Understanding ISCO Field Applications by Assessing Geochemical Data

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Soil & Groundwater Remediation

Webinar | April 26, 2023

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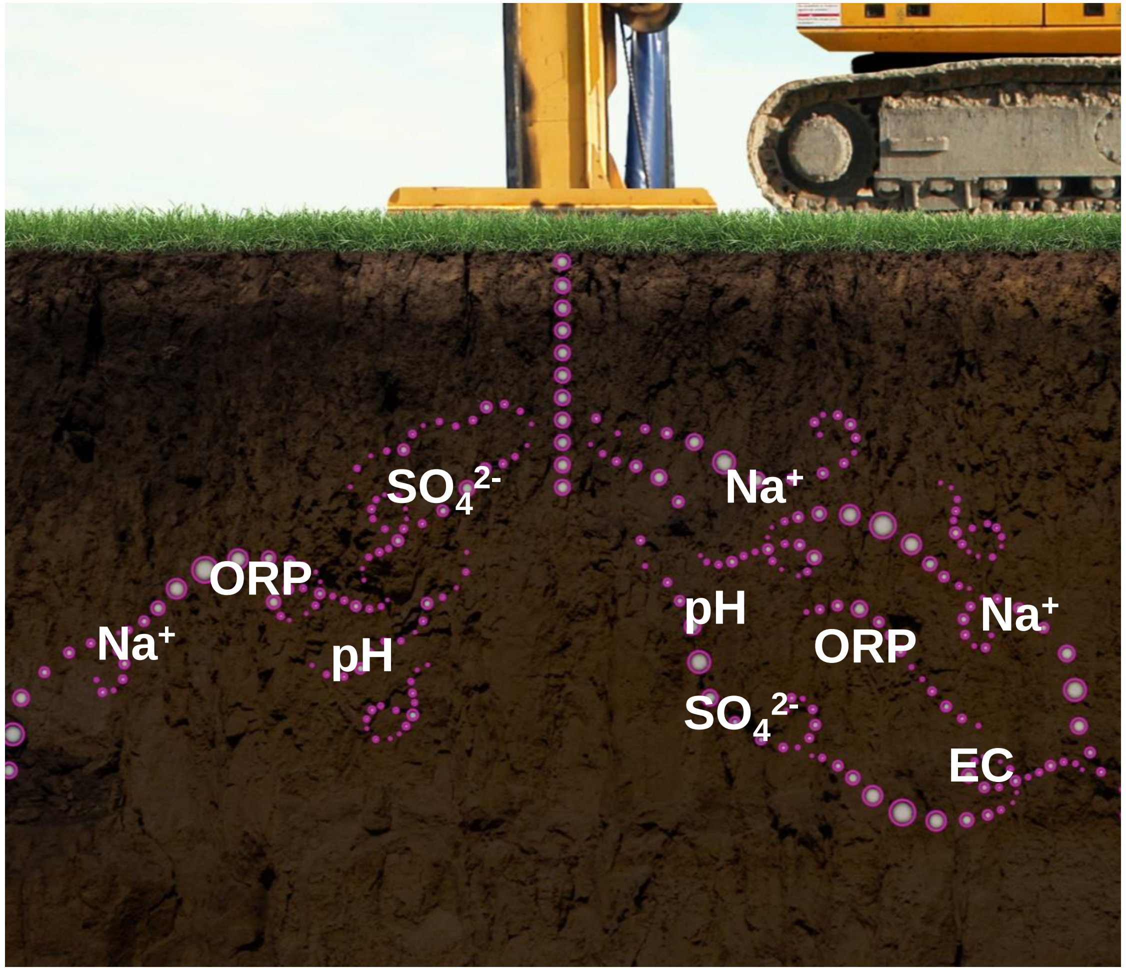
Presentation Outline

- **Introduction**
  - What can we learn from geochemical analyses
- **Review of key persulfate geochemical indicators**
  - Direct measurement of persulfate
  - Persulfate breakdown products
  - Changes to geochemical parameters
- **Case example**
  - Successful application
  - Underdosing (rebound)
  - Recontamination from inflowing groundwater
    Poor distribution



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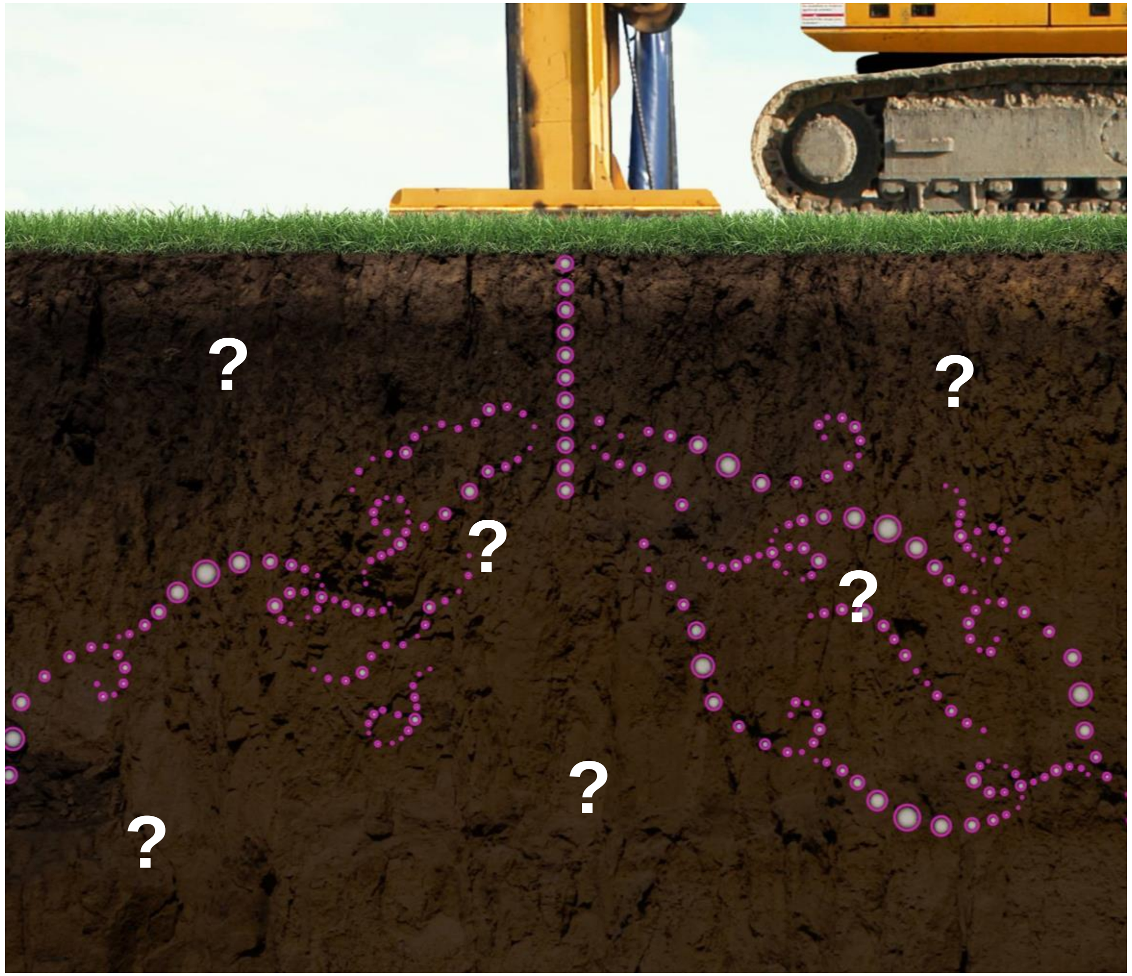
Common In Situ Remediation Challenges

- Dealing with unknowns / data gaps
- Dealing with heterogenic conditions
  – Lithology + contaminant distribution
- Uncertainties in reagent demand calculations
- Establishing contact (injection strategies)

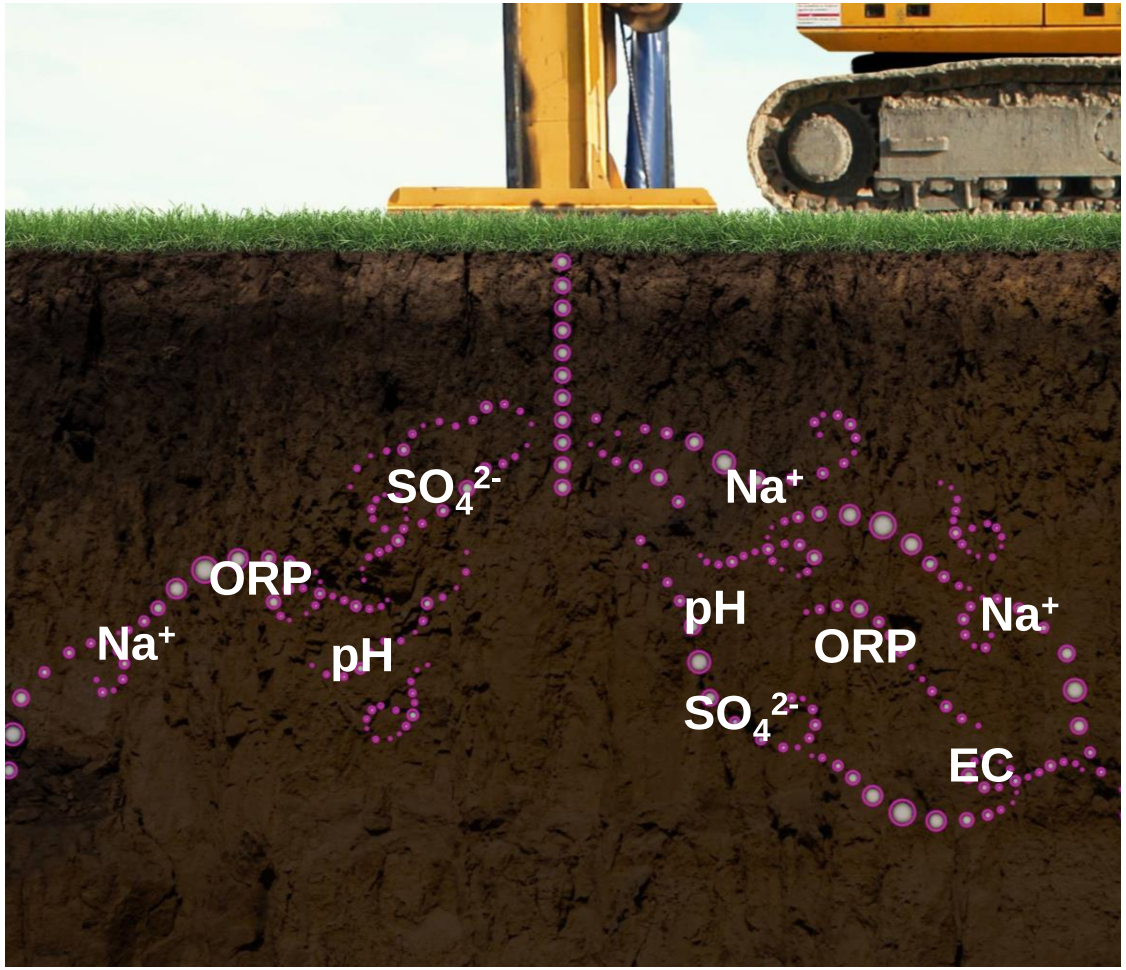
Successful *In Situ* remediation requires:

Sufficient dose of reagents to contact contaminants over a sufficient time period



Persulfate has a distinct chemical 'fingerprint'

- Following the successful application of persulfate, a distinctive signature of certain parameters would be expected:
  - Analyses of active persulfate in GW
  - Increase in persulfate breakdown products (sodium/potassium & sulfate)
  - Key geochemical parameters: EC, ORP, pH
- A detailed comparison of these parameters in combination with other site data can be used to better understand an application and the site.



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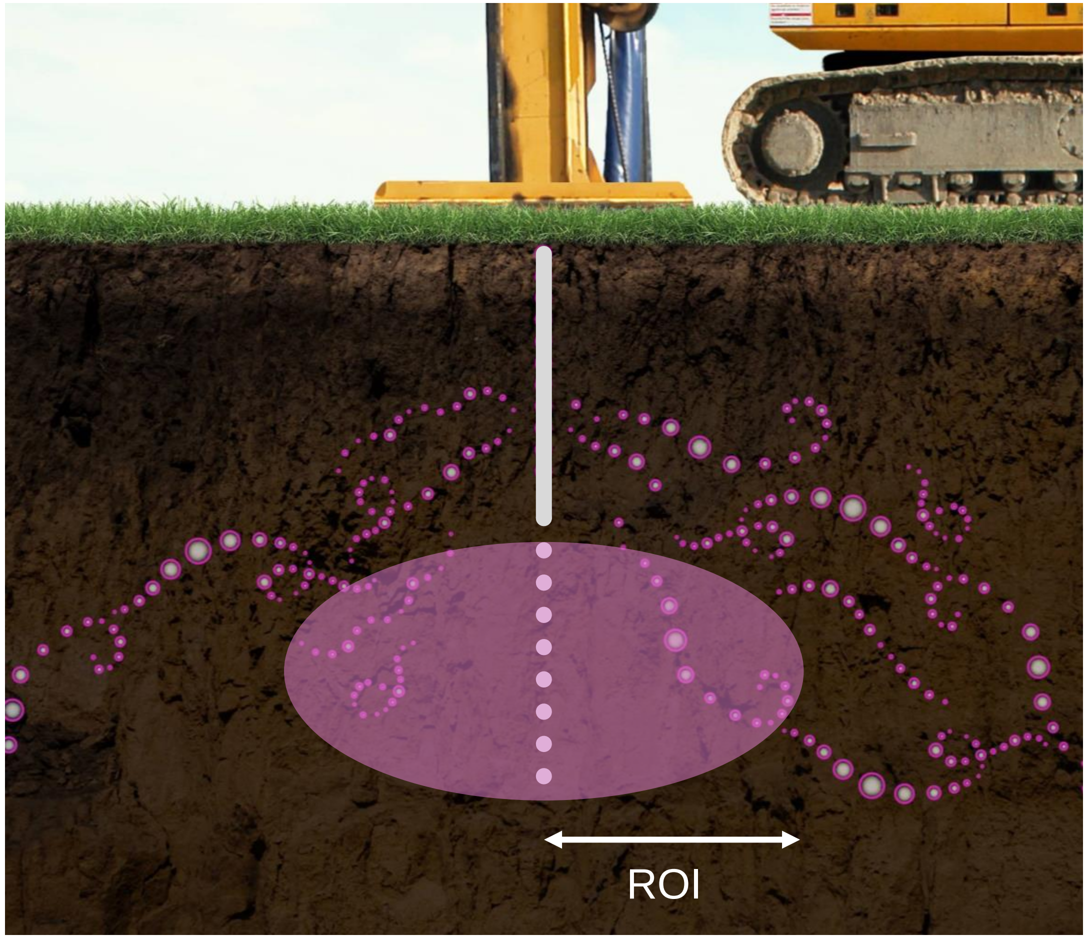
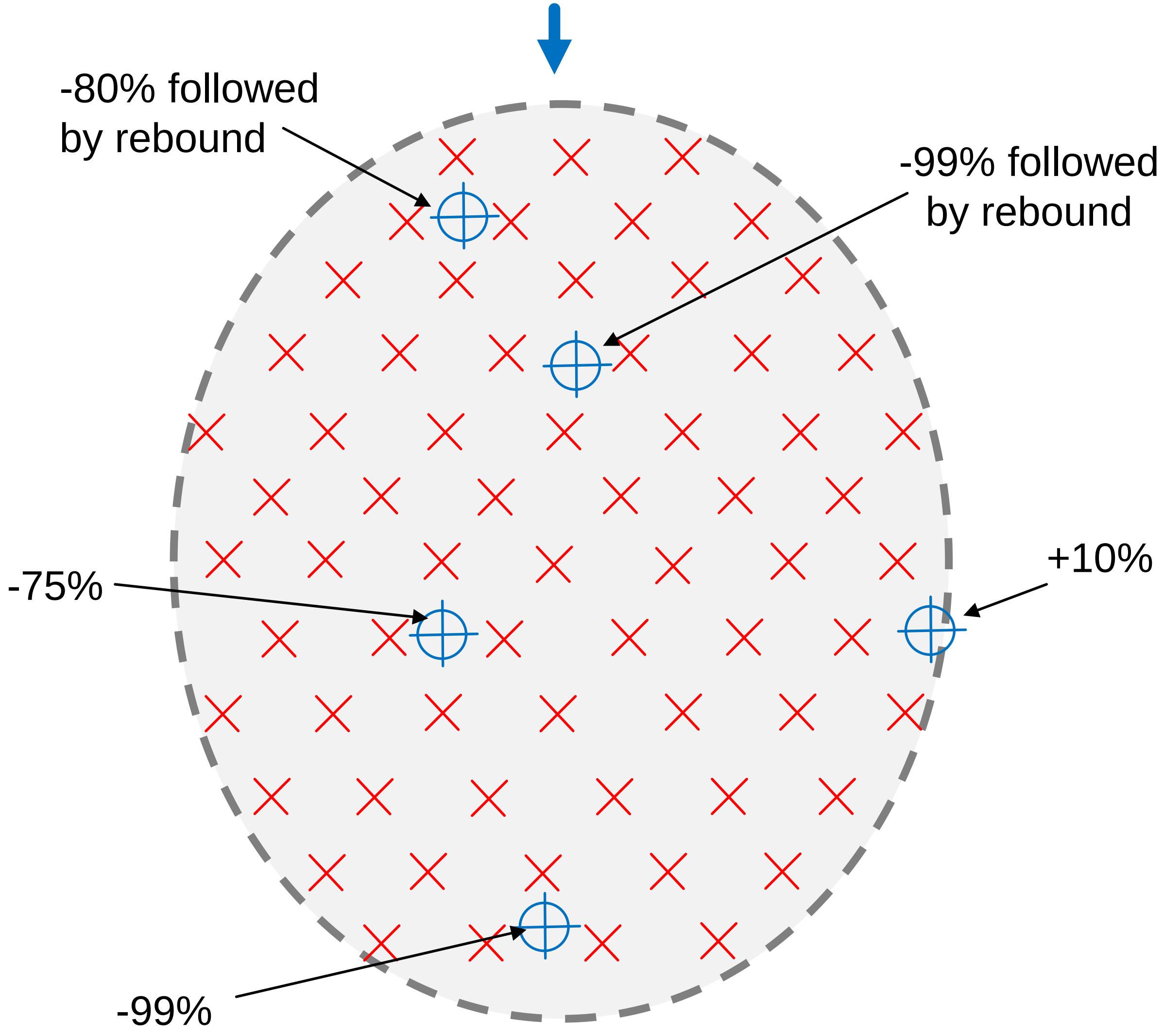
Geochemical Data could Help Evaluate:

- Reagent distribution / radius of influence (ROI)
- Reagent longevity
- Reagent transport
- Residence time of reagents within the target area
- Potential for continued treatment via anaerobic oxidation
- Groundwater velocity and flow paths
- Contaminant source areas



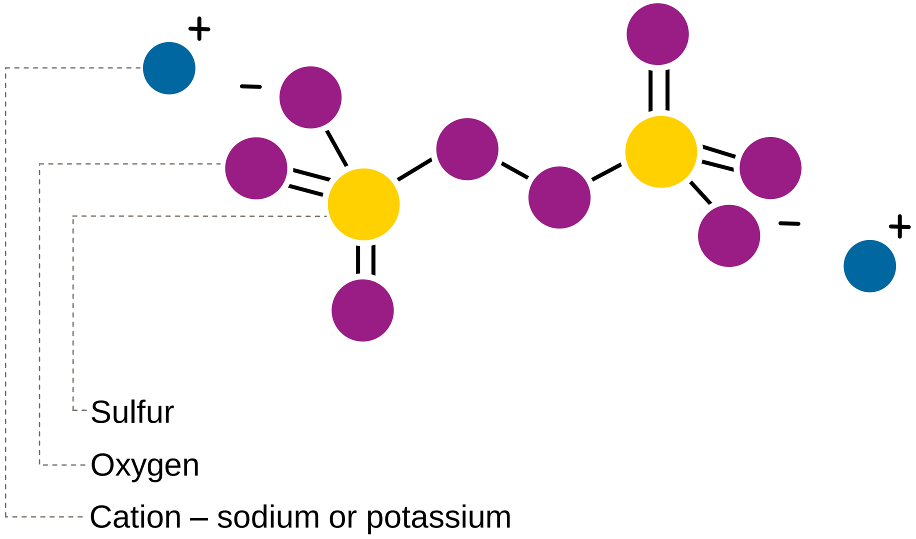
Geochemical Data can Help Interpret Performance



- Geochemical analyses can help distinguish between:
  - Underdosing
  - Lack of distribution / contact
  - Insufficient contact time
  - Rebound from sorbed mass (*ie*. under-dosing)
  - Recontamination from inflowing groundwater over time (*ie*. upgradient source remaining)

Understanding the problem allows modifying the remedial action plan appropriately for the next phase if needed.

Persulfate Geochemical 'Fingerprint'



Persulfate in Groundwater

Persulfate Breakdown Products

Na^+ / K^+ SO_4^{2-}

Key Geochemical Parameters

ORP   pH   EC

Direct Analyses of Persulfate = ‘Active’ Reagent

Klozur® Field Test Kits

Easy field measurements of persulfate:

- Distribution/ROI determination during injections
- Persulfate presence/absence in groundwater over time:
  - Concentrations of active persulfate remaining
- Persulfate Presence/Absence in Soil

- 10 samples per kit
- Range: 1 g/L to 100 g/L
- Accuracy:
  - Range 1 – 50 g/L (+/- 1 g/L)
  - Range 50 – 100 g/L (+/- 2 g/L)

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Direct Analyses of Persulfate = 'Active' Reagent

CHEMets Visual Kits

- Range: up to 70 mg/L
  - Below 'effective' range for persulfate (typically reaction kinetics drops below ~1-2 g/L)

- Interferences from oxidized minerals (Fe(III)) & common activators:
  - Not recommended for concentration monitoring

- Fast and inexpensive → could be used for positive / negative screening and then confirm concentration using Klozur® Field Test Kits

Recommended for positive / negative screening

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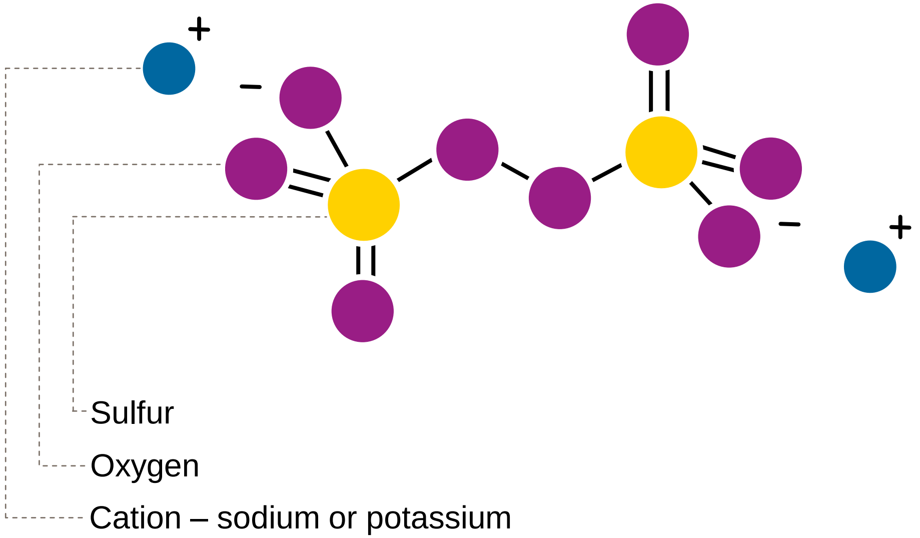
Persulfate Composition / Breakdown Products

- Two types of persulfate commonly used in environmental applications:

  – **Klozur SP – Sodium Persulfate:**
    – Highly soluble, injects as a liquid
    – Source zone / hotspot treatment

  – **Klozur KP – Potassium Persulfate:**
    – Solubility limited extended release
    – PRBs, low permeability soils, high Koc contaminants

- Both releases the persulfate anion:
  – Na^+ or K^+



	Klozur® SP $Na_2S_2O_8$	**Klozur® KP** $K_2S_2O_8$
Sodium	**19%**	**-**
Potassium	**-**	**29%**
Sulfate	**81%**	**71%**

Persulfate Residuals = both active and inactive (spent) persulfate

- **Klozur SP → analyze for sodium and sulfate**
- **Klozur KP → analyze for potassium and sulfate**

- Na^+ and K^+ typically conservative and stays in solution:
  – Assess distribution, migration and flow paths

- Sulfate can transform:
  – Precipitate to form minerals (*eg*. calcium sulfate)
  – Reduce to form sulfide (~-150 mV to ~-200 mV)

Persulfate activators may also add to fingerprint:

NaOH – 58% Na^+

$Ca(OH)_2$ – 54% Ca^{2+}

Persulfate Residuals – Expected Concentrations at Uniform Distribution

Example expected conc. breakdown products added to groundwater (uniform distribution):

	Klozur® SP $Na_2S_2O_8$	Klozur® KP $K_2S_2O_8$
	g/L	g/L
Example target dose	20	20
Sodium	3.8	-
Potassium	-	5.8
Sulfate*	16.2	14.2

*Sulfate may precipitate (not conservative)

Persulfate distribution:

Groundwater concentrations of Na^+ and K^+ could be directly compared to injected dose:

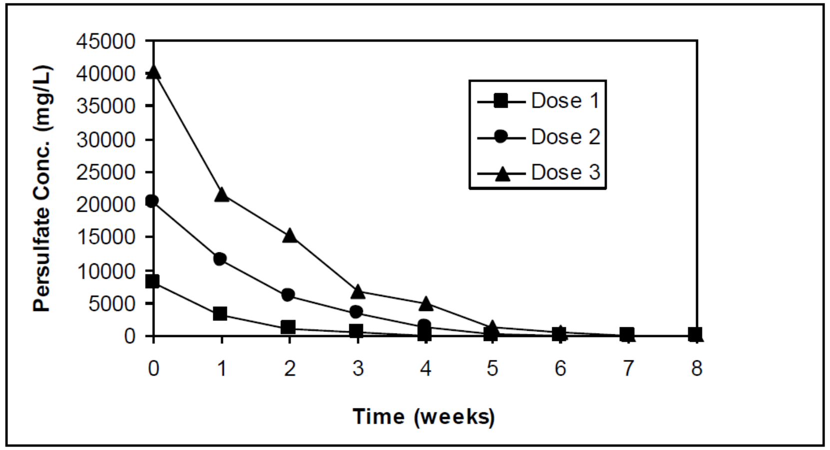
- Conc < expected – reagents displaced over larger area or outside of intended zone?
- Conc > expected – preferential pathways or smaller ROI?

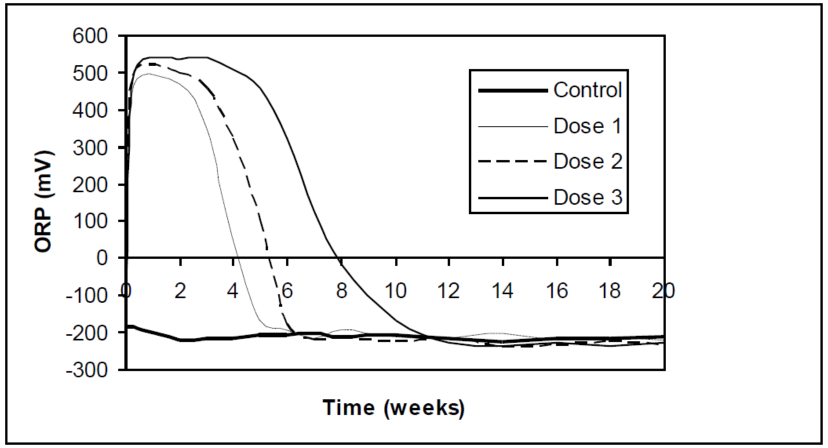
Key Persulfate Geochemical Indicators

- **Electric conductivity (EC)** – increases in response to persulfate and its breakdown products

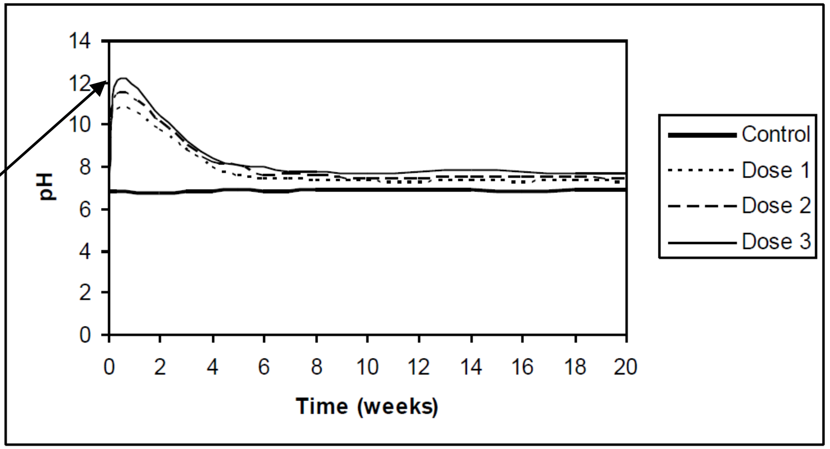
- **ORP** elevated while persulfate still active.

- **pH** - persulfate releases sulfuric acid as it decomposes → pH decreases:
  - Extent of pH effect depends on the buffering capacity of the soil and activation chemistry employed.
  - Alkaline activation: Initial increase in pH due to addition of base activator followed by gradual decrease as the persulfate reacts.



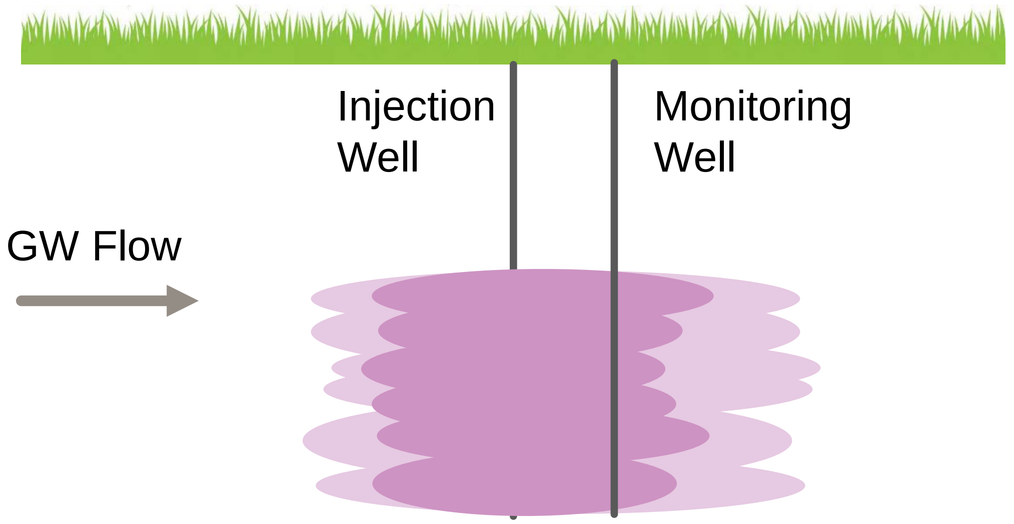


Initial pH increase due to alkaline activation



What We Like to See – Direct Zone of Influence

- Residual Persulfate: >50% of pore volume concentration
- Conductivity: 2 to 3 order of magnitude increase over background
- ORP: 300 mV to 600 mV
- pH: If alkaline activated pH should be >10.5 while persulfate is present
- Sodium/Potassium and Sulfate: Proportional to pore concentration
  - Sodium Persulfate: 19% sodium and 81% sulfate
  - Potassium Persulfate: 29% potassium and 71% sulfate

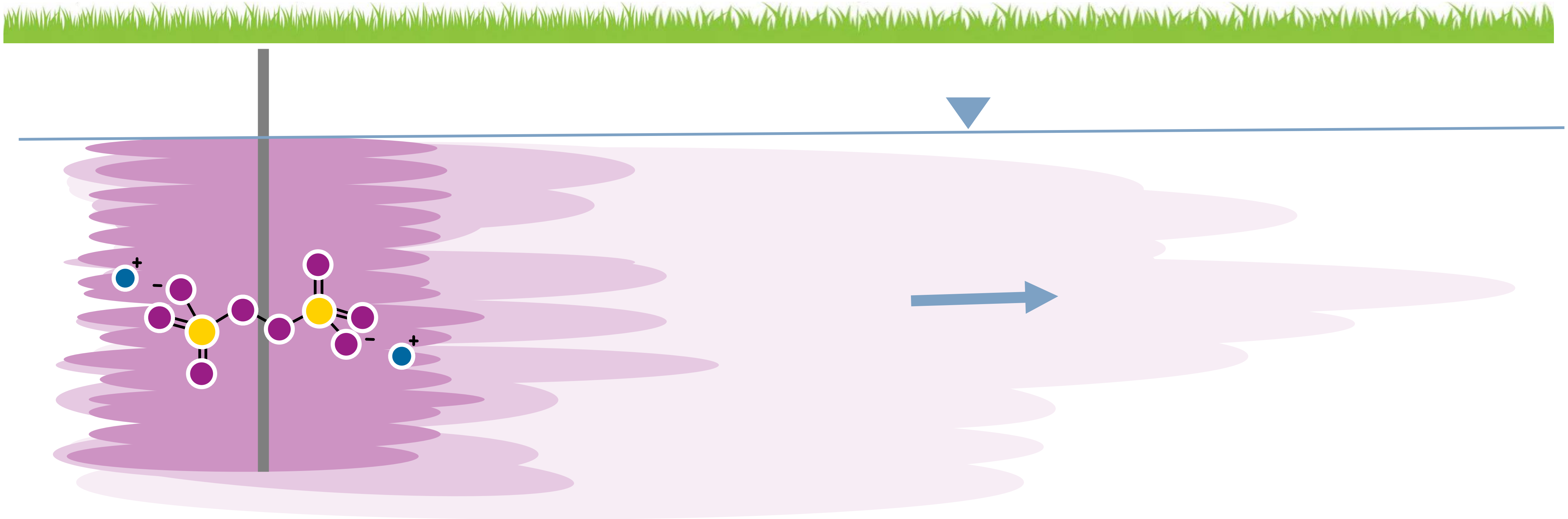


Evonik recommends minimum of:

10 g/L in a pore volume for petroleum hydrocarbons; and,

20 g/L persulfate for oxidized contaminants needing the reductive pathway

Timing of Geochemical Fingerprint



Direct zone of influence :

Immediate increase in <u>persulfate</u>, Na^+, EC & sulfate

Indirect zone of influence:

Delayed increase → persulfate & breakdown products migrated into area

Over time:

<u>No active persulfate</u>

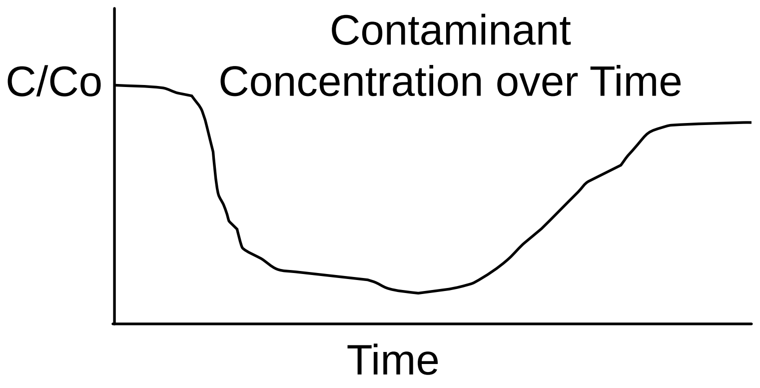
Geochemical signature

Disappearance of chemical footprint (EC, Na/K) over time → untreated groundwater is migrating into the area

Rebound vs. Recontamination

If contaminant concentrations rebounds after the persulfate has been spent, geochemical data can help distinguish between a true rebound vs recontamination from inflowing groundwater:

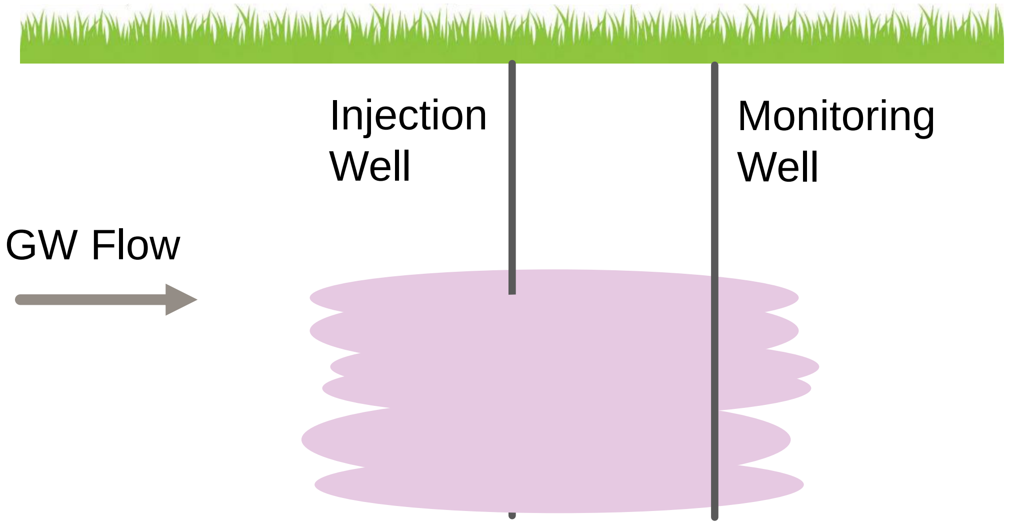
- **True Rebound:**
  - Contaminant partitions back into groundwater from soils → sorbed concentrations remaining
- **Recontamination:**
  - Untreated, contaminated groundwater migrates back into treatment area



EC and Sodium can Help Distinguish between Rebound vs. Recontamination

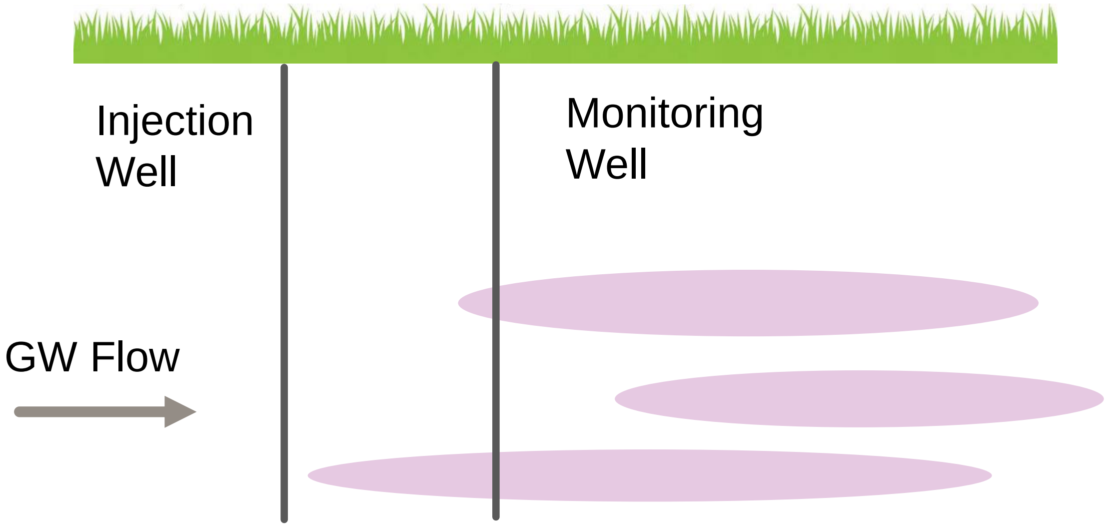
True Rebound – Repartitioning from Soils

Conductivity, sodium/potassium, etc stay similar to peak (no influx of fresh GW) while contaminant concentration increase



Possible Recontamination from Inflowing Groundwater

The disappearance of a geochemical footprint (EC & Na^+/K^+) suggests that new, untreated groundwater migrated into the area



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Why is this Difference Important

- **Rebound scenario:**
  - Indicates an insufficient dose:
    - Sorbed mass / non target demand not fully accounted for?
      - Adjust dose
    - Distribution issues? Didn’t receive intended dose?
      - Application method may need to be modified

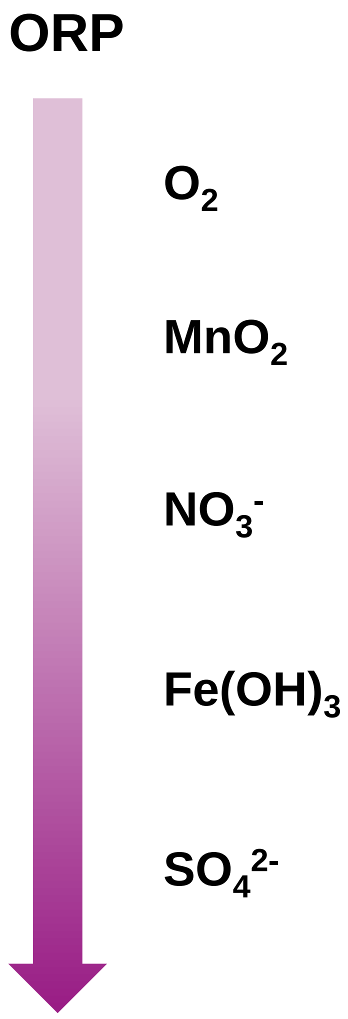
- **Recontamination scenario:**
  - May be indicative of upgradient contaminant source zone that requires treatment
  - Common in pilot tests:
    - Consider residence time and GW flow velocities

Potential for Anaerobic Oxidation / Sulfate Reduction

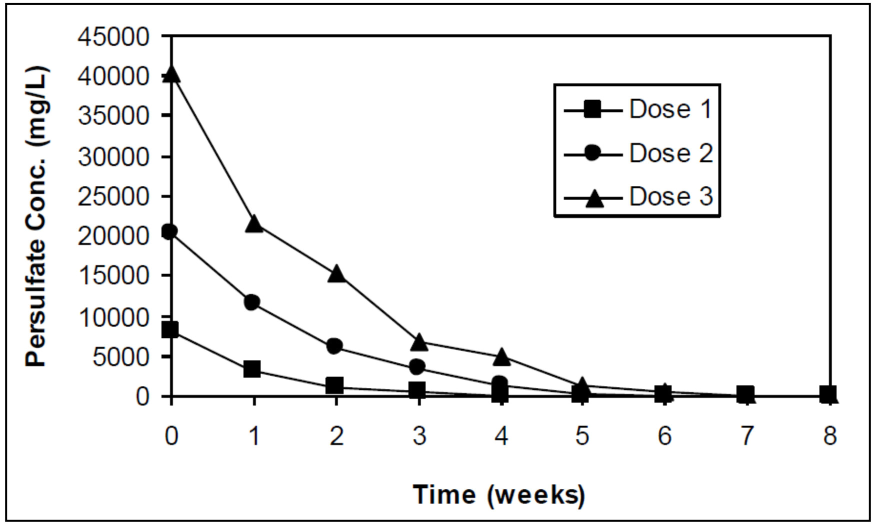
- Residual sulfate acts as an electron acceptor
  - Sulfate reducing bacteria (SRBs)
  - Weaker oxidative process
    - Treats benzene and other easily oxidizable petroleum hydrocarbon

- Requires sulfate reducing conditions
  - ORP ~ -150 mV to -200 mV
  - Often can take 1-2 years

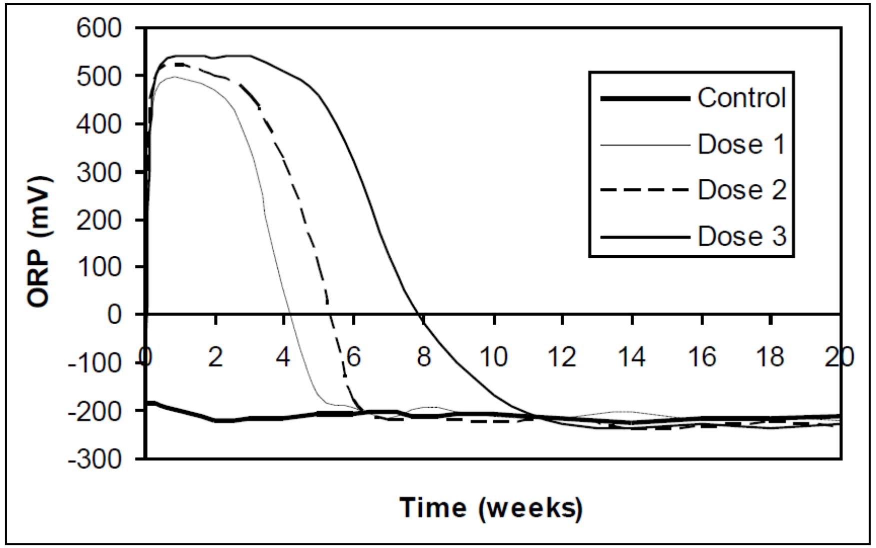
- Sodium to sulfate ratio will change if sulfate is being consumed (precipitation or reduction)

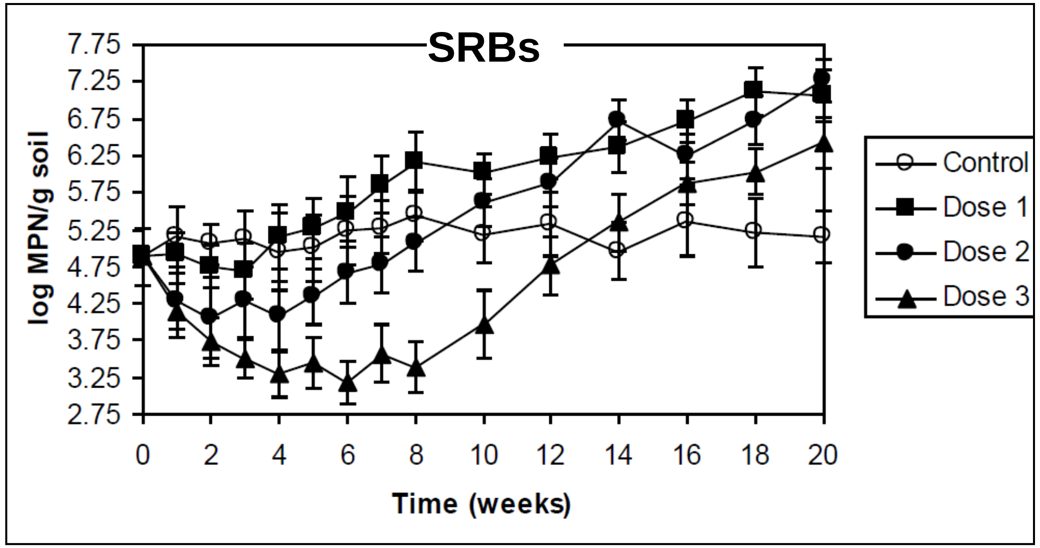


Potential for Anaerobic Oxidation / Sulfate Reduction:
Example Data from Western Michigan University Bench Study: PAHs in Sediments



- Sulfate reduction evaluated in batch study with Klozur CR
- ORP drops back in to reducing conditions once persulfate is spent
- ORP drop coupled with increase in SRB counts
- ORP and sulfate/sulfide monitoring will indicate potential for anaerobic oxidation





Reference: Lab Study by Dan Cassidy - Western Michigan University

Likely Anaerobic Oxidation following a Klozur® Persulfate Application

Sampling Event (Months)	BTEX (ug/L)	Nap (ug/L)	SP (g/L)	ORP (mV)	Sulfide (mg/L)	Sulfate (mg/L)
Baseline	3,000	170	0	-100	0	0
Application			Up to 140	Up to 350		
6	500	30		-120	1.2	8,500
9	300	20		-140	2.8	5,000
12	180	15		-110	0	4,000

- Alkaline activated persulfate application in NYC
- Remedial Goals Met
- Site Closed
- No rebound was observed

Potential Monitoring Program

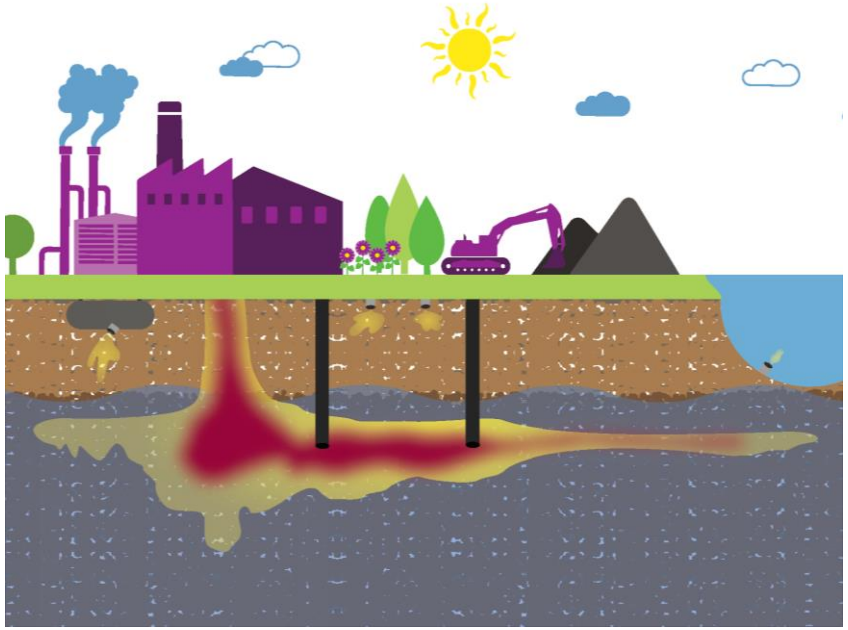
	Baseline Monitoring	Application Monitoring	Distribution Monitoring	Performance Monitoring
	To set a baseline to compare against	During application	Immediately post application	Typically, 4-10 weeks post application
Contaminants	x			x
Fraction Organic Carbon, foc	x			x
Persulfate		x	x	x
Sodium/Potassium/Activator Ions	x		x	x
Sulfate	x		x	x
Electric Conductivity	x	x	x	x
ORP	x	x	x	x
pH	x	x	x	x
DOC	x			x

Example Case Study – Confidential Site

- Main Contaminants: BTEX, MTBE, TBA

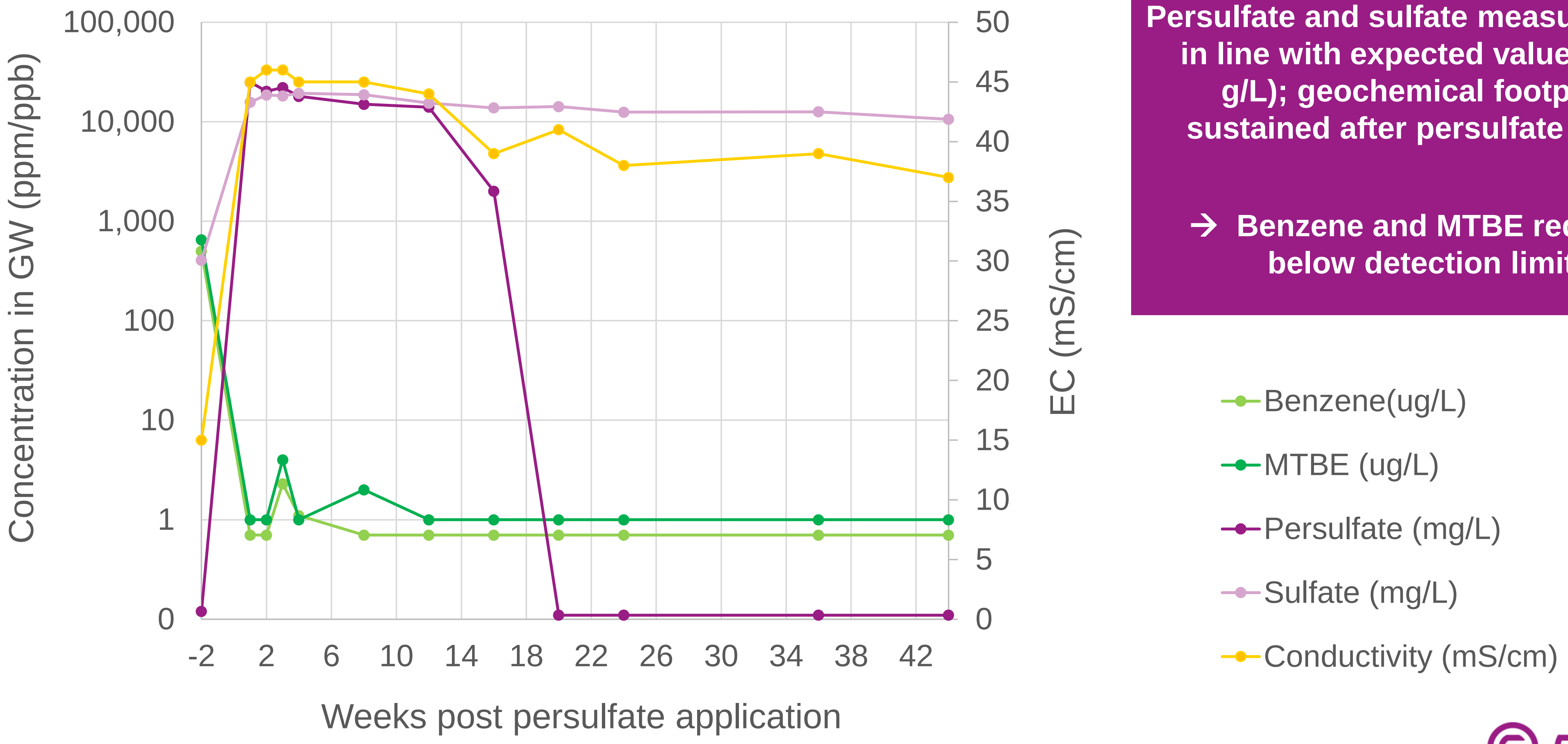
- Dose applied:
  – 2 g Klozur SP per kg soil
  – Total porosity (35%): 8.2 g/L persulfate / 6.6 g/L sulfate
  – Effective porosity (15%): 19.1 g/L persulfate / 15.5 g/L sulfate

- Results:
  – Varied – ranging from >99% reduction to no treatment
  – Rebound of contaminant concentrations were observed over time



- A comprehensive data review was completed to guide next steps

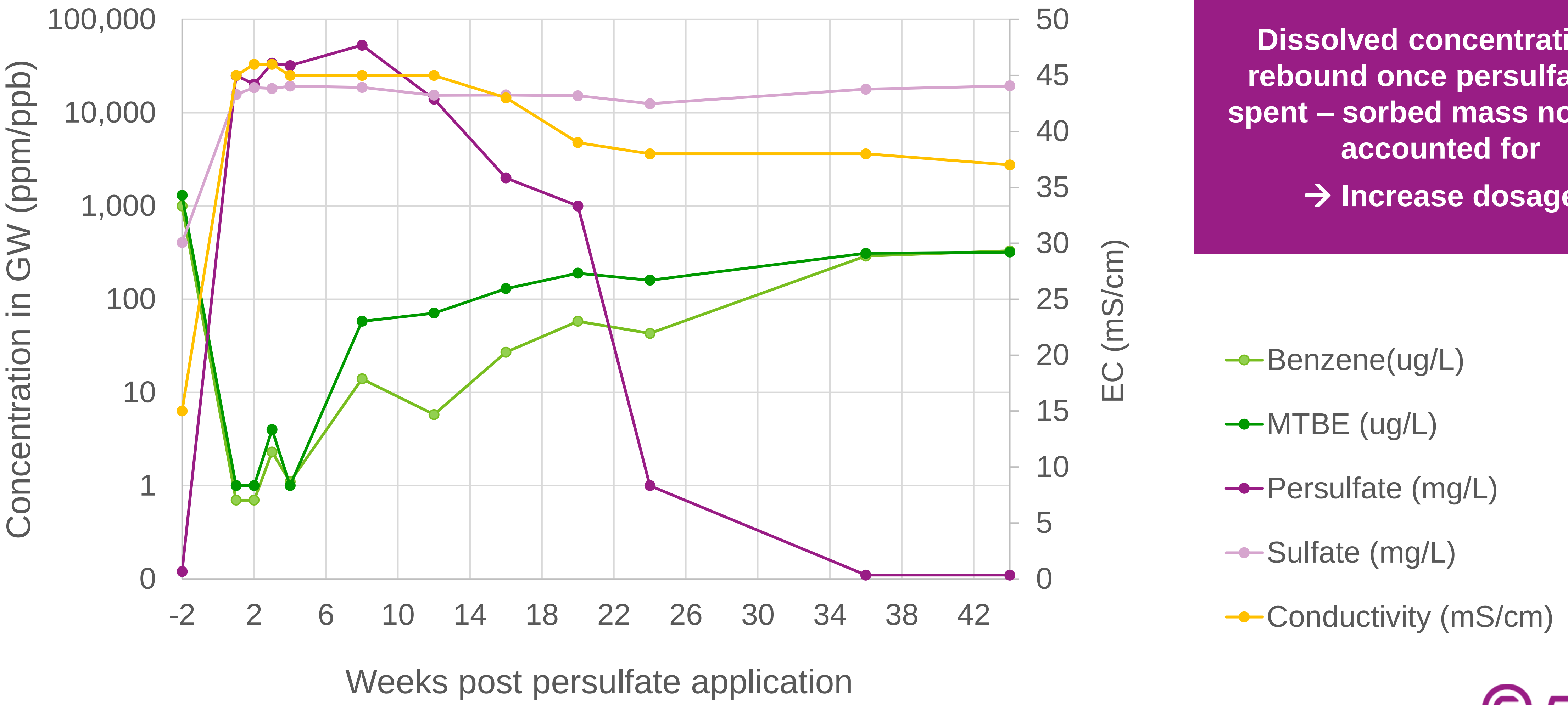
Example of Monitoring Well with Succesful Sustained Results



Persulfate and sulfate measurements in line with expected values (~20 g/L); geochemical footprint sustained after persulfate spent

→ Benzene and MTBE reduced below detection limit

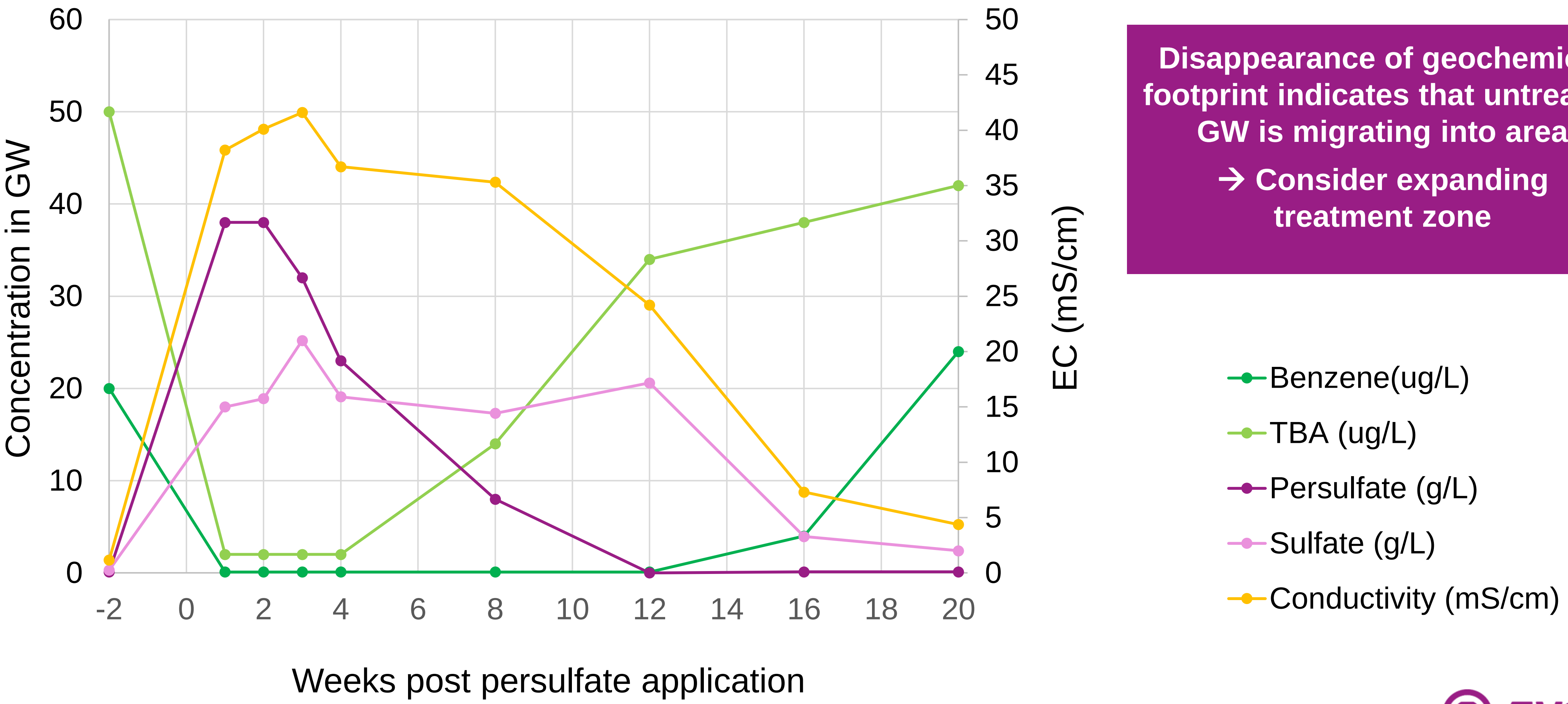
Example of True Rebound (underdose)



Dissolved concentrations rebound once persulfate is spent – sorbed mass not fully accounted for

→ Increase dosage

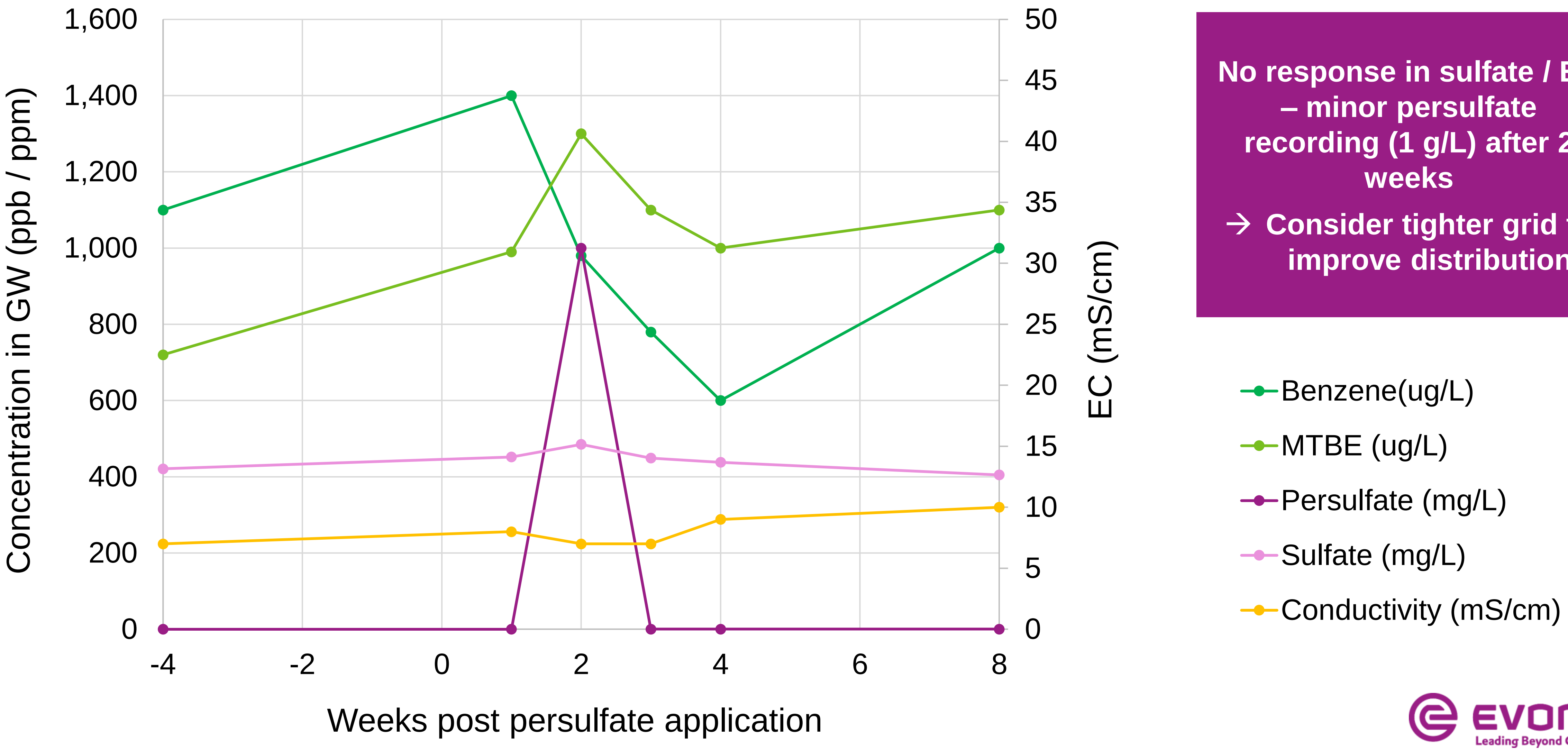
Example of Possible Recontamination



Disappearance of geochemical footprint indicates that untreated GW is migrating into area

→ Consider expanding treatment zone

Example of Unsuccesful Application



No response in sulfate / EC – minor persulfate recording (1 g/L) after 2 weeks

→ Consider tighter grid to improve distribution

Some things to consider..

- Establishing contact:
  - Preferential pathways - isolate target intervals (injection)
  - Injection volumes vs. target ROI & effective porosity
  - Review feasible application strategies. Is soil mixing an option?
  - Consider reagent distribution properties and longevity
    - Klozur SP vs. Klozur KP
- Consider flux and residence time!
  - Location of monitoring locations relative grid
- Dosing:
  - Consider sorbed and non-target demand

Successful *In Situ* remediation requires:

Sufficient dose of reagents to contact contaminants over a sufficient time period

Summary

- Geochemical analyses is helpful to gain a better understanding of:
  - Application: Persulfate distribution, longevity & residence time
  - Site: Flow paths, flow velocities, potential for upgradient sources, source zones

- This detailed analysis allows modifying the remedial action plan appropriately for the next phase if needed.

Parameters to Monitor:

- Residual persulfate
- Geochemical parameters (conductivity, ORP, and pH)
- Sodium / potassium and sulfate
  - Common cations and anion
- Dissolved organic carbon
- Total organic carbon on soil

Thank You!

Questions?

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