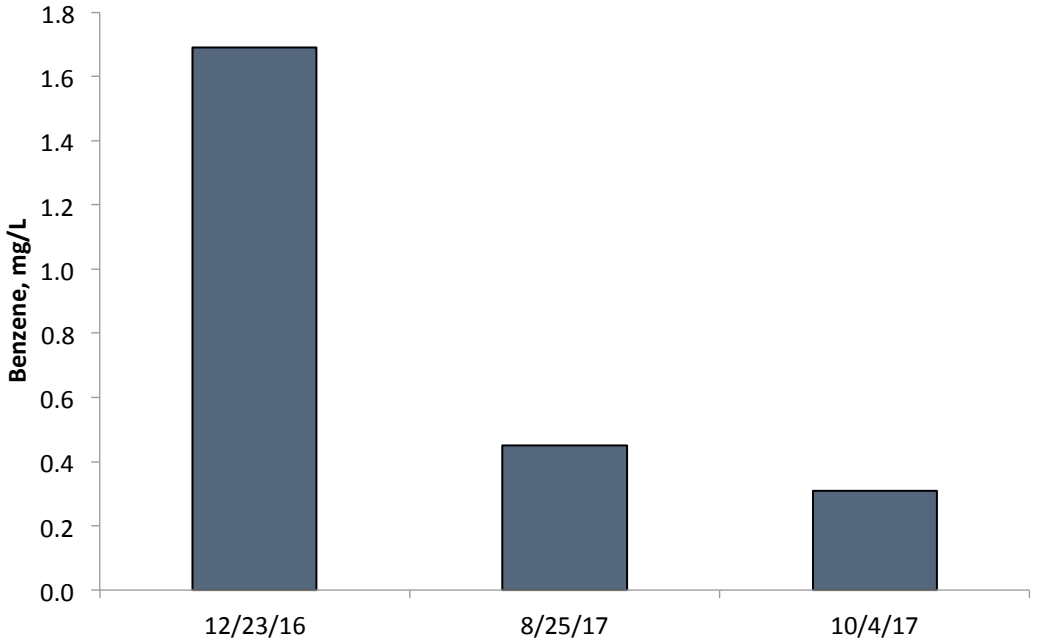


Benzene concentrations -- source area





Active fueling station in Lakewood, CO



Former bulk plant facility in Lafayette, CO

Field Applications of E-Redox® (O)

Site	Location	Contaminant	Matrix
Former gas station	Pine Ridge, South Dakota	BTEX, TPH-DRO	Groundwater
Former and operating gas stations, 2x	Lakewood, Colorado	BTEX	Groundwater
Operating gas stations, 2x	Denver, Colorado	BTEX	Groundwater
Operating gas station	Wheat Ridge, Colorado	BTEX	Groundwater
Former bulk station	Lafayette, Colorado	BTEX	Groundwater
Former gas station	Montrose, Colorado	BTEX	Groundwater
Operating gas station	Pueblo, Colorado	BTEX	Groundwater
Former products terminal	Northern California	BTEX, TPH-DRO	Groundwater, saturated and vadose zone soils
Operating MWTP x2	Beijing, China	COD, N, P	Municipal wastewater

BioRemeter™

- "Miniature" modifications from E-Redox® configuration
- For real-time measurement of microbial activities
  - "Collects" and measures electrons from microbial reactions in the matrix
- Survey by using existing groundwater wells
- A new tool for site assessment and real-time evaluation of enhanced bioremediation, NSZD, and MNA

BioRemeter™ Field Survey for Biodegradation Activities

Conditioning BioRemeter

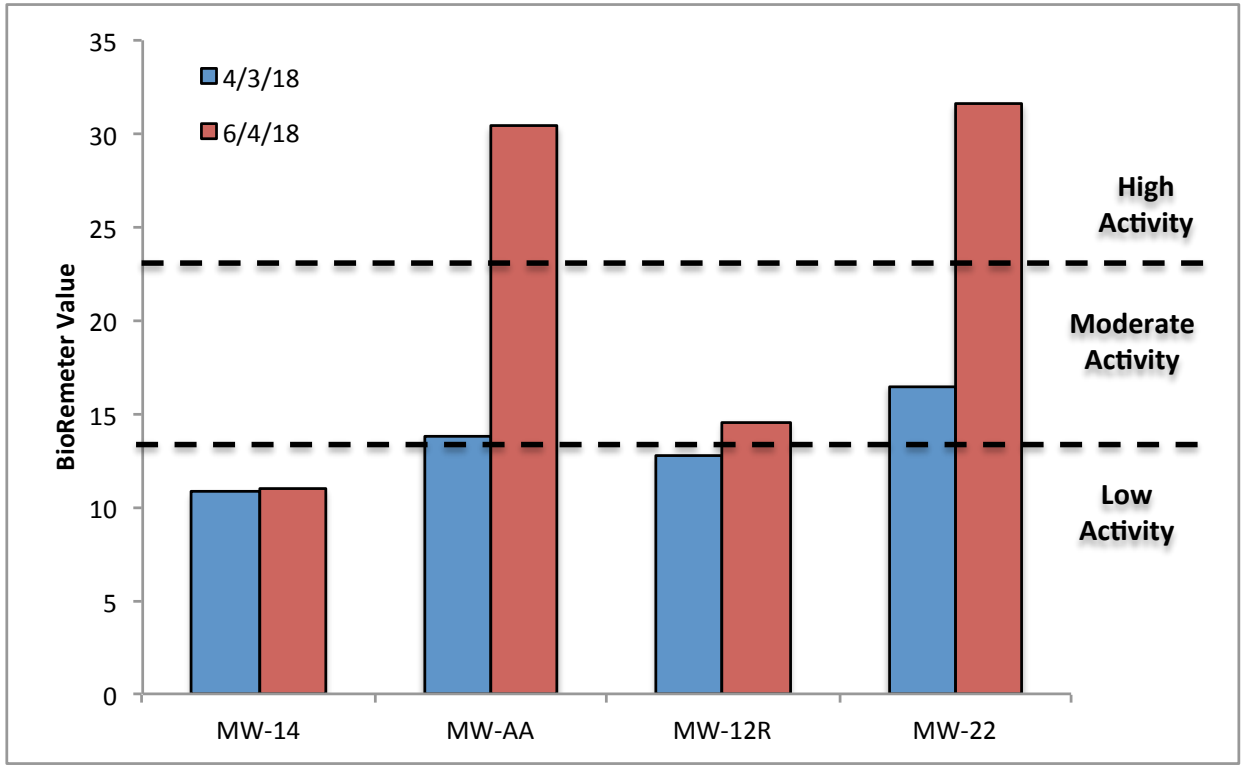
Calibration

BioRemeter in well

Measurement of voltage

Close well and rinse probe

Case Study of BioRemeter™: Active Fuel Station in Denver, CO



E-Redox® (O) Summary

- ✓ **E-Redox®**-O technology is a "passive" but active treatment for BTEX, TPH-GRO, TPH-DRO and other petroleum hydrocarbons, e.g., >5x rate for benzene in GW, >10x for TPH-DRO in sediments
- ✓ Voltage profiles in the E-Redox® device correlate with active biodegradation activities, resulting in an *in situ* tool for real-time monitoring of biodegradation – **BioRemeter ™**
- ✓ Modular, sustainable, no energy input, minimum maintenance
- ✓ E-Redox® works best when matrix conductivity is high and electron acceptor is deficient (most sites)
- ✓ E-Redox® can be a stand-alone remedy or synergistically used with other remedial technologies (e.g., bioaugmentation, nutrients addition, carbon, chemOx, SVE, etc.)

Mechanism Studies

- The anode (in contact with the contaminated matrix) and the established biofilm at the anode-matrix interface serve as a solid and highly conductive electron collector for electrons released from biodegradation. The circuit and specific resistance load serve as the conduit to transfer electrons to the cathode (exposed to oxygen in ambient air), and electricity is generated during the electron transfer. Meanwhile, protons migrate through the matrix towards the cathode. The cathode (at its interface with air) serves as a perpetual electron acceptor that consumes the electrons and protons and completes the electron transport *(Morris and Jin, 2009, 2012*).
- The extracellular transfer of electrons to the remote O2 at the E-Redox-O system can revive, stimulate, and sustain aerobic respiration/degradation in an otherwise anaerobic matrix. The matrix-wide electron transfer via a number of biological (certain cells and cell organelles) and abiotic (ions, metals, humic materials, other small organic constituents) shuttles has been well documented (e.g., ***Müller, et. al., 2016; Lovley, 2017***). Such electron movements can trigger two processes: competition with petroleum-degrading microbes for electrons, stimulating microbial enzyme production and higher degradation rate to "make up" the loss; certain opportunistic microbes in the matrix can harvest "free electrons", helping microbial growth and subsequent degradation.
- E-Redox-O system creates a higher redox at its immediate proximity and beyond (with time), which further enhances electron flow towards the system and consumption at the cathode by O2. This weak redox gradient helps shift microbial population composition (***Lu et al., 2017; Lu et al., 2018, under review***). This shift towards thermodynamically more favorable species further benefits biodegradation at distant location but within the ROI of the E-Redox-O system (***Lu et al., 2018, under review***).
- The E-Redox-O system stimulates biological oxidation by expediting electron transfer from the biodegradation process, “pulling” electrons to ambient O_2, the favorable electron acceptor, competing with microorganisms for extracellular electrons, thus accelerating metabolic rates, and maintaining low electron density and H_2 levels in the matrix to eliminate potential product feedback and inhibitory influence (***Jin and Ren, 2018, unpublished***).
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Thank You

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