ARCADIS

Geochemical Battery

Aquifer Tuning at CVOC in situ remediation

Dr. Marcus Alter, Laura Simone (Arcadis Germany)

Introduction

Innovative in-situ remediation concepts for chlorinated solvents (CVOC) remain crucial despite decades of experience and advanced technological developments in the field. This is due to the large number of contaminated sites and the significant duration and cost of ongoing remediation efforts. In this context, the focus is shifting from process-related aspects to the more sustainable concept of "aquifer tuning".

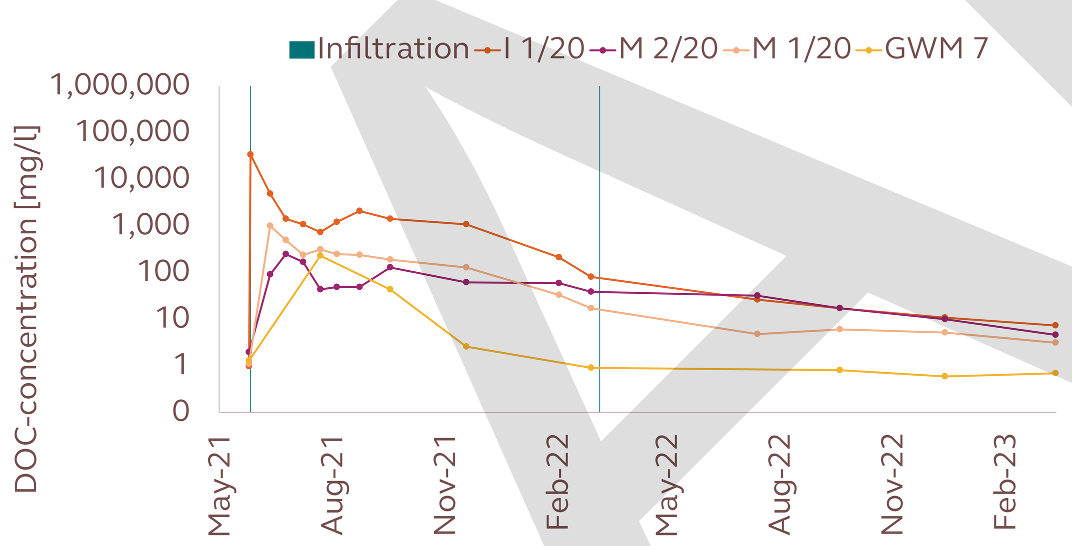
The term "aquifer tuning" refers to the alignment of planning and optimization of in-situ remediation measures with site- and process-specific conditions, considering natural conditions. The goal is to achieve an efficient use of substrates and minimize the technical effort required for their application.

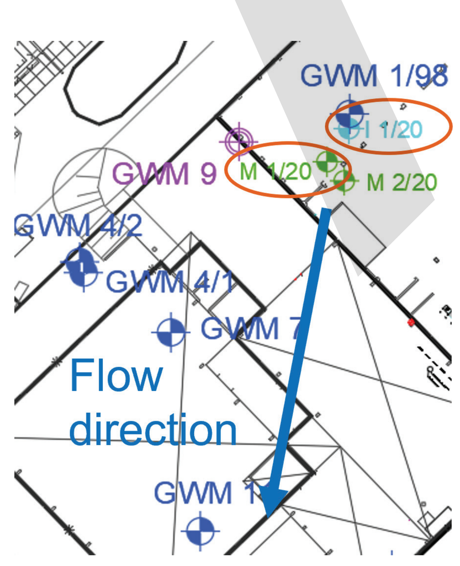
Hypothesis

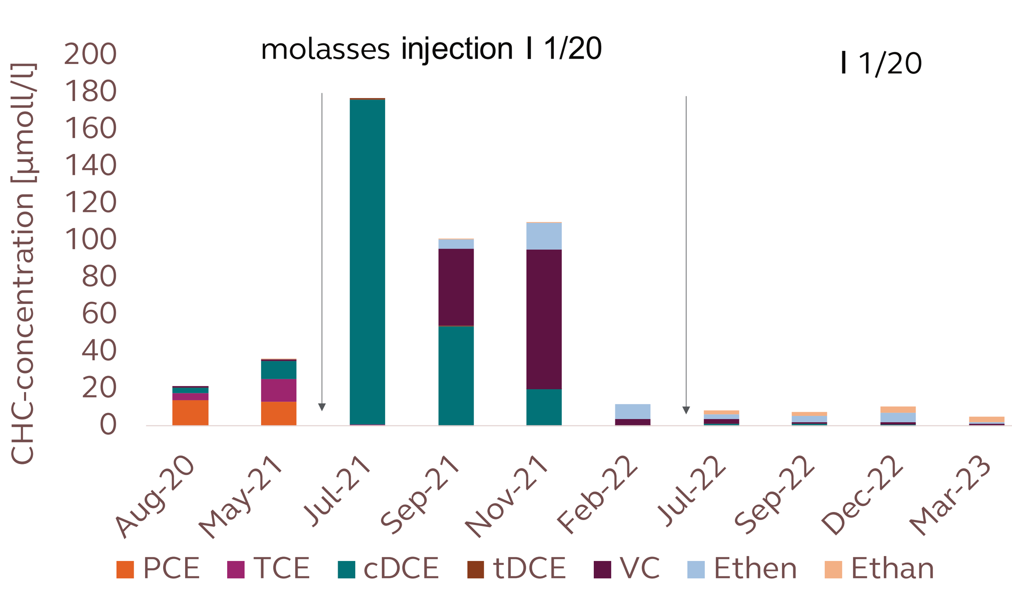
- Secondary electron donator: EPS (extra polymer substances released by bacteria) and previously formed biomass decay
- Support of a pool of reduced species of electron acceptors like reactive mineral species (iron sulphide mineral precipitates, iron-bearing minerals)
- (sometimes): longer persistence of reagents (molasses, vegetable oil)
- Less rebound than other methods like P&T or ISCO

Example in Germany

- Long lasting effect of molasses infiltration in the test field area
- Second infiltration: lower concentration of molasses and less corresponding DOC-effect
- Effective dechlorination around injection well, no rebound!







CSM for in situ dechlorination – battery model

Biotic - Abiotic Conceptual Model for Electron Transfer and Tuning

			Illustrated Example of Remedial Phases			
Role	**Process Description**	**Compounds of Interest**	**Background/Baseline**	**Active Treatment (Early)**	**Active Treatment (Late)**	**Transition to Passive Monitoring**
Geochemistry			Oxic	Anoxic	Anoxic	Anoxic
Bulk reductant	Serves as electron donor to mediator and/or electron acceptor	Organic carbon (nominal, organic carbon substrate, biomass recycling) Iron (magnetite, green rust, iron sulfides, ferrous iron species) Sulfur (hydrogen sulfides and polysulfides) Titanium citrate	Limited electron donation	Increasing electron donation	High degree of electron donation	Sustained electron donation (from electron shuttling and/or biomass recycling)
Mediator	Transfers electrons between the electron donor and acceptor; depending on redox state, can serve as an electron donor to chlorinated compounds or as an electron acceptor from bulk reductant(s)	Nominal organic matter (humic substances) Mixed valents state iron minerals (magnetic, green rust, ferrous hydroxide) Metalloenzymes (vitamin B_{12})	Limited electron shuttling	Active electron shuttling	Active electron shuttling	Active electron shuttling
Electron acceptor	Accepts electrons from electron donor (either bulk reductant or mediator)	Oxygen Nitrate Mangenese	O_2 reduction	NO_3 - reduction Mn(IV) reduction	Mn(IV) reduction	Mn(IV) reduction
		Iron Chlorinated compound Sulfate Carbon dioxide		Fe(III) reduction Chlororespiration SO_4^{2-} reduction Methanogenesis	Fe(III) reduction Chlororespiration SO_4^{2-} reduction Methanogenesis	Fe(III) reduction Chlororespiration SO_4^{2-} reduction Methanogenesis
Iron sulfide mineral formation			No	Yes	Yes	Yes
Battery strength	Relative size of available electron pool					

Source: Horst et. Al 2022 (GWMR)

Heat Map for Assessing Likelihood and Optimal Conditions for FeSx Formation Within In Situ Reaction Zones

Parameter			Conditions Indicating Potential Presence of Iron Sulfide Minerals			Example Application		
Parameter Description	**Parameter ID**	**Approximate Costs, Specialty Analyses Vendors**	**Favorable**	**Possible**	**Unfavorable**	**In Situ Reactive Zone (Ideal Conditions)**	**Fringe of In Situ Reactive Zone**	**Background (Non-Ideal Conditions)**
Field measurements: low cost, poor accuracy	GW DO (mg/L)	NA	<0.1	<1, >0.1	>1	0.52	0.98	2.62
	GW ORP (mV)	NA	<–50	<150, >–50	>150	–277	–104	86
Geochemical evidence (proxy): easy/fast sampling; low costs; good accuracy; low precision	GW-dissolved Fe (mg/L)	$30	>20	<20, >1	<1	3.7	23.8	0.0559
	GW Δ sulfate (mg/L)	$25	>200	<200, >25	<25	870	158	227
	GW sulfide (mg/L)	$30	>1	Detectable		7.15	0.0426	0.0905
	GW methane (mg/L)	$65	>5	<5, >0.5	<0.5	0.02	0.47	0.0033
	GW acetylene (µg/L)	$65	Detectable			0.89	<0.28	<0.28
	GW TOC (mg/L)	$40	>20	<20, >5	<5	35.3	89.7	21.9
Geochemical evidence (conclusive): longer deployment/ sampling times; higher costs; good accuracy; low precision	Black-tinted Min-Trap	$300 per sampler (Microbial Insights)	Significant presence of black precipitates	Limited distribution of gray/black precipitates	Absence of black precipitates	Significant presence of black precipitates	Significant presence of black precipitates	Absence of black precipitates
	Min-Trap total Fe (mg/kg)	$30	>100	>50	<50	78	97	107
	Min-Trap AMIBA: (WAS-Fe^{2+}+ SAS-Fe^{2+})/ (WAS-Total Fe + SAS-Total Fe)	$1000	>0.75	<0.75, >0.25	<0.25	1.02	1.03	0.28
	Min-Trap AMIBA: AVS+CrES (if SAS Fe^{2+} detected) (mg/kg)		>20	Detectable	Non-detectable	48	26.3	11.23
	Min-Trap SEM-EDS	$1200-$1800 per sample	Extensive co-location of Fe and S	Limited co-location of Fe and S	No significant S	Extensive co-location of Fe and S	Limited co-location of Fe and S	Not analyzed
Microbiological evidence: fast sampling; high costs; good accuracy and precision	Iron-reducing bacteria and sulfate-reducing bacteria	$300-600 individual targets $750-$950 per array	<1.00x10^3	<1.00x10^2 – 1.00x10^3	Non-detectable	8.83x10^3 – 2.67x10^6	6.17x10^4–1.23x10^5	Not analyzed

Success requirements

- Well-developed initial conceptual site model
- Intensive long-term monitoring, data harvesting for future applications