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Bioelectrochemical Biodegradation of 1,4-Dioxane under Anaerobic Conditions – a feasibility study

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Bio(oxidative)degradation

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

E-Redox® (O)

(Photo) Bioelectrochemical Remediation

E-Redox®

Boosts bio(oxidative)degradation

Abiotic redox reactions for COC destruction and desorption

Desorption of mass into water phase

E-Redox® ($O_{\text{-oxidation}}$)

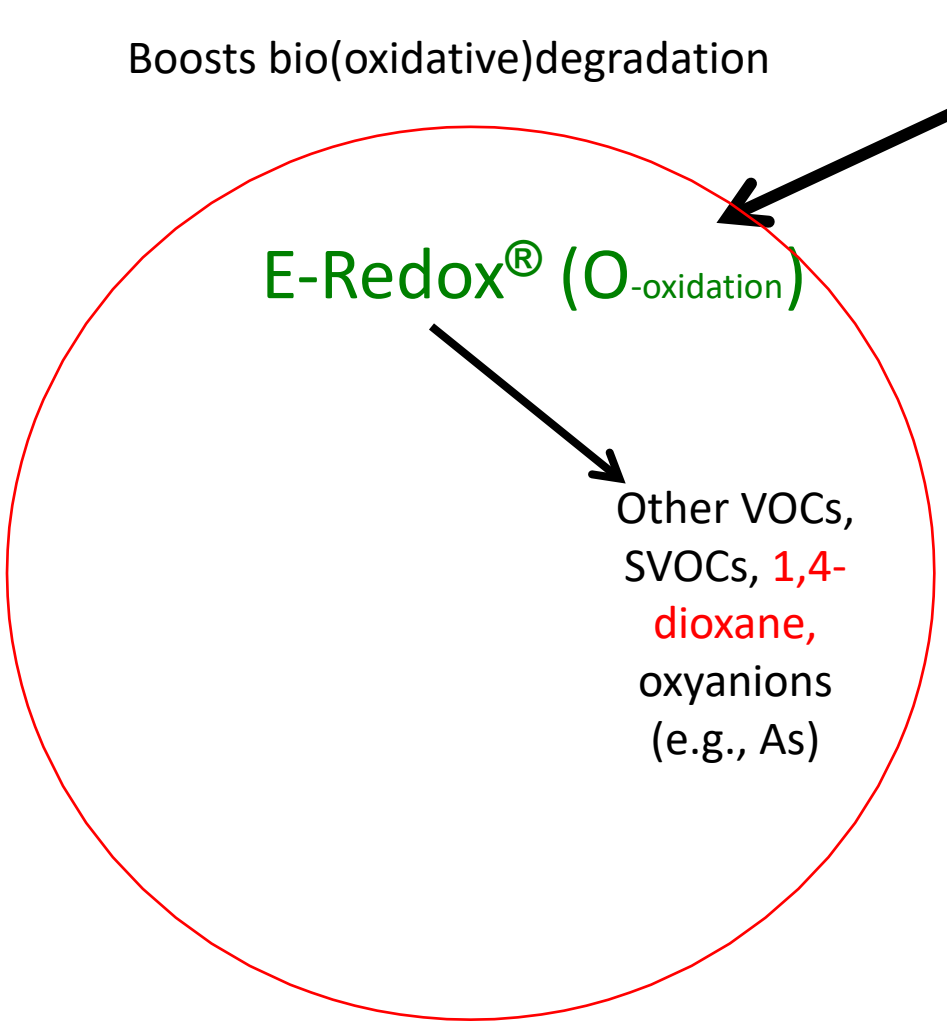
- Typical Petroleum Hydrocarbons (e.g., BTEX)
- Some PAHs
- Other VOCs, SVOCs, 1,4-dioxane, oxyanions (e.g., As)

E-Redox® ($I_{\text{-Reduction}}$)

- Certain Oxyanionic Metals (e.g., CrVI)
- Nitro-aromatic Compounds
- Chlorinated Solvents, Some PFAS
- PCBs
- Nitrate/Nitrite, Perchlorate

(Photo) Bioelectrochemical Remediation

E-Redox®



A respiratory conduit to perpetual electron acceptor to support and expedite biodegradation in matrices depleted of electron acceptors; without physical injection of any e-acceptors (air/oxygen/nitrate/sulfate)

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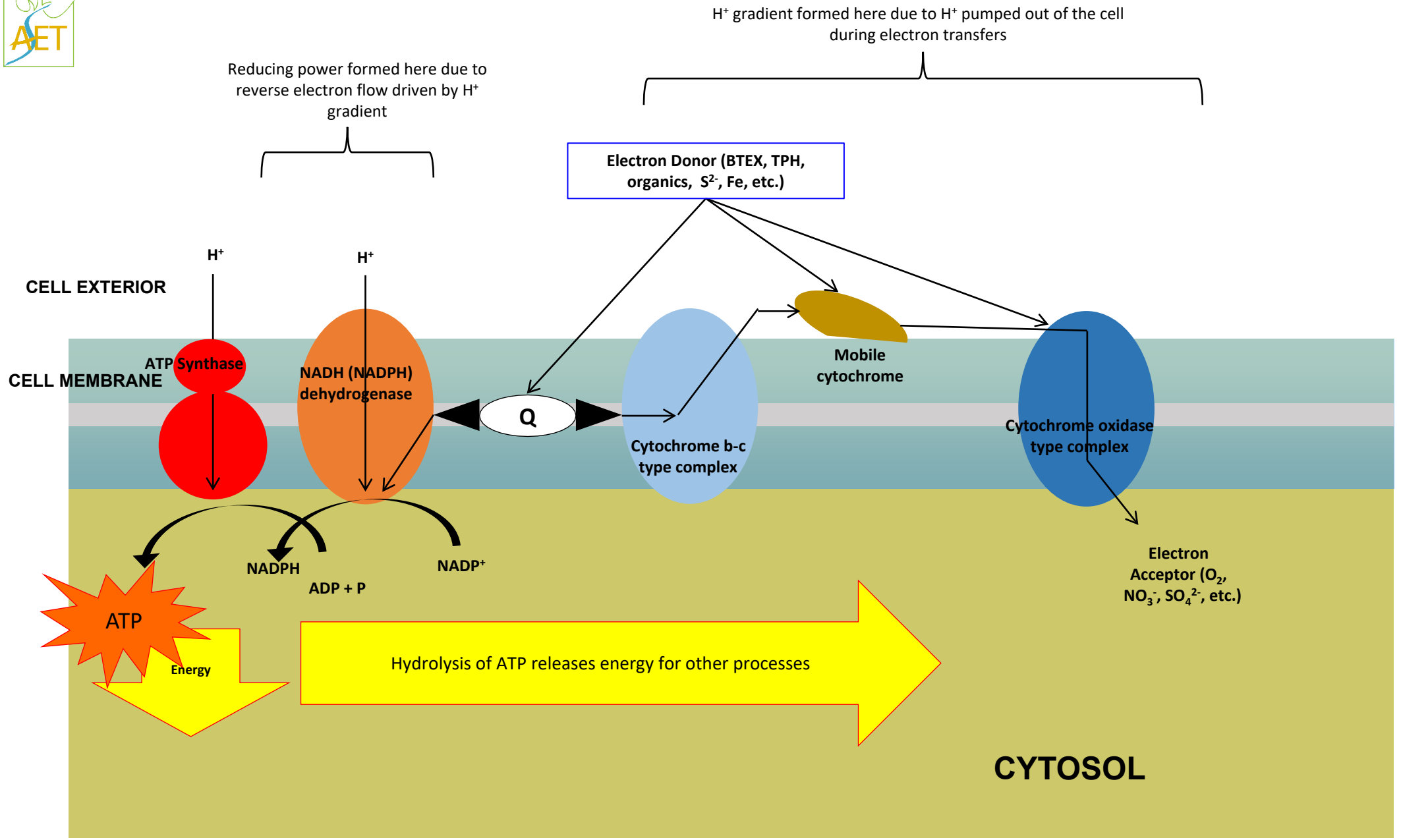
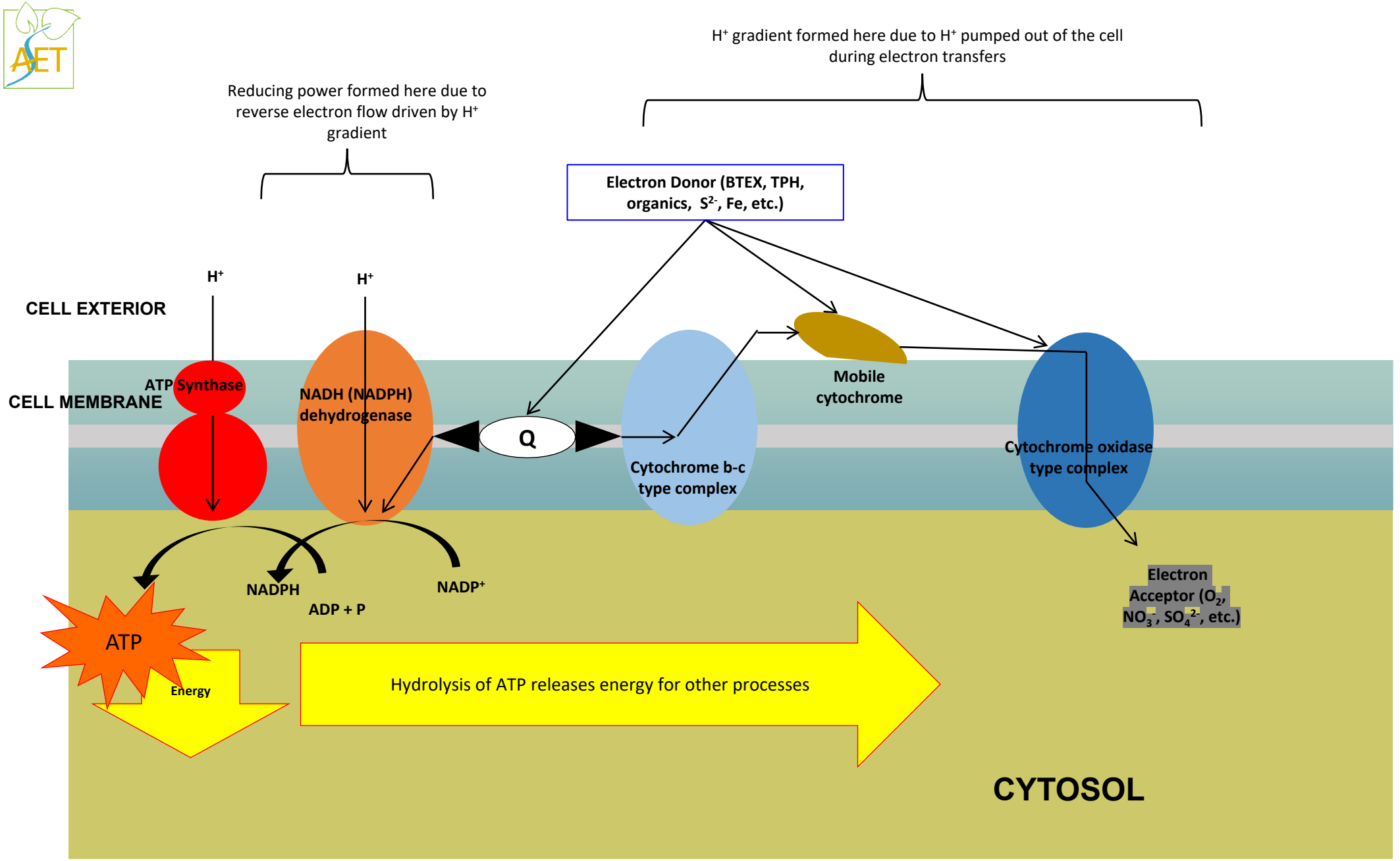
CO OPS listed remedial technology


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.)
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-, SO4 2-, etc.)
NADPH
NADP+
ADP + P
ATP
Energy
Hydrolysis of ATP releases energy for other processes
CYTOSOL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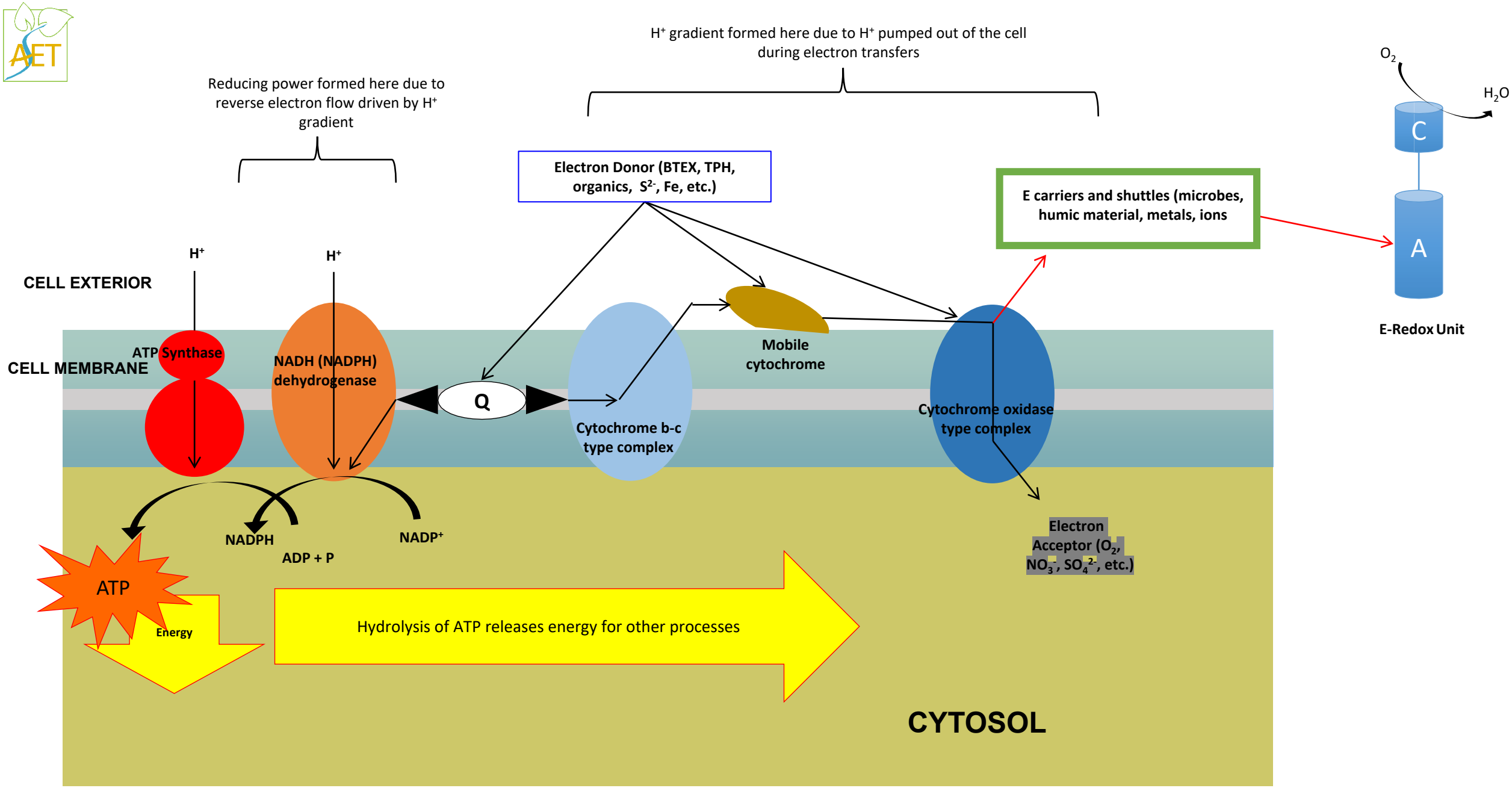
H+ gradient formed here due to H+ pumped out of the cell during electron transfers
Reducing power formed here due to reverse electron flow driven by H+ gradient
Electron Donor (BTEX, TPH, organics, S2-, Fe, etc.)
E carriers and shuttles (microbes, humic material, metals, ions
O2
H2O
C
A
E-Redox Unit
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-, SO4 2-, etc.)
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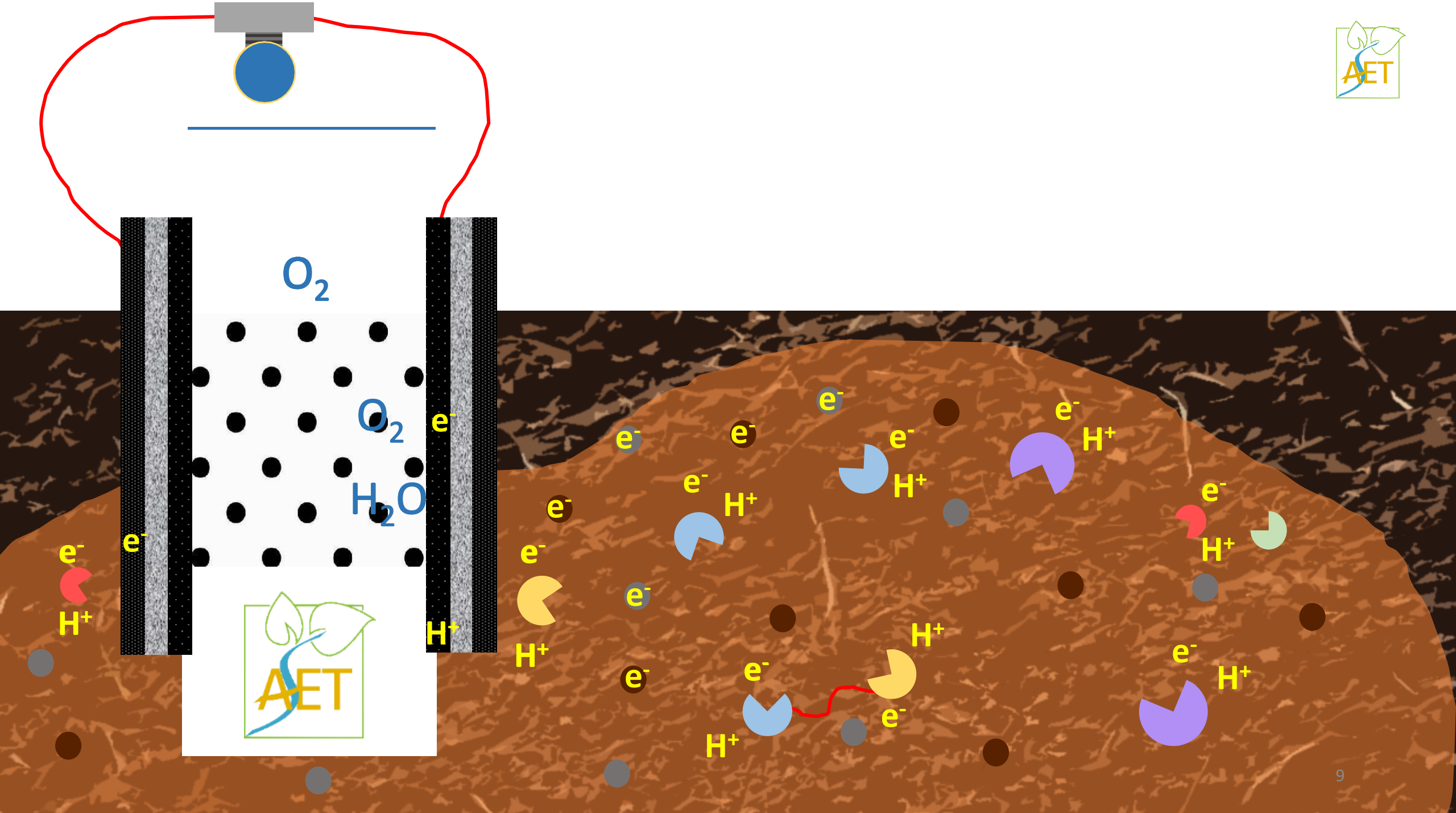
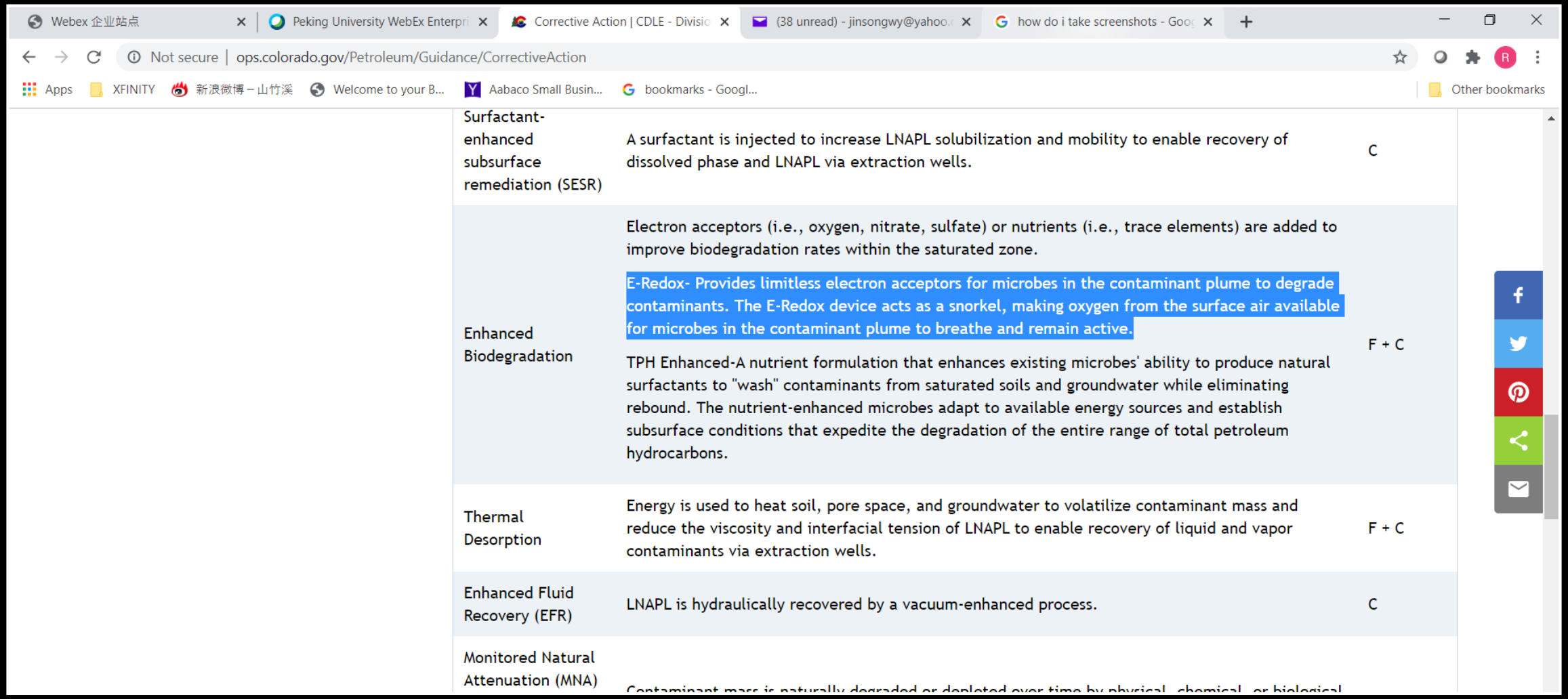

O_2
O_2
H_2O
e⁻
H⁺



CO Oil and Public Safety Guidance: Corrective Action Technologies

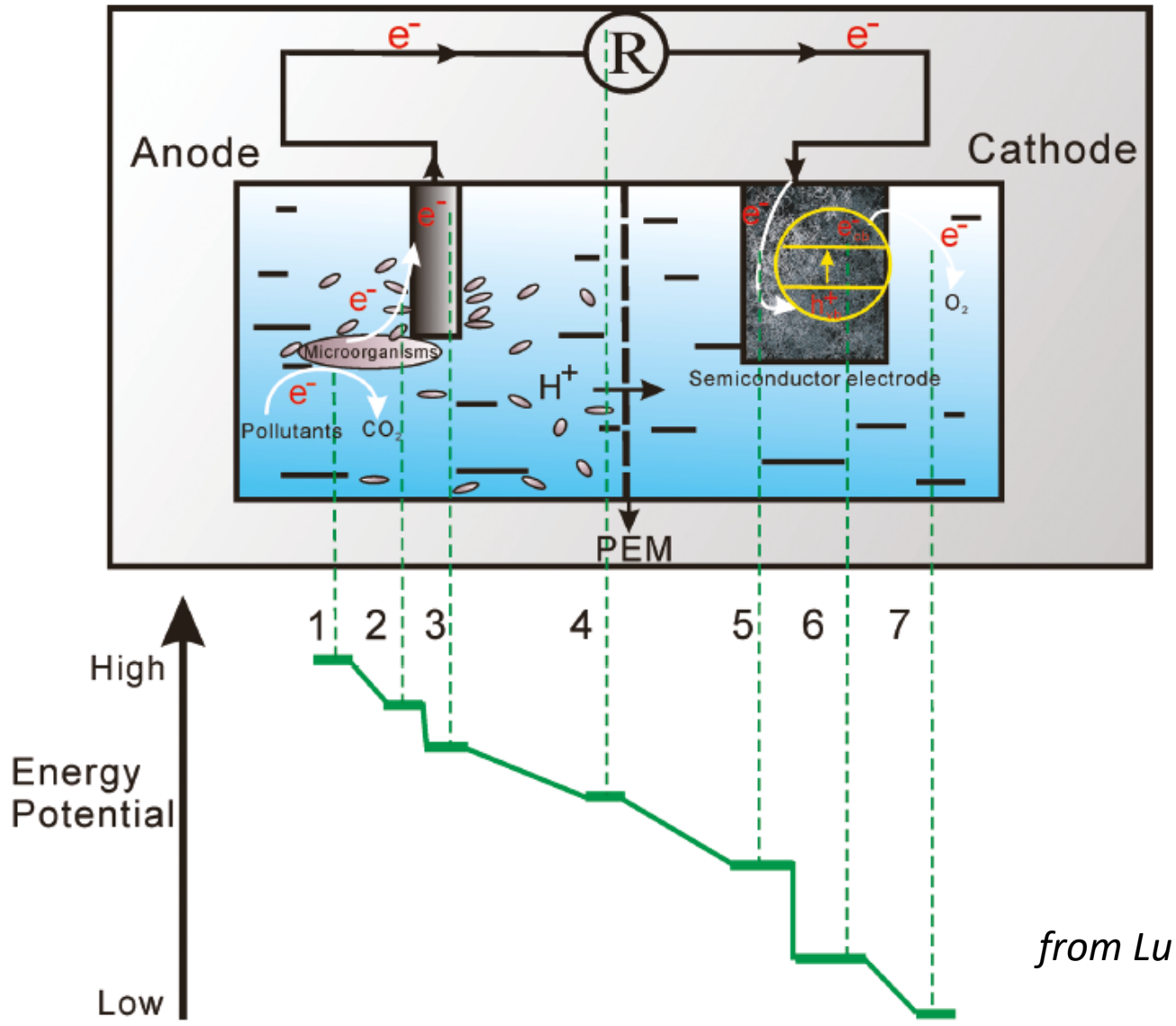
- E-Redox® applied to dozens of field sites since 2015 and achieved “no further action” determination
- E-Redox® listed as a remedial option by the State of Colorado in its guidance documents





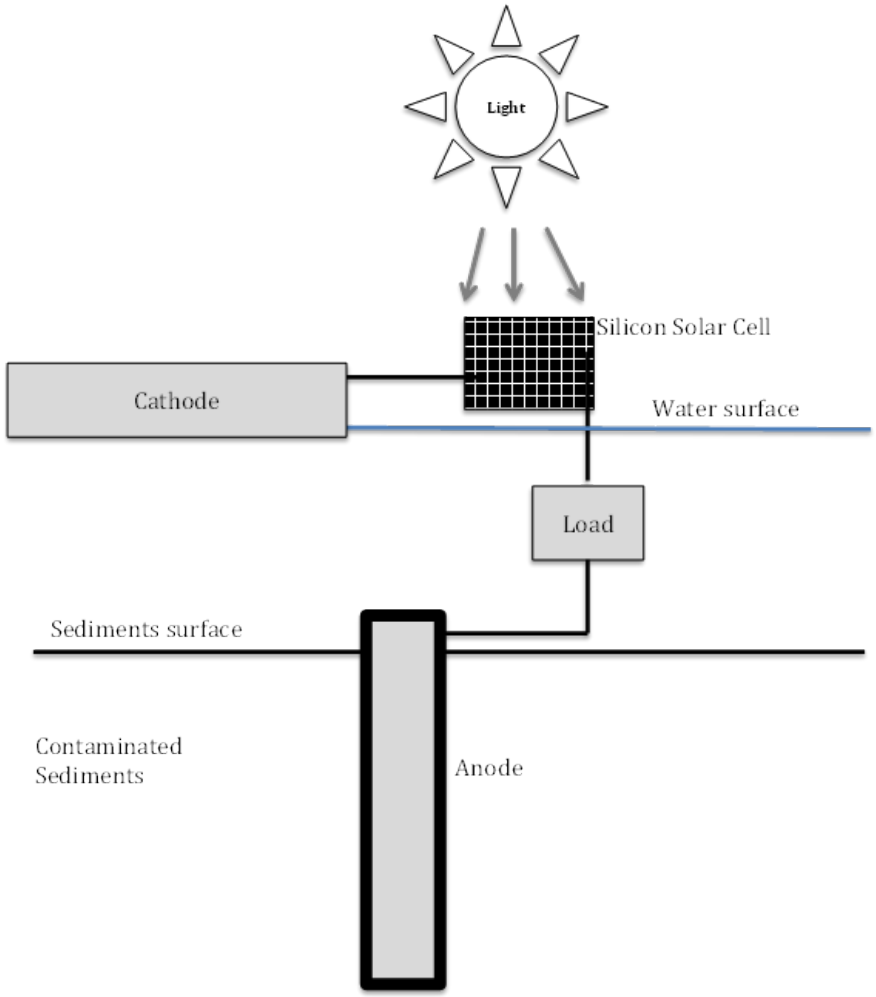



Photo-enhanced E-Redox® (E-Redox® Plus)



- ✓ Integrating semiconducting material into E-Redox® expedites electron movement and strengthens bioelectrochemical reactions
- ✓ Photochemical process triggers an “electron pumping” effect that accelerates oxidative biodegradation

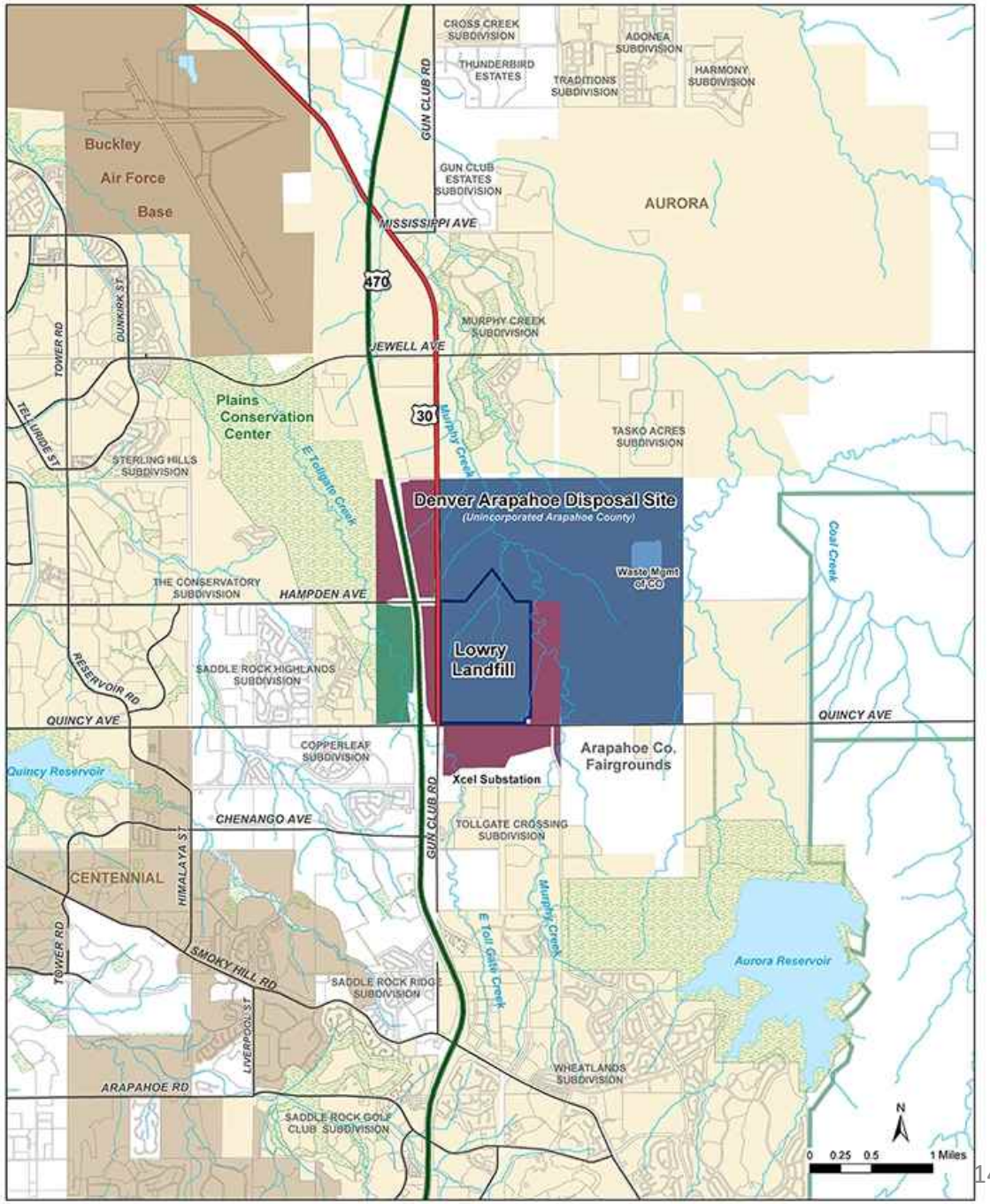
from Lu et al. Nature Communications, 2010



E-Redox® Plus has been applied for treating organic wastes in lake sediments, and petroleum hydrocarbons at a former refinery, and at a remote site in Alaska

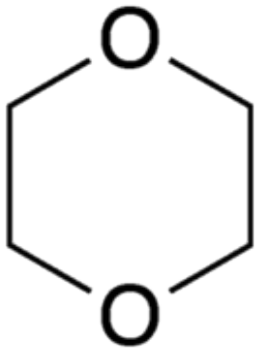
Lowry Landfill

- Located in the Denver Metro area
- Owned and operated by the City and County of Denver and Waste Management of Colorado
- 508 acres
- Accepted industrial waste from mid-1960s to 1980, resulting in groundwater contamination
- Listed as a Superfund site in 1984
- **1,4-Dioxane** is one of the recalcitrant contaminants in the groundwater



1,4-Dioxane Biodegradation

- 1,4-Dioxane has been found biodegradable by certain capable bacteria under aerobic conditions
- Co-occurrence of multiple contaminants usually results in the recalcitrance of 1,-4 dioxane due to anerobic conditions in the matrix



Growth

Pseudonocardia dioxanivorans CB1190

Cordyceps sinensis

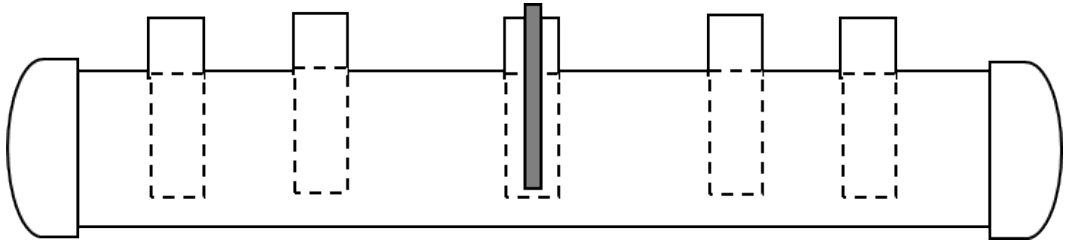
Mycobacterium austroafricanum JOB5

Rhodococcus jostii RHA1

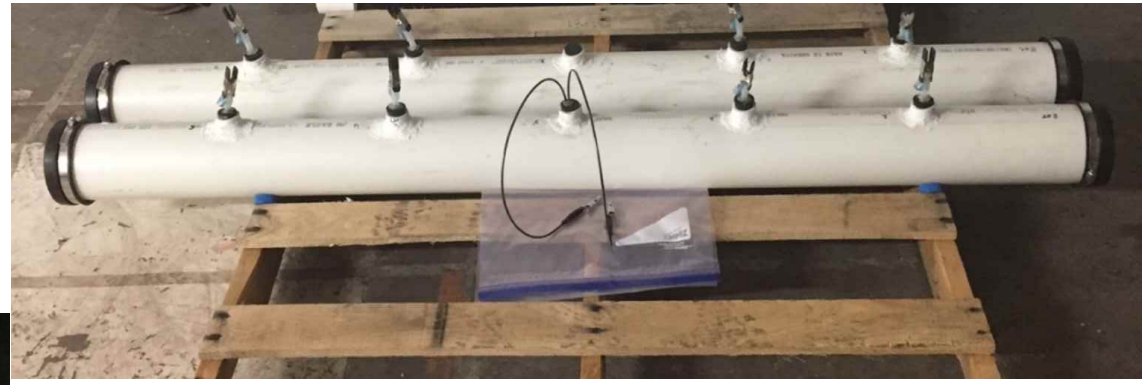
Non-Growth

Laboratory Treatability Study

- Groundwater and soil samples were collected from the Lowry Landfill site in an area with elevated 1,4-dioxane
- Samples contained sufficient nutrients but were under anaerobic condition for a long period
- Two lab-scale E-Redox® units were setup (1 active, 1 disconnected control)
- Both units were eventually inoculated with a culture containing 1,4-D degrader *Pseudonocardia dioxanivorans (*CB1190 DSM 44775, ATCC 55486, JCM 13855)

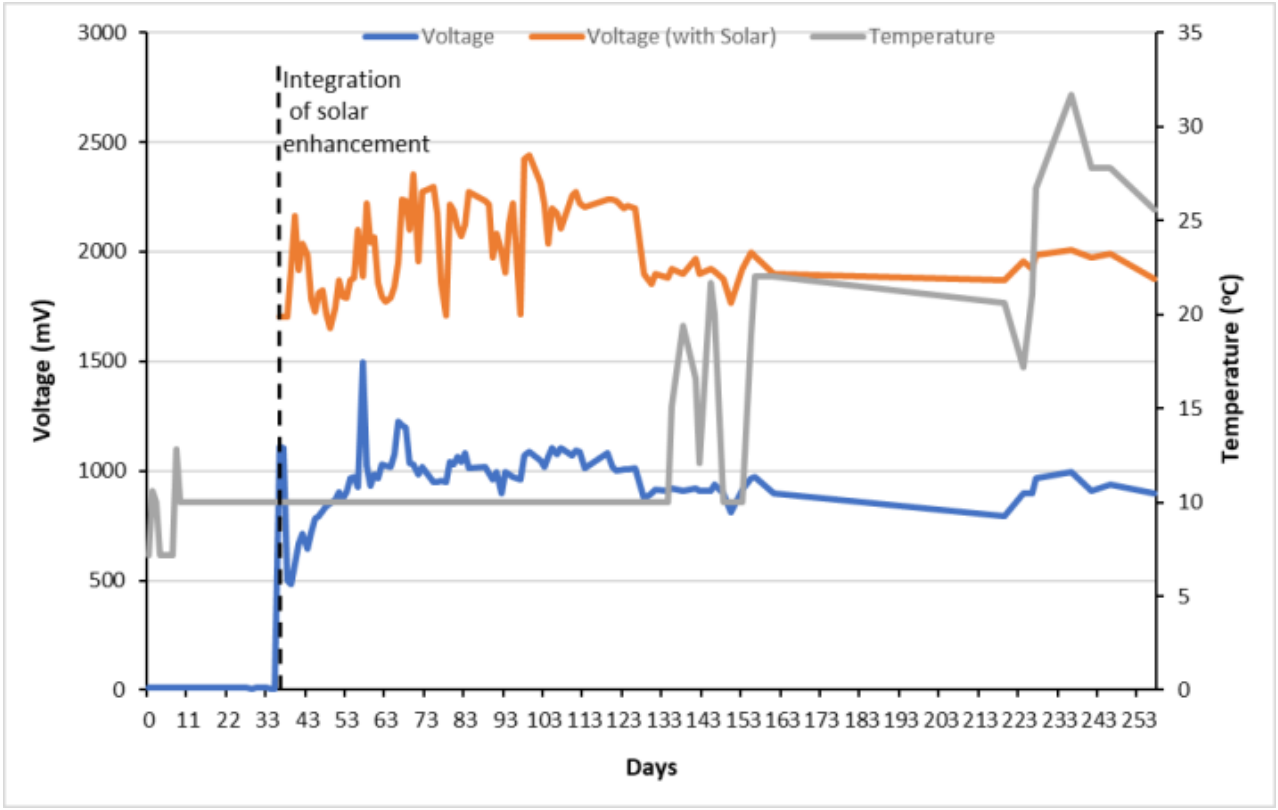


Lab scale E-Redox® units (~5 ft L x 4" ID) with multiple sampling ports

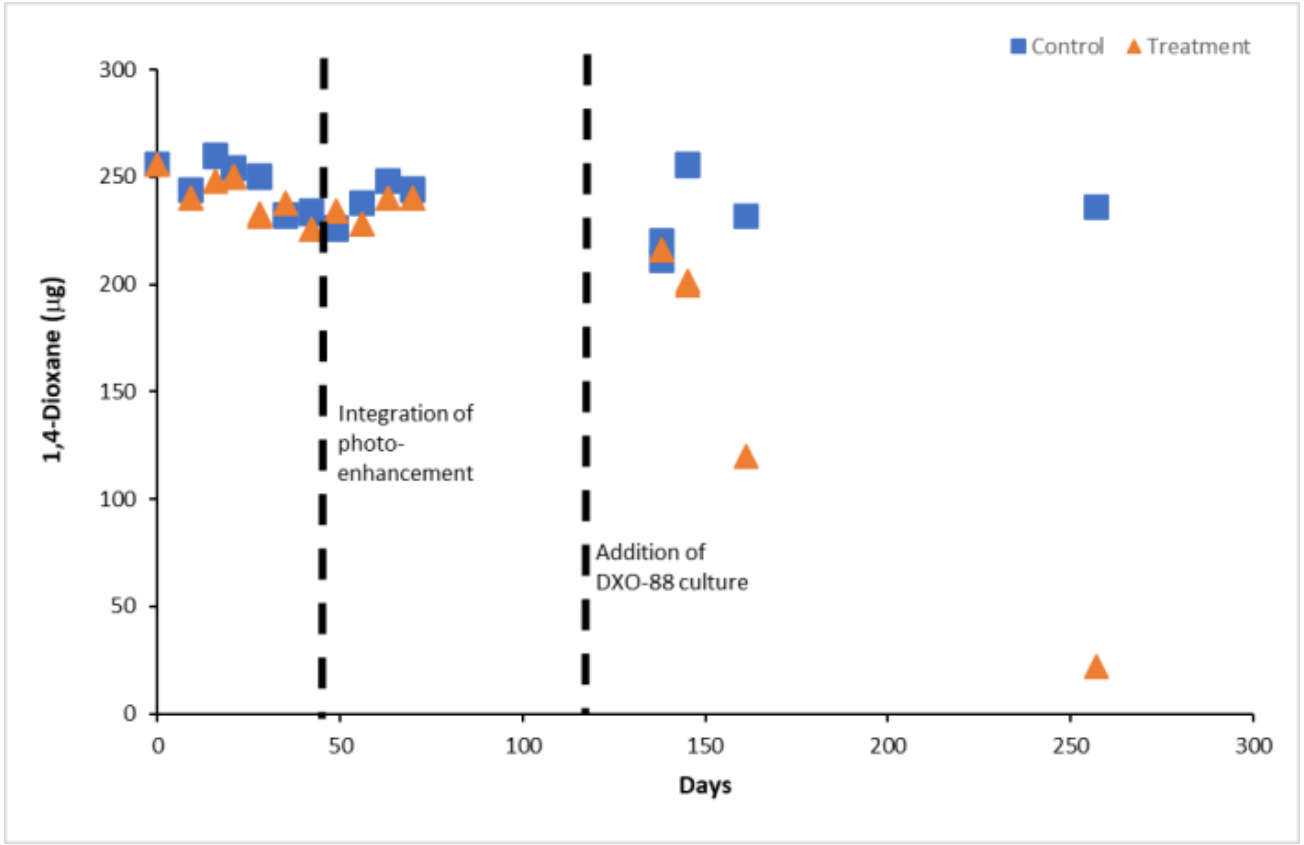


Results

- E-Redox® voltage monitoring indicated baseline microbial activity increased with the integration of the semiconducting material
- Microbial assay results indicated that microbial activity was lacking in both active and control units during the first 35 days
- *P. dioxanivorans* CB1190 culture was inoculated after the first 35 days



- After inoculation, 1,4-dioxane was degraded at 90% in the E-Redox® unit but stable in the control
- Robust microbial growth/metabolism was detected in the E-Redox unit vs. none to low bioactivity in the control
- Results indicate E-Redox® can significantly enhance 1,4-dioxane biodegradation when capable microorganisms are present



Summary

- E-Redox® technology provides a conduit for electrons to be transferred to ambient O2 as the terminal electron acceptor
- It offers a “snorkel” for aerobic microbes in an anaerobic environment
- E-Redox® technology is applicable to CLAY and other tight lithology. No physical injection is involved
- E-Redox® is modular, compatible and synergistic to other remediation tools

✓Due to absence of capable indigenous microorganisms, bioaugmentation with *P. dioxanivorans* culture was conducted

✓Compared to the non-E-Redox, bioaugmented control, E-Redox® significantly enhanced the biodegradation of 1,4-dioxane

E-Redox®

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Enhanced biodegradation of hydrocarbon-contaminated sediments using microbial fuel cells

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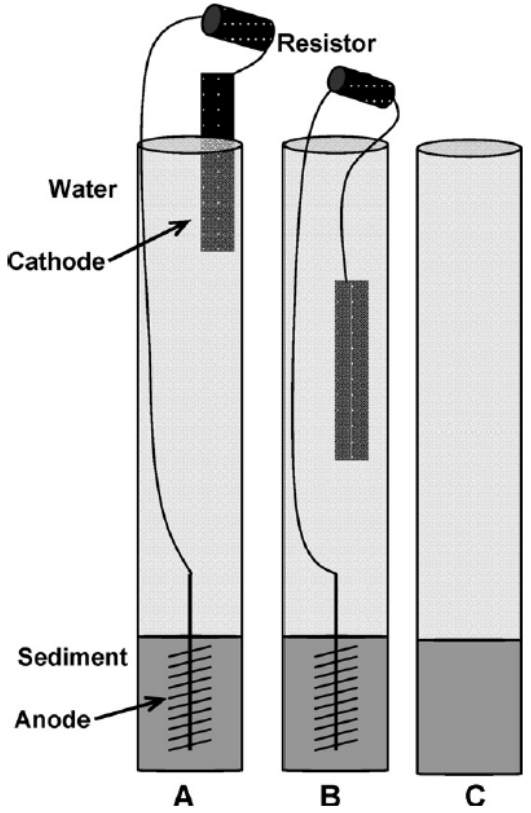
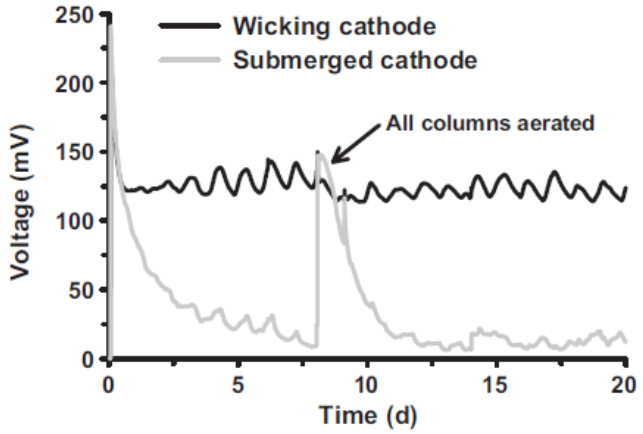
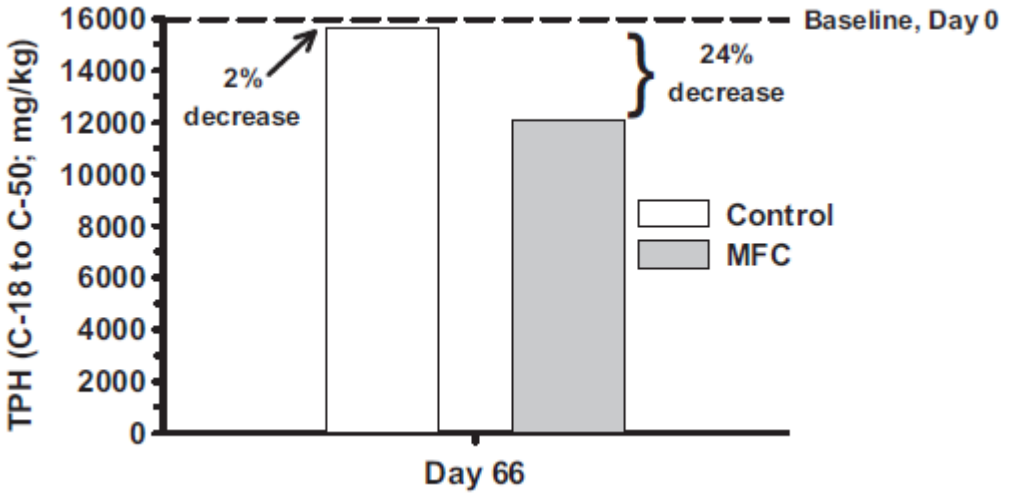
[b] Advanced Environmental Technologies LLC, Fort Collins, CO 80525, USA
[c] Department of Civil and Architectural Engineering, University of Wyoming, Laramie, WY 82071, USA

The 1st published research for bioelectrochemical system in biodegradation of petroleum hydrocarbons in sediments

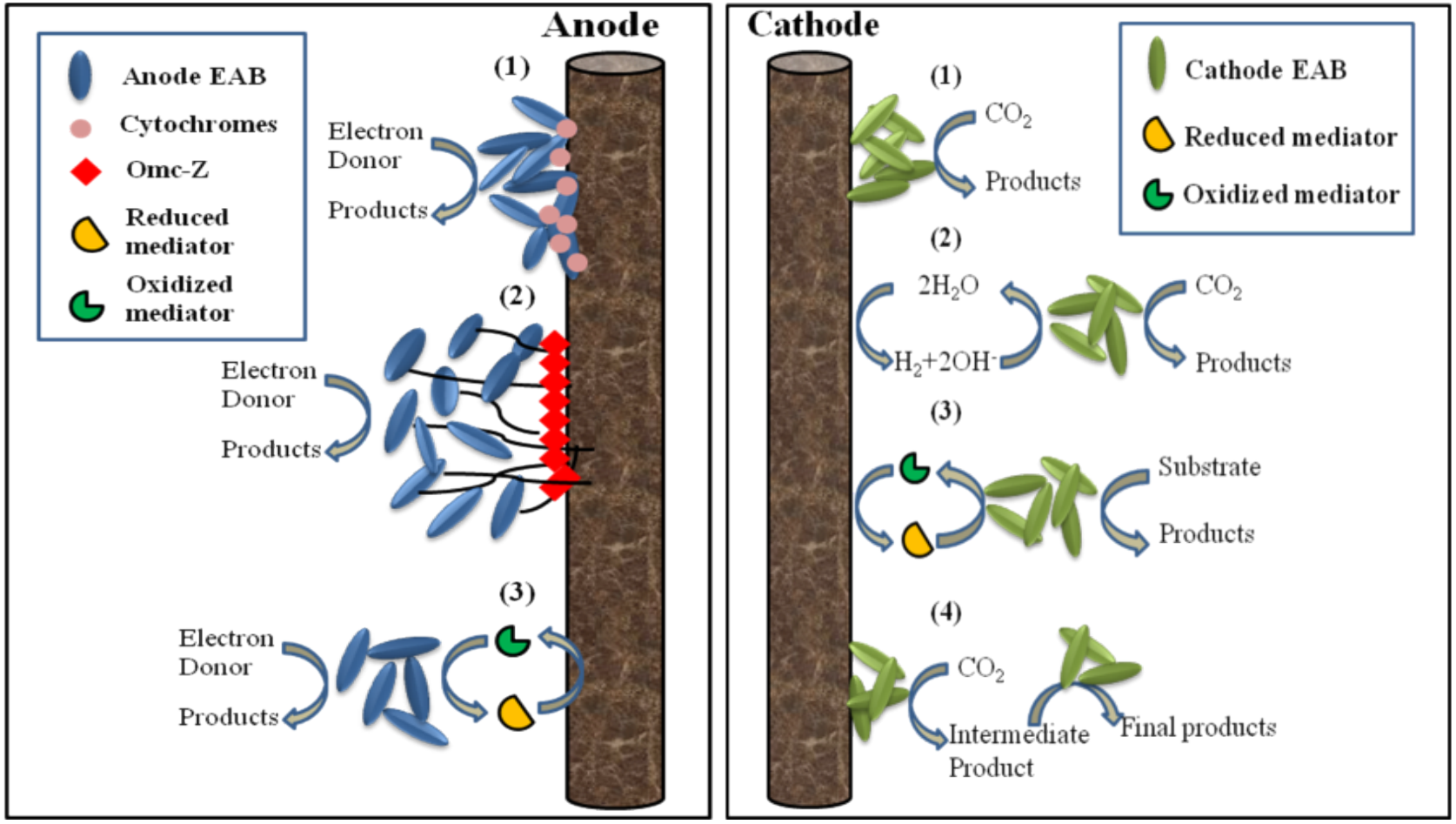
- Contaminated sediments from U.S. Pacific Coast
- TPH concentration = 16,000 mg/kg
- Bench-scale test systems operated for 66 days
- Voltage production from biodegradation as high as 190 mV
- TPH degradation 12 times greater for bioelectrochemical system compared to control

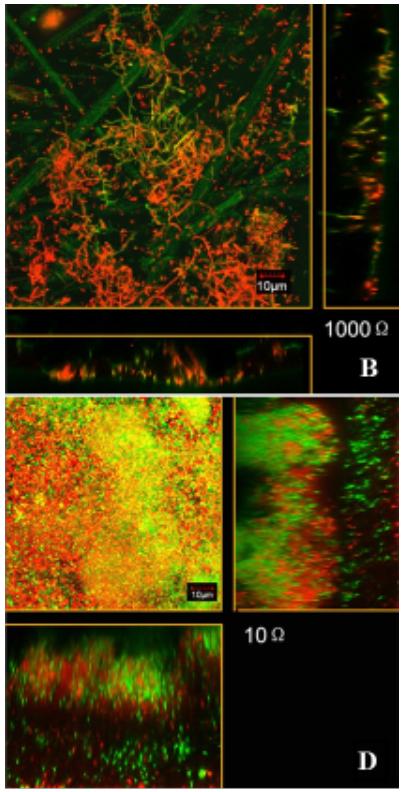






Pathways for microbial electron transfer in a bioelectrochemical system: electron shuttles in the matrix *(mediators)*, microbial contact, conductor (BECS electrodes), and TEA – *modified from Ren*





[Left] Anode EET mechanisms (1) Direct contact through Cytochromes; (2) Direct transfer through Nanowires; (3) Indirect transfer through matrix mediators;
[Right] Cathode EET mechanisms (1) Direct contact with the electrode; (2) through H2 conversion; (3) through mediators; (4) through other intermediate products.