Introduction & ISCO Primer

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Welcome and Background

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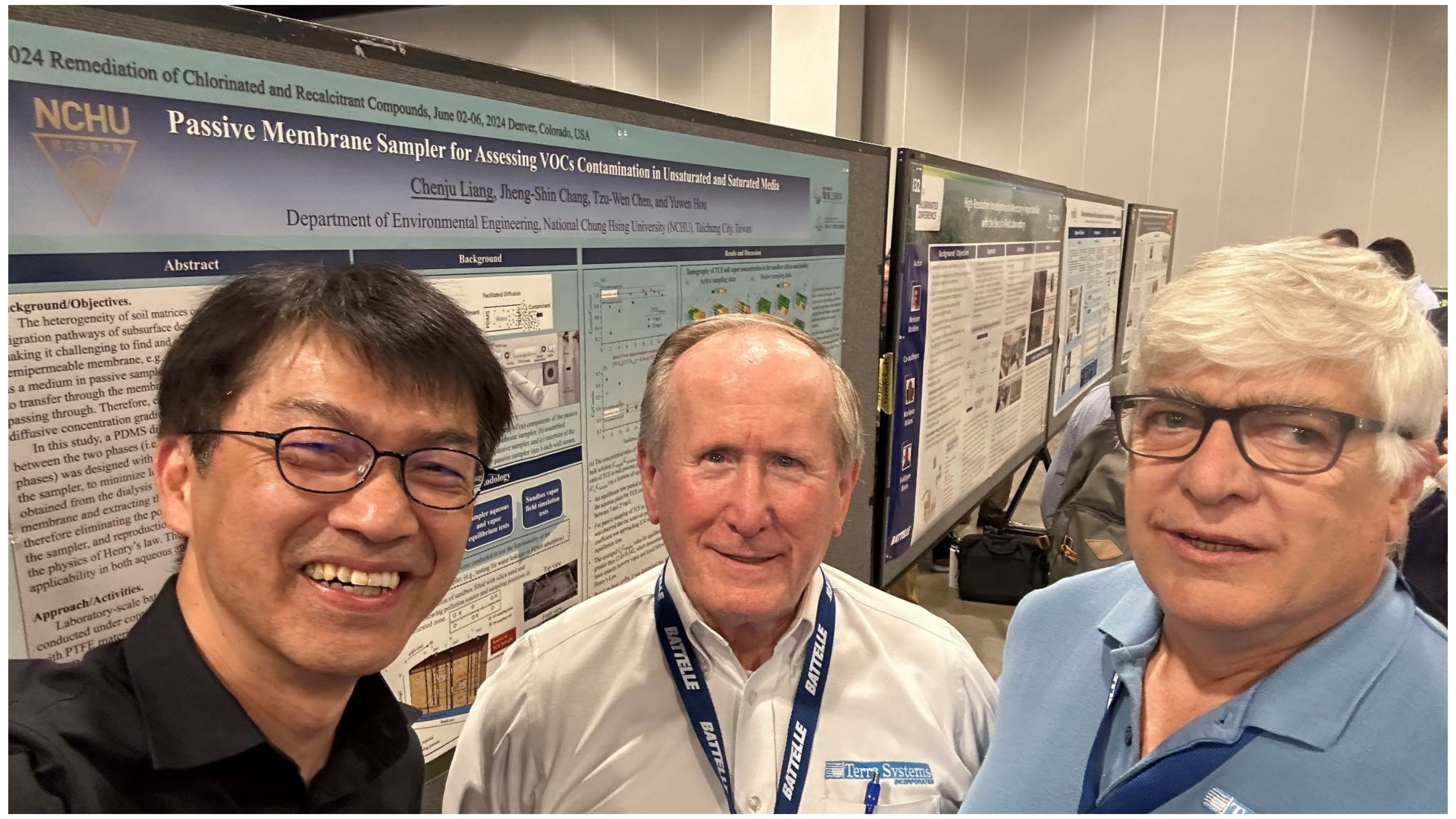
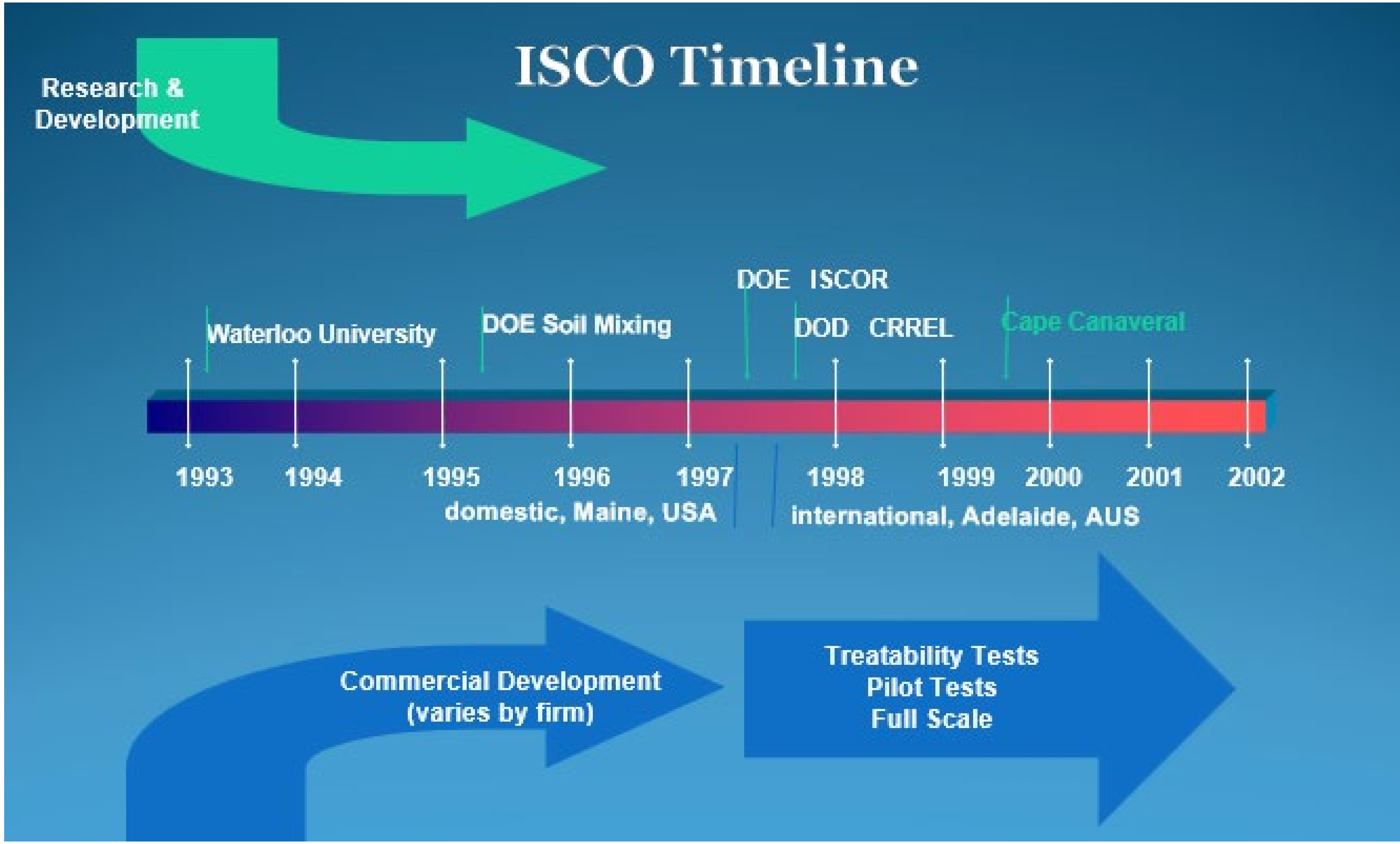
- Who Am I?
  - Career start in 1984 in original LNAPL recovery firm
  - Multiple firms as industry consolidated and changed
  - Focus on remediation, In-Situ Chemical Oxidation and Safety
  - Global technical presenter for last 40 years
- Why am I here?
  - Supporting local projects in Taiwan – ISB and ISCO
  - Met Dr. Liang at Battelle 2024 while reviewing his poster and research
  - Information sharing!



Groundwater Technology

What is In-Situ Chemical Oxidation (ISCO)

- ISCO is another remedial tool in the remedial toolbox
  - Highly flexible and modifiable
  - Not applicable to any Site (no silver bullet)
- Accepted mainstream technology (no longer considered innovative, some even consider “traditional”)
  - Educational ISCO ~ 1994
  - DOE Soil Mixing ~1996
  - First Field ISCO 1997
  - Commercialization post 1997



What is In-Situ Chemical Oxidation (ISCO)

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- ISCO is the application of chemical oxidants to destroy contaminants in the subsurface.
- The oxidant is the chemical applied to mineralize (i.e., destroy) target compounds into innocuous byproducts.
- Oxidation is the chemical reaction where electrons are lost by the reduced species and absorbed by the oxidant (i.e., redox reactions):

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

- Applying this half reaction to various contaminants, the corresponding “stoichiometric” requirements for oxidation can be calculated.

In-Situ Chemical Oxidation (ISCO)

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1. Selection and Loading

2. Delivery and Distribution

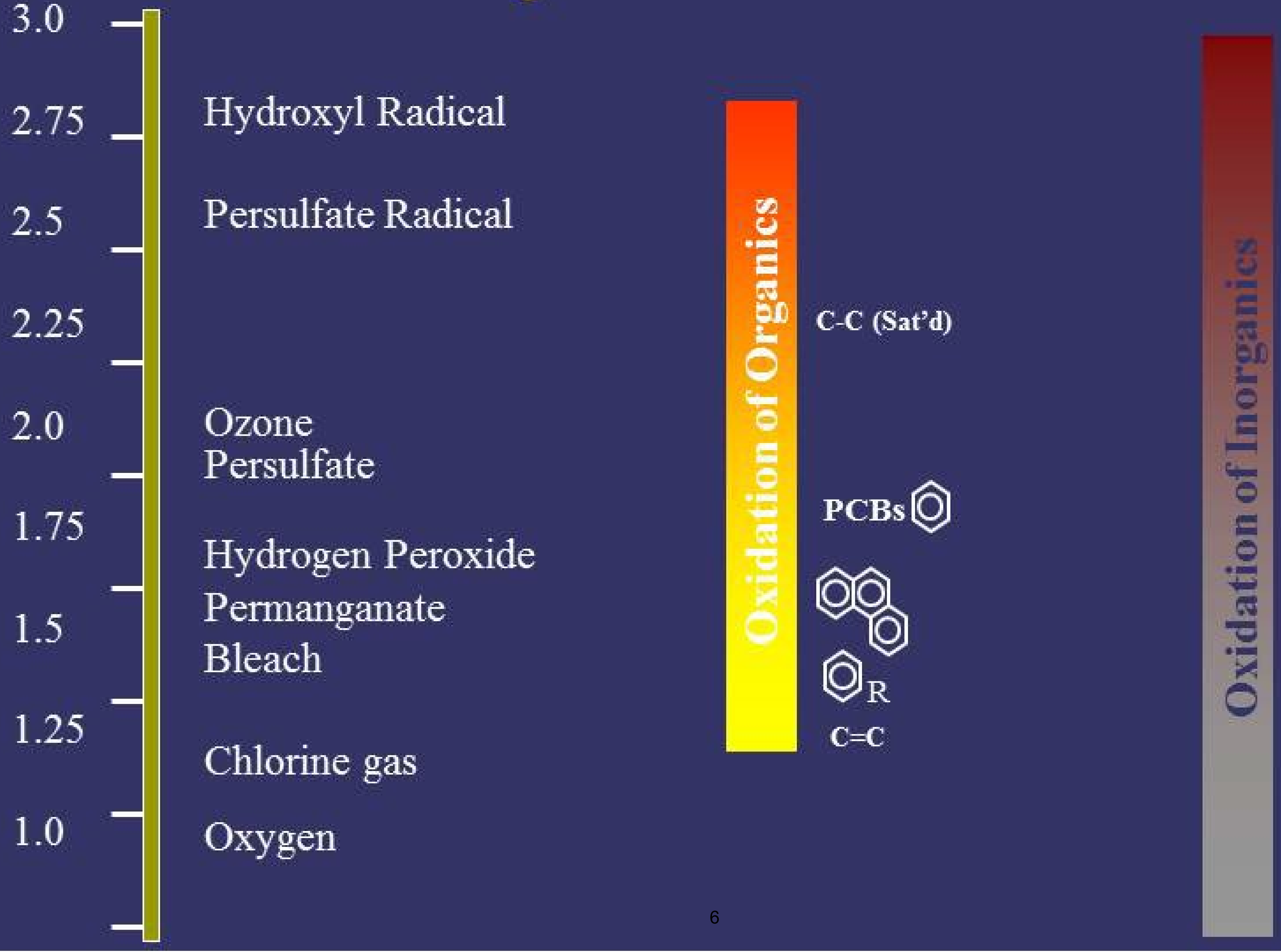
Performance is:

applying *enough oxidant* *in contact* with the contaminant for a *long enough period of time* to *react effectively*

3. Contact and Persistence

4. Reaction and Contaminant Destruction

Reactivity of Available Oxidants



Oxidant Selection

Selection is a function of many factors:

- Site specific issues – lithology, groundwater hydraulics, access, sensitive receptors, target mass location, heterogeneity and anisotropy
- Time – available, single vs. multiple treatments, permeability
- Cost – labor, equipment, capital, expenses, subcontractors, availability
- Oxidant – loading, effectiveness, stability, end products of reaction
- Optimization strategies – surfactants, coupling, controlled release
- Focus is on permanganate ISCO, technology is however applicable to many injectates

Delivery

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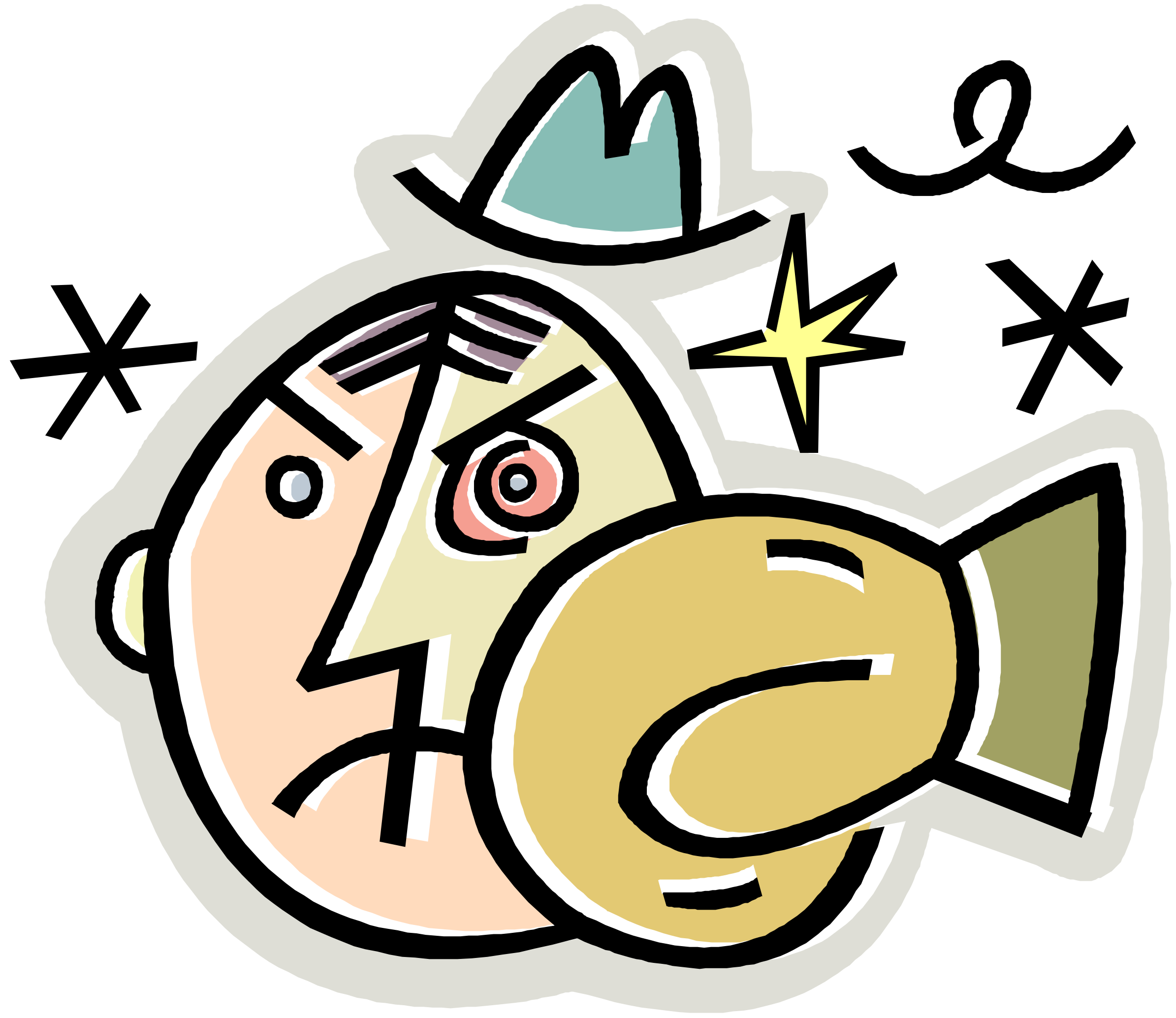
<u>**Delivery** is, remains, and always will be, the single most important component of an ISCO success or failure</u>

- Contact – contact – contact! – redox is contact process
- Emplacement is only the beginning –
- End point – persistence vs. reactivity



Delivery Examples

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"Passive"	*"Active"*	*"Destructive"*
Encapsulation Flow through Constant head Push-Pull	Existing Wells Temporary Wells Recirculation Pore dilation Electrokinetics Thermal Methods	Excavation / Engineering Media Fracturing Soil Mixing

Increasing Disruption →

Increasing Energy Input and Short-Term Cost →

Increasing Time Required and Long Term Cost ←

Passive Methods

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Allow unimpeded natural processes

- Do nothing – or very little
- Encapsulation/isolation – Cap and cover
- Flow through systems – PRBs, mulch walls
- Dissolvables - candles
- Contact Head injection –
- Push-Pull – with surfactant

Active Methods

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Accelerate Natural Processes

- **Pressurized injection – wells, probes, multiple level**
- Recirculation – P&T and infiltrate, ART wells
- Pore Dilation –
- Electro kinetics -
- Thermal (?) -

Destructive Methods

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Site conditions get in the way – destroy them

- Excavation
- Soil Mixing
- Media Fracturing

Oxidant Misconceptions

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- In porous media, the application of oxidants **will not "clog"** the formation (< 10% void infilling at high loading). Due to small pore throats and limited connectivity, this is not necessarily true in low permeability materials or fractured media
- Oxidation **does not sterilize** formation, biota recovers quickly and fully
- Effective and appropriate **delivery is critical** to ISCO success
- Oxidant can **persist** in presence of contaminant
- Excess oxidizer lead to **false negative** confirmatory samples (also may damage to lab equipment)
- Treatment trains - biological methods (ERD using QRS™ or SRS®) provide **follow-up** to ISCO

ISCO with Sodium Persulfate

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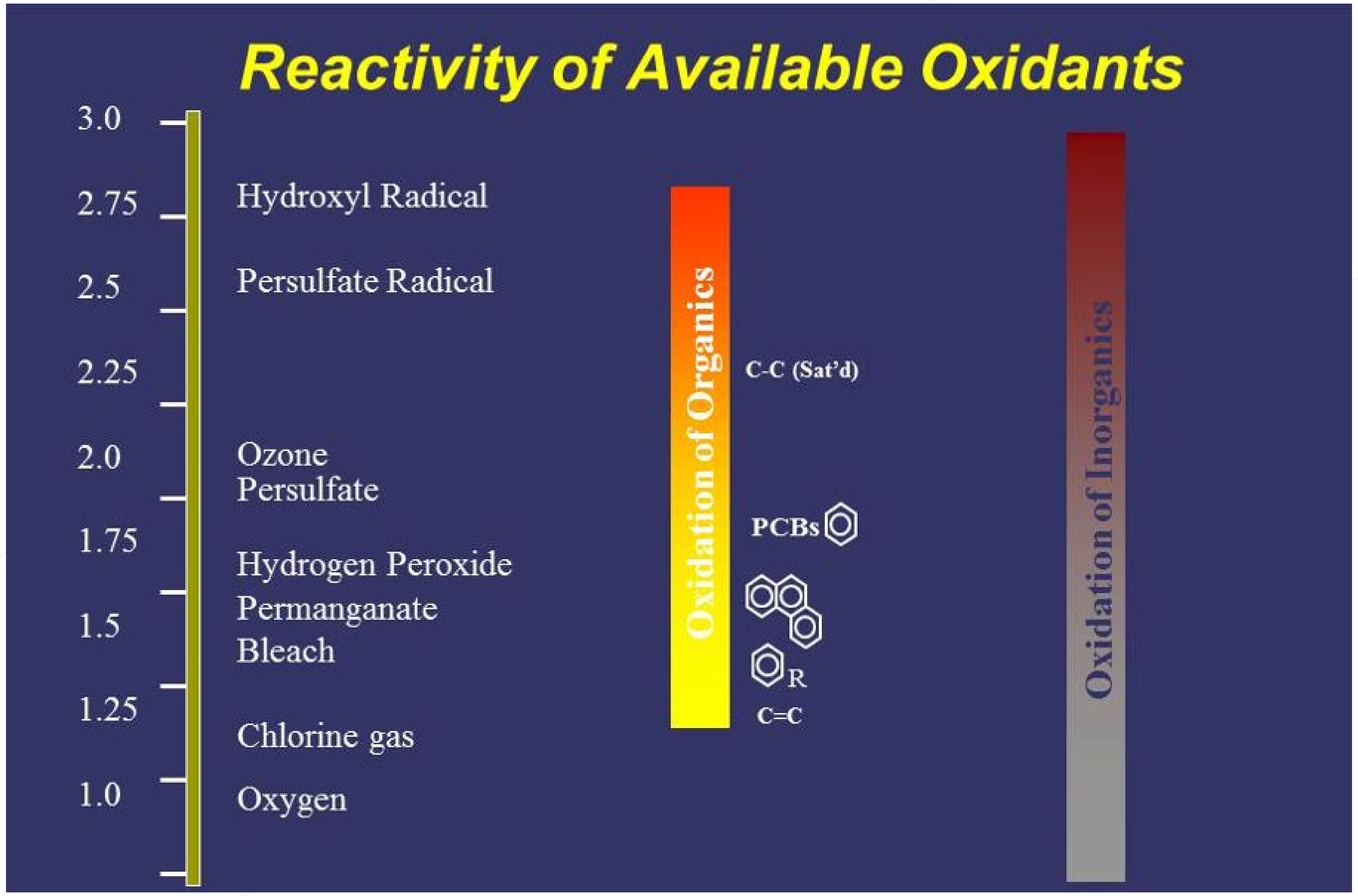
- Two Reaction Pathways

activated (radical) - $S_2O_8^{-2}$ + TSI-FSA™ → $S_2O_8^{-}$, SO_4^{-}•, OH•, O_2^{-}

- Why Activation?

unactivated (oxidation) – $S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2H_2SO_4^-$

1. combined oxidative and reductive pathways
2. stronger, kinetically fast, localized
3. degrade recalcitrant compounds (Cl-ethanes, CT, pesticides, etc.)



Commonly Used Persulfate Activation Methods

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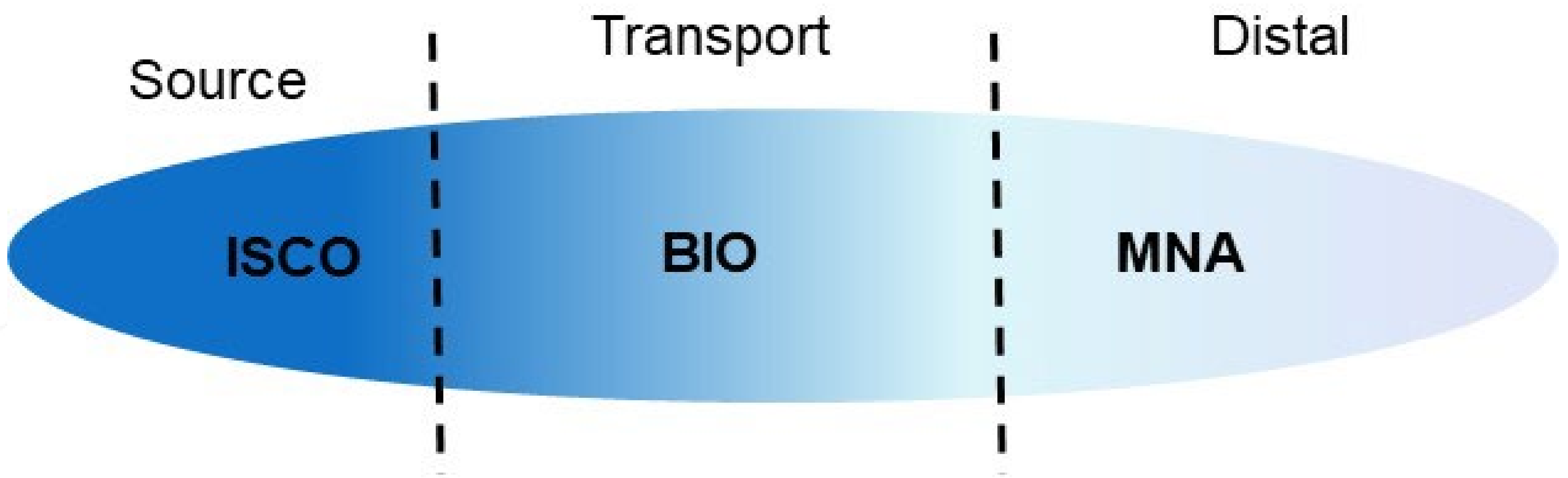
Method	Drawbacks	Patent Holder
Sodium Hydroxide	Hazardous (pH, worker safety)	Evonik (Block et al.)
Fe-EDTA	Requires 160 to 600 mg/L Iron	Evonik (Block et al.)
Hydrogen Peroxide	Rapid decomposition of persulfate and peroxide	Evonik (Sethi et al.)
Stabilized Hydrogen Peroxide	Precise monitoring and control of pressure and temperature	Cronk (JAG)
Carbohydrate	Licensed technology	ISOTEC (Watts et al.,)
Ferrous Sulfide TSI-FSA™	Limited field experience	**None**

Combined Remedies: Chemical Oxidation & Bioremediation

- Technology Coupling – “Best of Both Worlds”
  - maximize effectiveness while minimizing cost
  - spatially – sequentially over distance
  - temporally – sequentially over time
  - better respond to changes in conditions
  - mutually supportive
- Remedial Life Cycle Approach



State of the Practice

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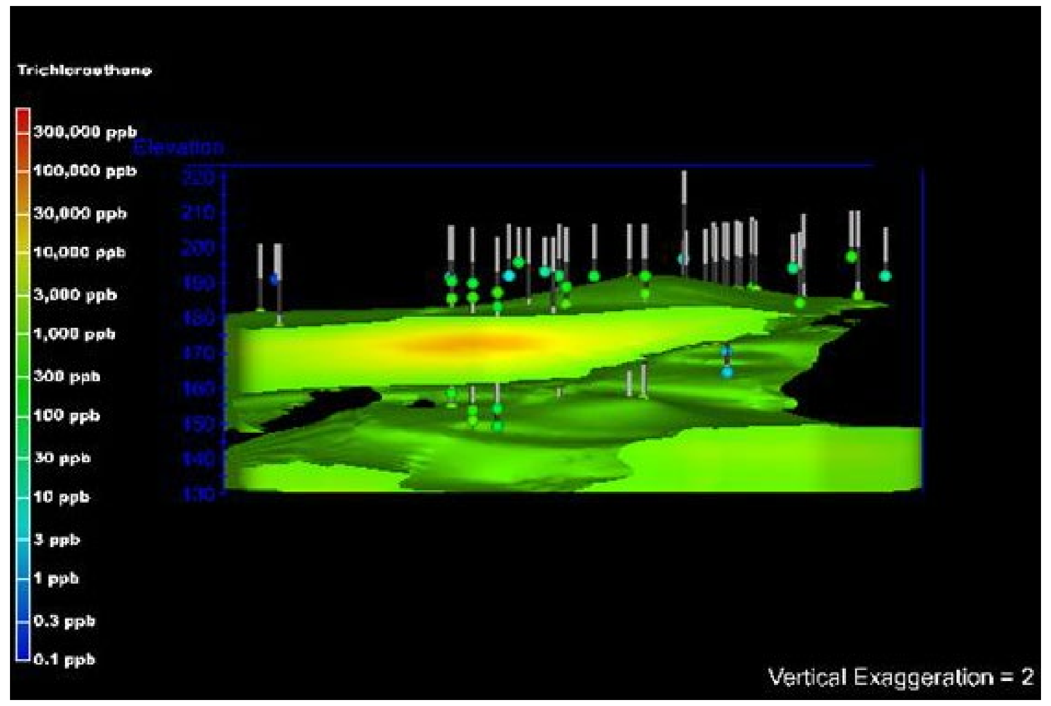
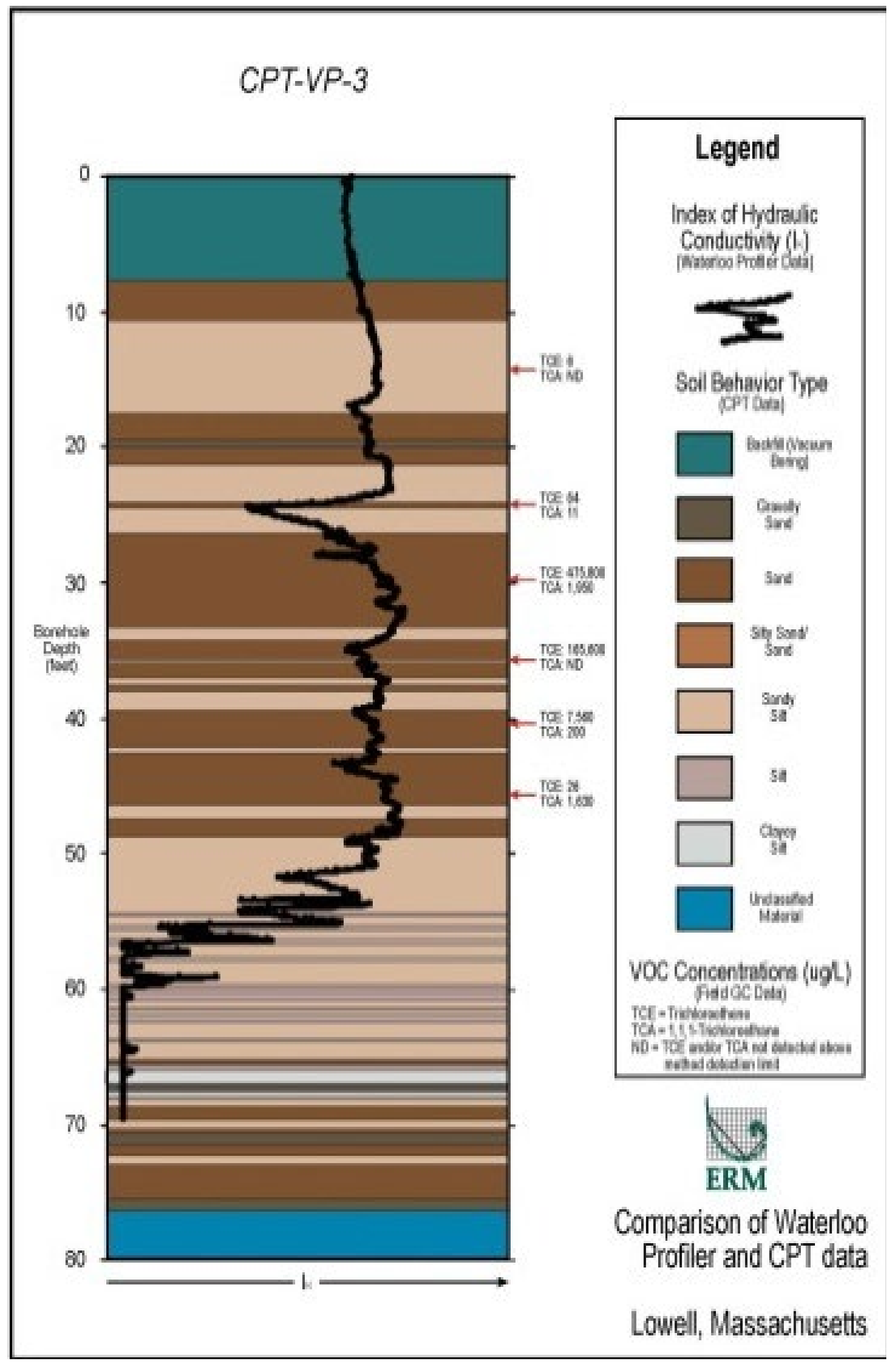
- Sites are increasingly complex
- Rapidly changing characterization tools
- Improved ISCO understanding
- Overpromised unrealistic expectations
  - Multiple incidences of technology failures
  - No technology works everywhere



Something you never want to see…



State of the Practice

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"... because as we know, there are **known knowns**; there are things we know we know.

We also know there are **known unknowns**; that is to say we know there are some things we do not know.

But there are also **unknown unknowns** – the ones we don't know we don't know.

And if one looks throughout the history of our country and other free countries, it is the latter category that tend to be the difficult ones,"

(Rumsfeld, 2002)

Questions?

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