

Understanding ISCO Field Applications by Assessing Geochemical Data

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Soil & Groundwater
Remediation

Remtech East | June 1, 2023



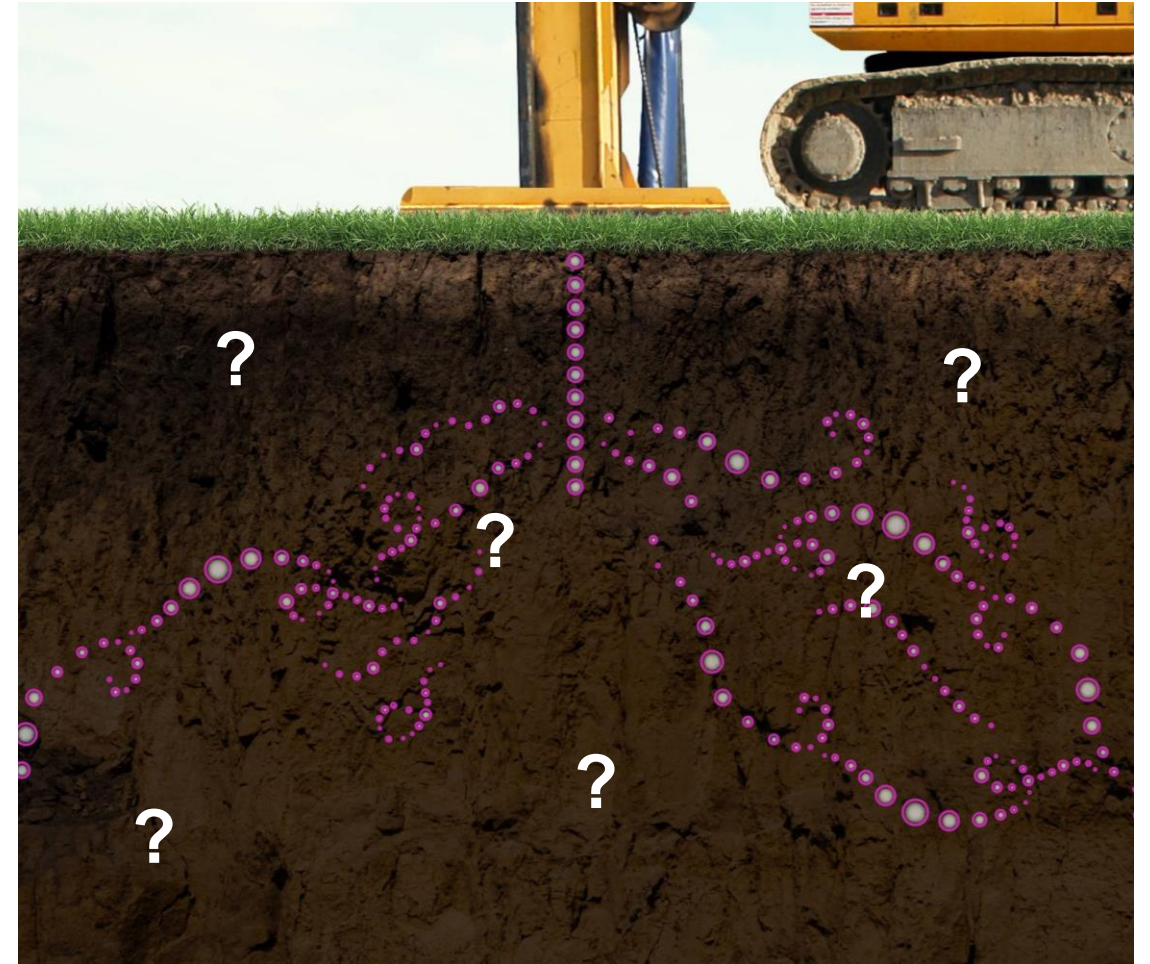
Key Elements of Designing and Applying Klozur® Persulfate

- **Chemistry**: Is the contaminant degraded by activated Klozur® Persulfate?
- **Design**: Is there sufficient oxidant mass to react with non-target demand and the contaminant mass?
 - Safety factors
- **Application**: How will the persulfate chemistry establish contact with the contamination in the subsurface?
- **Monitoring Program**: Designed to answer key questions regarding the persulfate application

How to use data that is commonly collected to better understand the application and site

Presentation Outline

- **The Persulfate “Fingerprint”/Signature**
- **Understanding How Persulfate is Applied**
- **Key Scenarios on how this can be used**
 - Successful application
 - Underdosing (rebound)
 - Recontamination from inflowing groundwater
 - Poor distribution

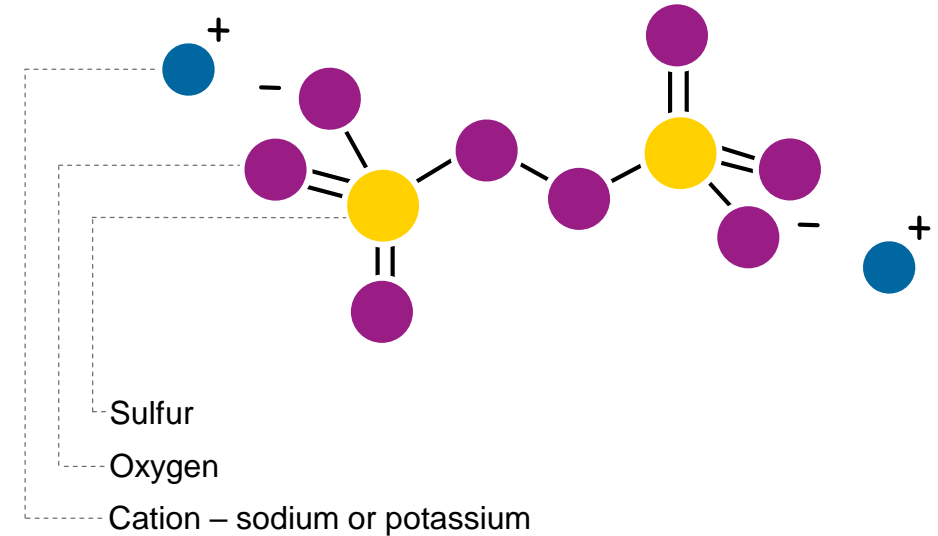


Persulfate Composition / Breakdown Products

- Two types of persulfate commonly used in environmental applications:
 - **Klozur SP – Sodium Persulfate**
 - Sodium and sulfate residuals
 - **Klozur KP – Potassium Persulfate**
 - Potassium and sulfate residuals

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

- Sulfate can transform:
 - Precipitate to form minerals (e.g., calcium sulfate)
 - Reduce to form sulfide (~ -150 mV to ~ -200 mV)



	Klozur® SP Na₂S₂O₈	Klozur® KP K₂S₂O₈
Sodium	19%	-
Potassium	-	29%
Sulfate	81%	71%

Persulfate Residuals = Both Active and Inactive (spent) persulfate

- Activators also have residuals
- Difference between Active and Inactive (spent) persulfate
 - Active persulfate used for chemical oxidation
 - Inactive persulfate has been consumed
 - Solution can have all the same characteristics except for active persulfate

Persulfate activators may also add to fingerprint:

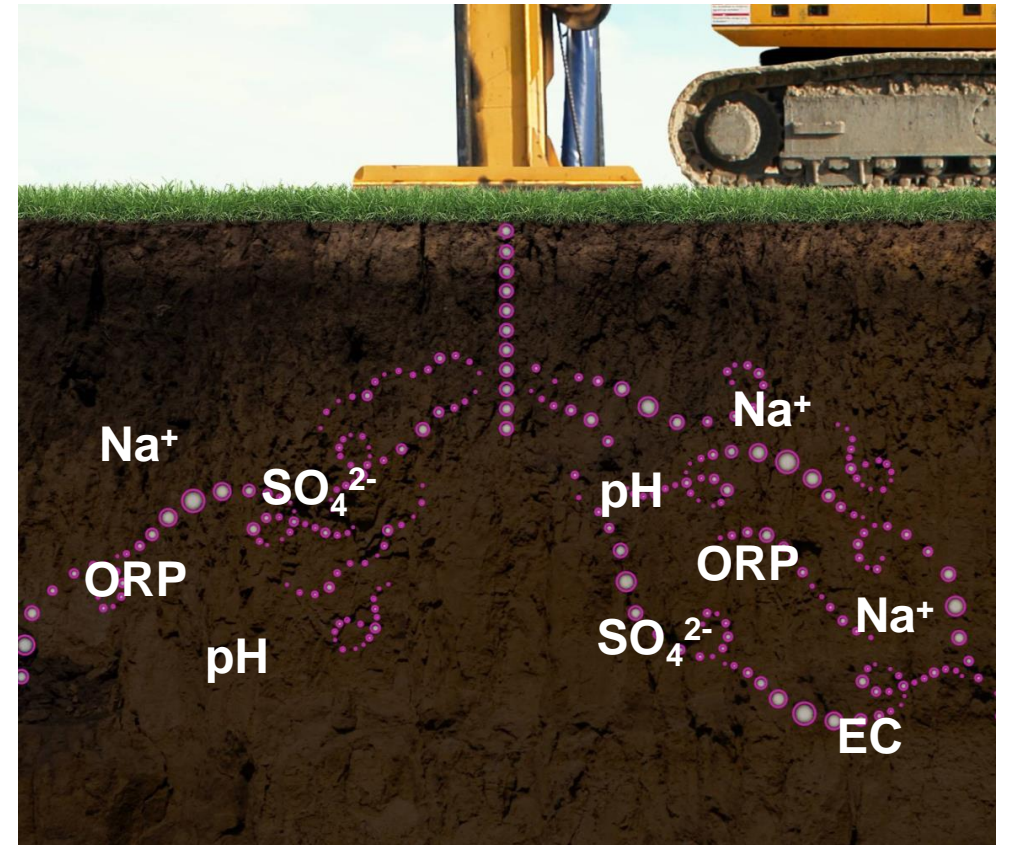
NaOH – 58% Na⁺

Ca(OH)₂ – 54% Ca²⁺



Klozur® Persulfate “Fingerprint” or “Signature”

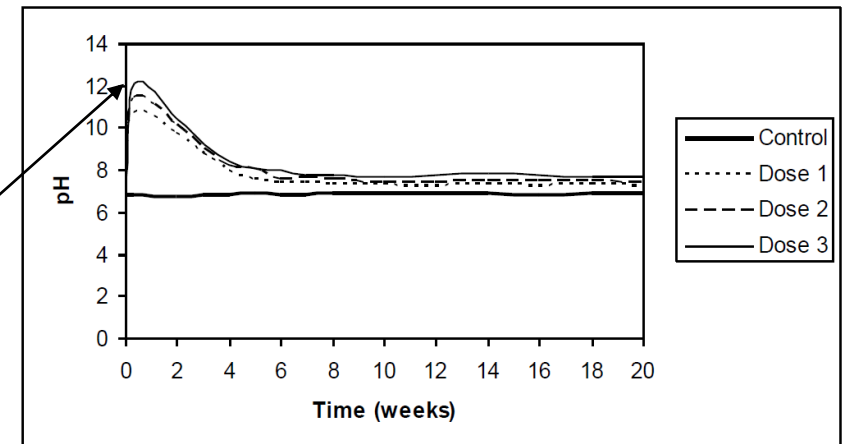
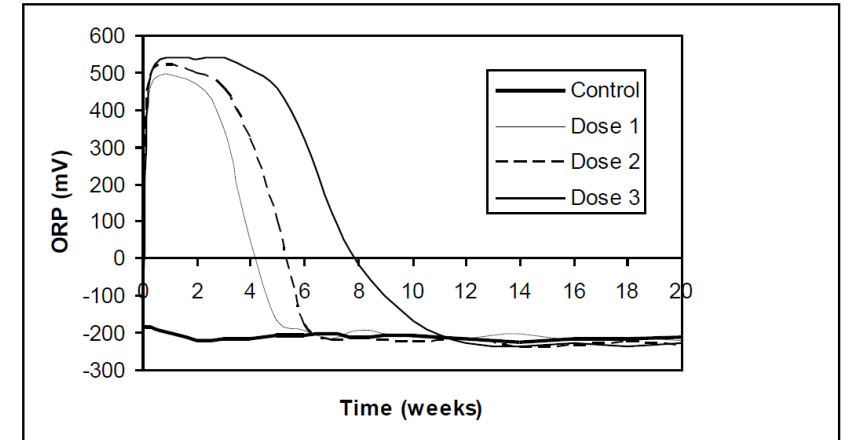
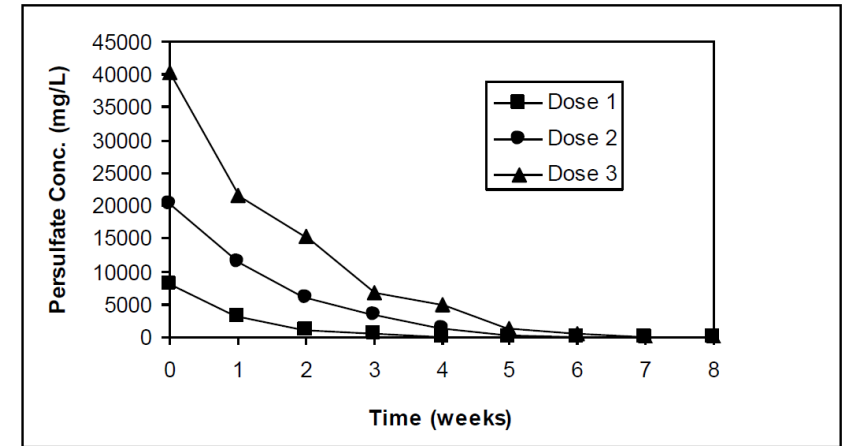
- Active reagent solution = Quantified active persulfate
- Reagent solution geochemical parameters:
 - Residual ions result in increased **Electrical Conductivity**
 - Klozur® caustic (25% NaOH or hydrated lime) should increase **pH**
 - In absence of Klozur® caustic, Klozur® Persulfate should decrease **pH**
 - Klozur® Persulfate should increase **ORP**
 - Analytical
 - Sodium/potassium and sulfate can be directly measured
 - Ratio of sodium/potassium to sulfate changes if sulfate is not conservative



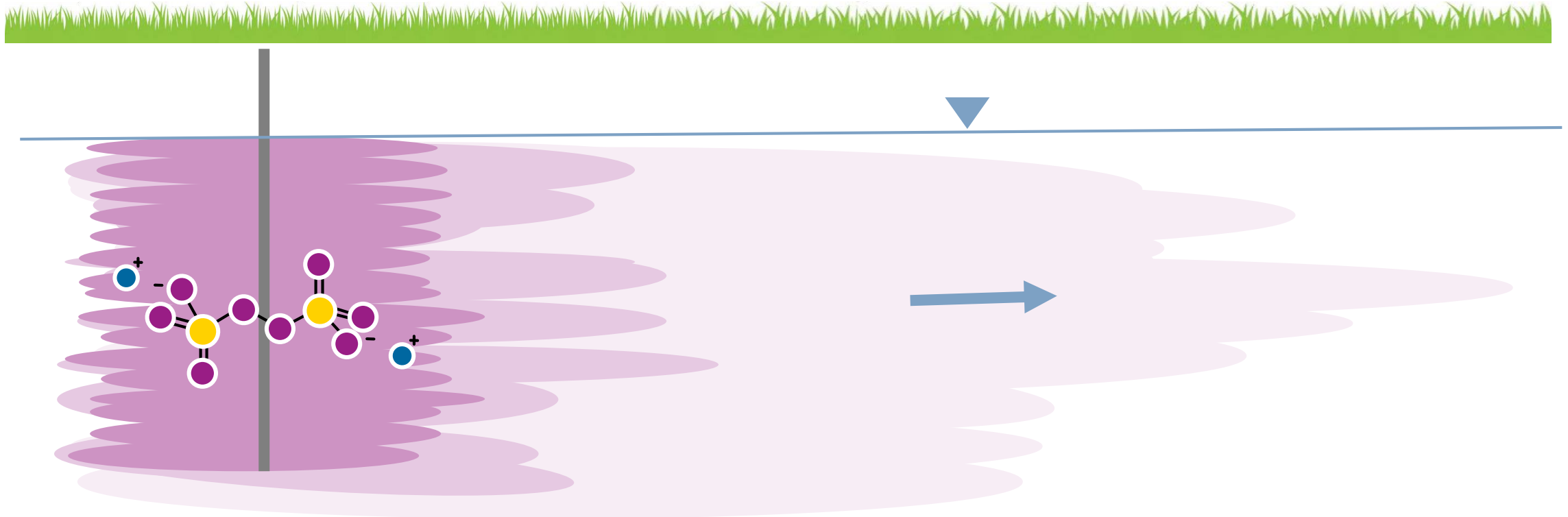
Key Persulfate Geochemical Indicators

- **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



Direct Zone of Influence



Direct zone of influence :

Immediate increase in persulfate, Na⁺, EC & sulfate

Indirect zone of influence:

Delayed increase → persulfate & breakdown products migrated into area

Over time:

**No active persulfate
Geochemical signature**

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

How Can the Sodium Persulfate Fingerprint be Used



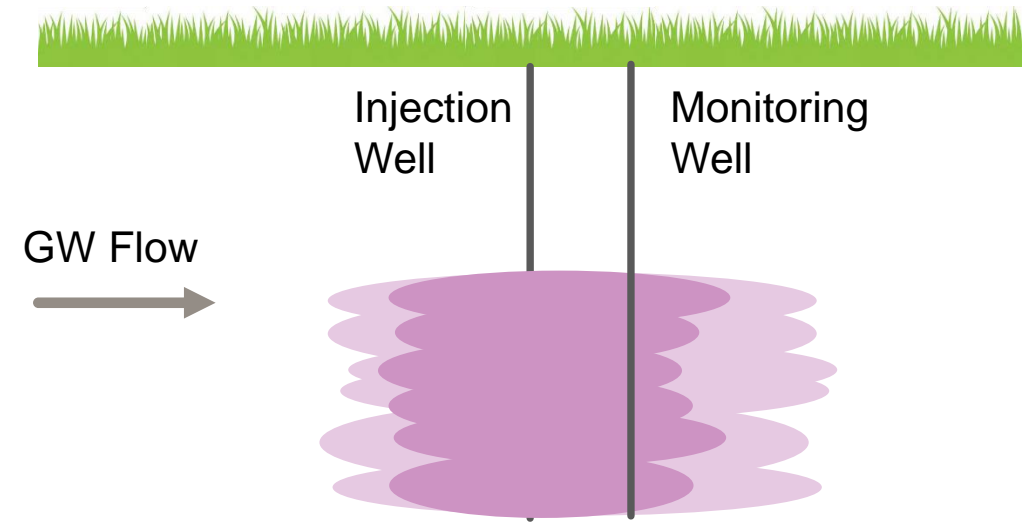
ISCO-ISS being applied by Arkil in Sweden

Geochemical data can help evaluate:

- Reagent distribution
- Reagent longevity
- Residence time of reagents within the target area
- Recontamination vs. rebound
- Potential for secondary treatment methods such as anaerobic oxidation

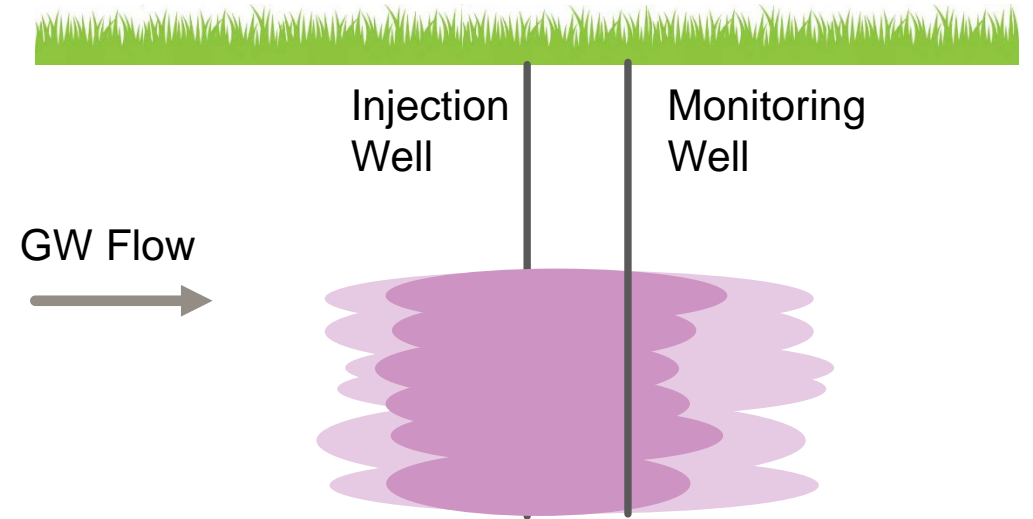
Understanding Reagent Distribution

- Reagent solution:
 - Geochemical parameters
 - Conductivity
 - pH
 - ORP
 - Sodium/sulfate (if monitored)
- Active reagent
 - Persulfate
- Contaminant concentrations



Scenario 1: What We Like to See

- 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



Scenario 1 Continued: Estimating Persulfate based on Residuals

- Injection concentration: 150 g/L
 - Expected residuals from injection solution:
 - Sodium: $150 \text{ g/L} * 0.19 = 28,500 \text{ mg/L}$
 - Sulfate: $150 \text{ g/L} * 0.81 = 121,500 \text{ mg/L}$
- Injection volume as a percent of total pore volume: 40%
 - Target concentration in total pore volume: $150 * 0.4 = 60 \text{ g/L}$
 - Expected residuals from injection solution:
 - **Sodium: $60 \text{ g/L} * \sim 0.19 = \sim 11,400 \text{ mg/L}$**
 - **Sulfate: $60 \text{ g/L} * \sim 0.81 = \sim 48,600 \text{ mg/L}$**

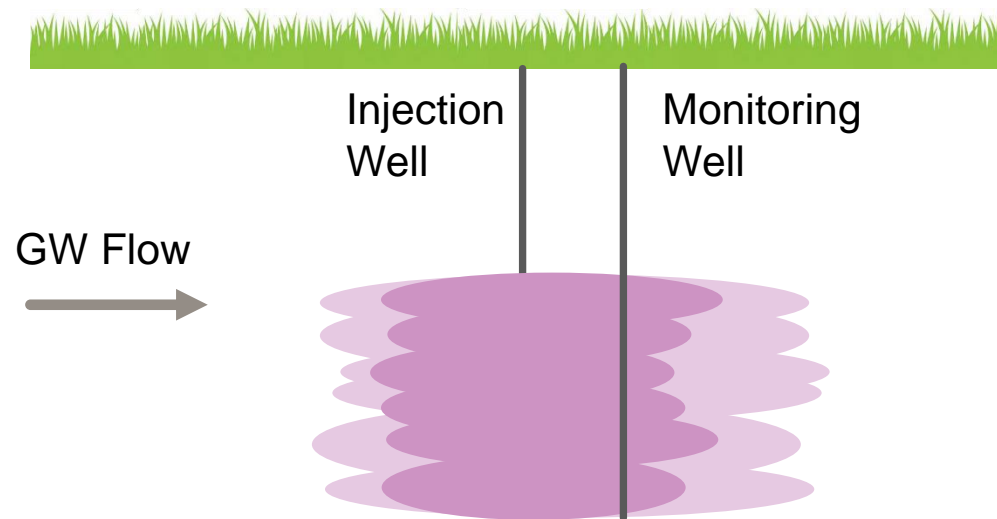
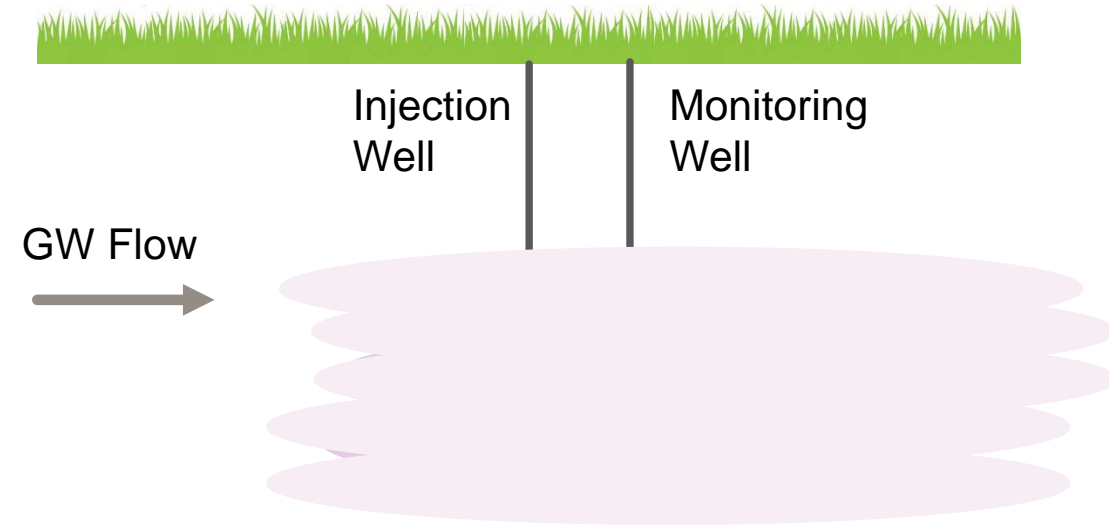
Evonik recommends minimum of:
10 g/L in a pore volume for petroleum hydrocarbons; and,
20 g/L persulfate for oxidized contaminants needing the reductive pathway

Scenario 2: Longevity of Active Persulfate

- All reagent solution:
 - Conductivity, sodium/potassium, sulfate, ORP, etc
- Active reagent solution
 - Concentrations of persulfate (>1-5 g/L preferred)

Top Scenario: Persulfate reacted in place.
Indirect parameters stay elevated but persulfate not-detected

Bottom Scenario: Injection solution migration.
Indirect and persulfate concentrations decrease as injectate migrates downgradient and is replaced with upgradient groundwater

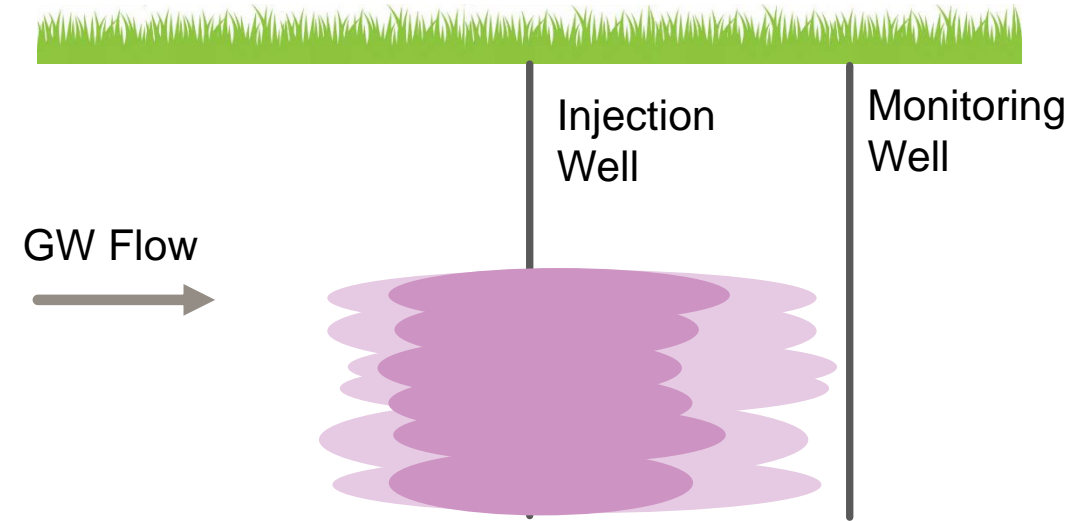


Why is this Important?

- Persulfate decomposing in target zone is preferred.
- Persulfate migrating out of treatment zone indicates limited contact time and may want to make adjustments:
 - More aggressive activation method
 - Increase concentrations of iron-chelate
 - Hydrogen peroxide
 - Higher pH
 - Flow down strategy (moving injection area upgradient)
 - Use solid state persulfate such as Klozur® KP (potassium persulfate)

Scenario 3: No Observed Change At Monitoring Well

- Contaminant mass reduction is not typical for monitoring locations that never observed signature
 - Insufficient injection volume
 - ~50 to 100% of an effective pore volume is recommended
 - Physical impediment between MW and IW
 - Preferential flow path led reagents away from MW



Signature

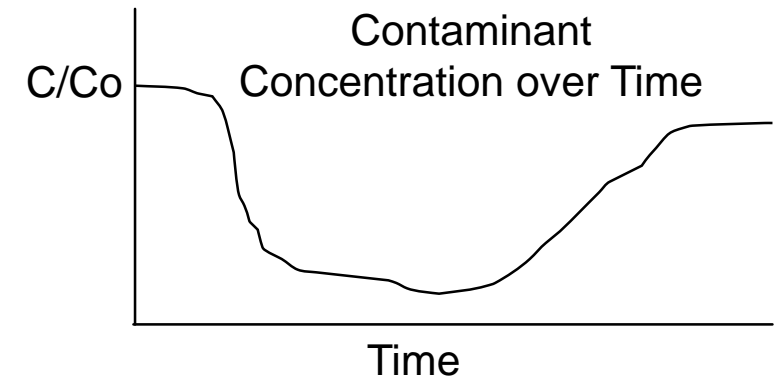
MW sees little to no change in fingerprint.

Conclusion: Reagent solution never impacted MW or has already flowed past MW

Scenario 4: 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:

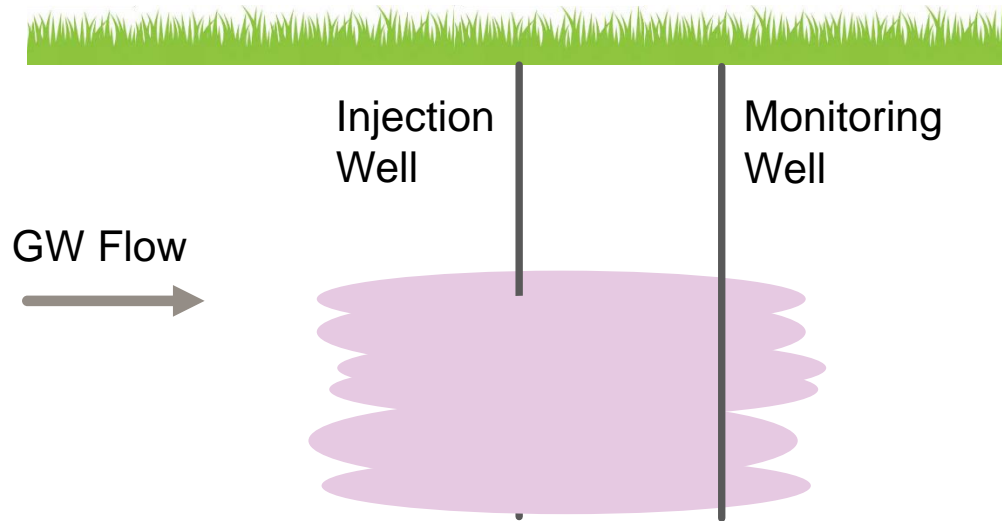
- **True Rebound:**
 - Contaminant partitions back into groundwater from soils → sorbed concentrations remaining
- **Recontamination:**
 - Untreated, contaminated groundwater migrates back into treatment area



EC and Sodium can Help Distinguish between Rebound vs. Recontamination

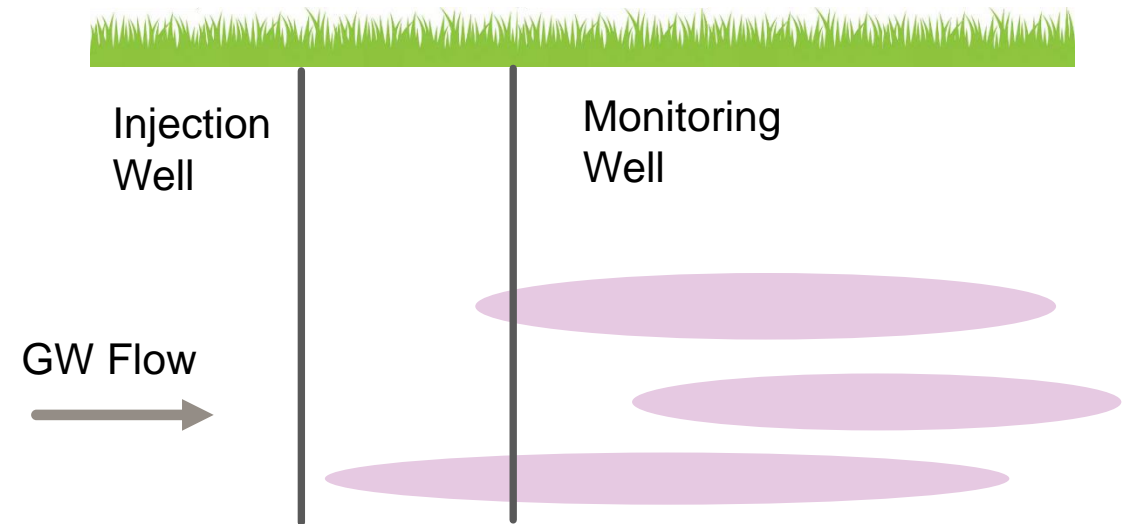
True Rebound – Repartitioning from Soils

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



Why is this Difference Important

- **Rebound scenario:**

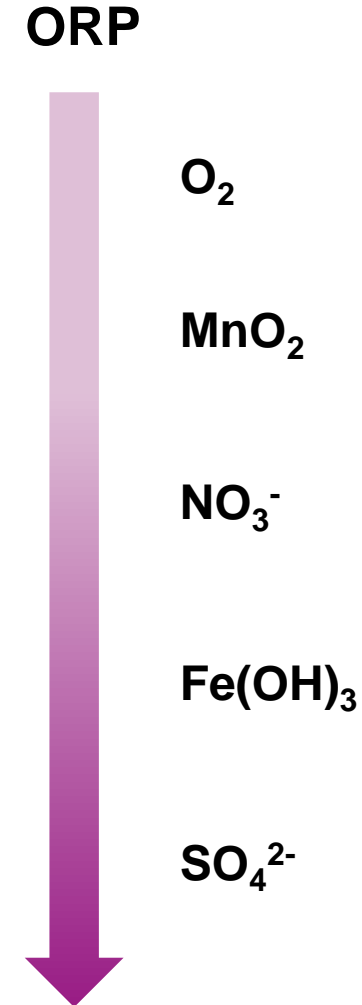
- Indicates an insufficient dose:
 - Sorbed mass / non target demand not fully accounted for?
 - Adjust dose
 - Distribution issues? Didn't receive intended dose?
 - Application method may need to be modified

- **Recontamination scenario:**

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

Scenario 5: 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)



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

Summary: Proper Monitoring can Support Better Site Understanding

Monitoring

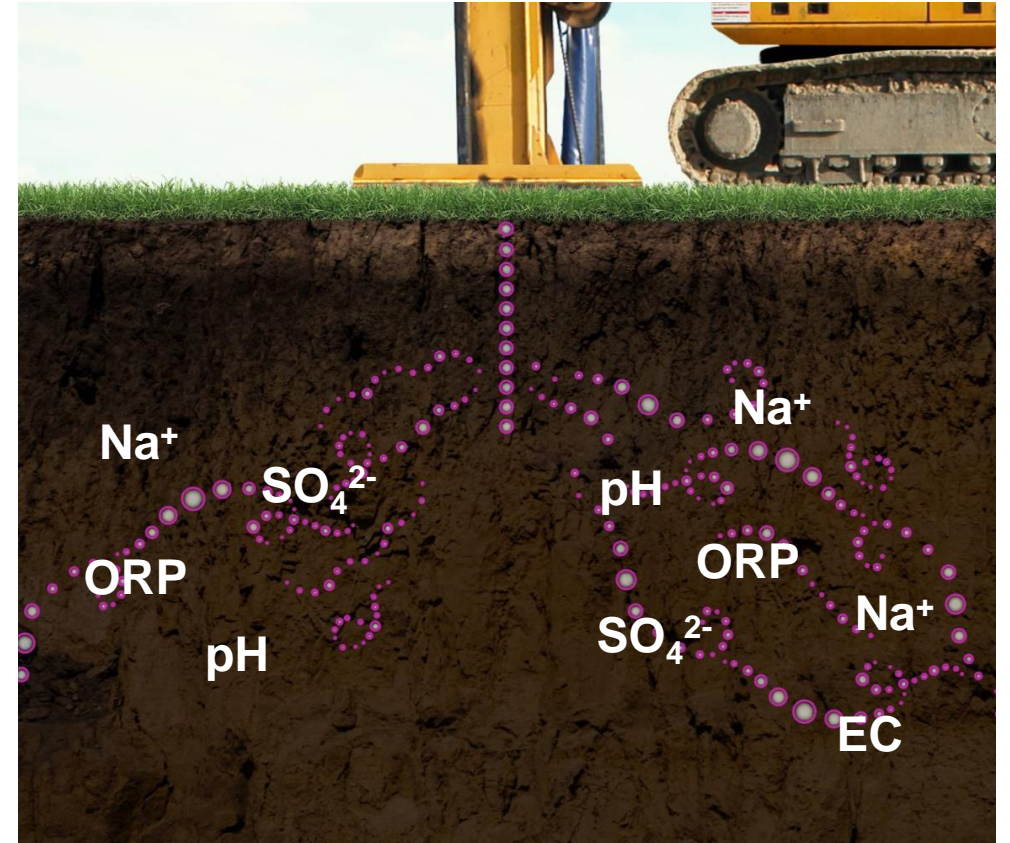
- Residual persulfate
- Geochemical parameters (conductivity, ORP, and pH)
- Sodium/potassium, calcium and sulfate
 - Common cations and anion
- Dissolved organic carbon
- Total organic carbon on soil
- Contaminant concentrations



- Reagent distribution
- Aquifer flow paths and flow velocities
- Reagent longevity
- Residence time of reagents within the target area
- Recontamination vs. rebound
- Potential for secondary treatment methods such as anaerobic oxidation
- Contaminant distribution/residual hotspots

Summary

- Geochemical analyses helpful to understand an application and troubleshoot varied performance
- Can be used to gain a better understanding of the site including flow paths, flow velocities, potential for upgradient sources, hot-spots
- This detailed analysis allows modifying the remedial action plan appropriately for the next phase if needed.



Questions?



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