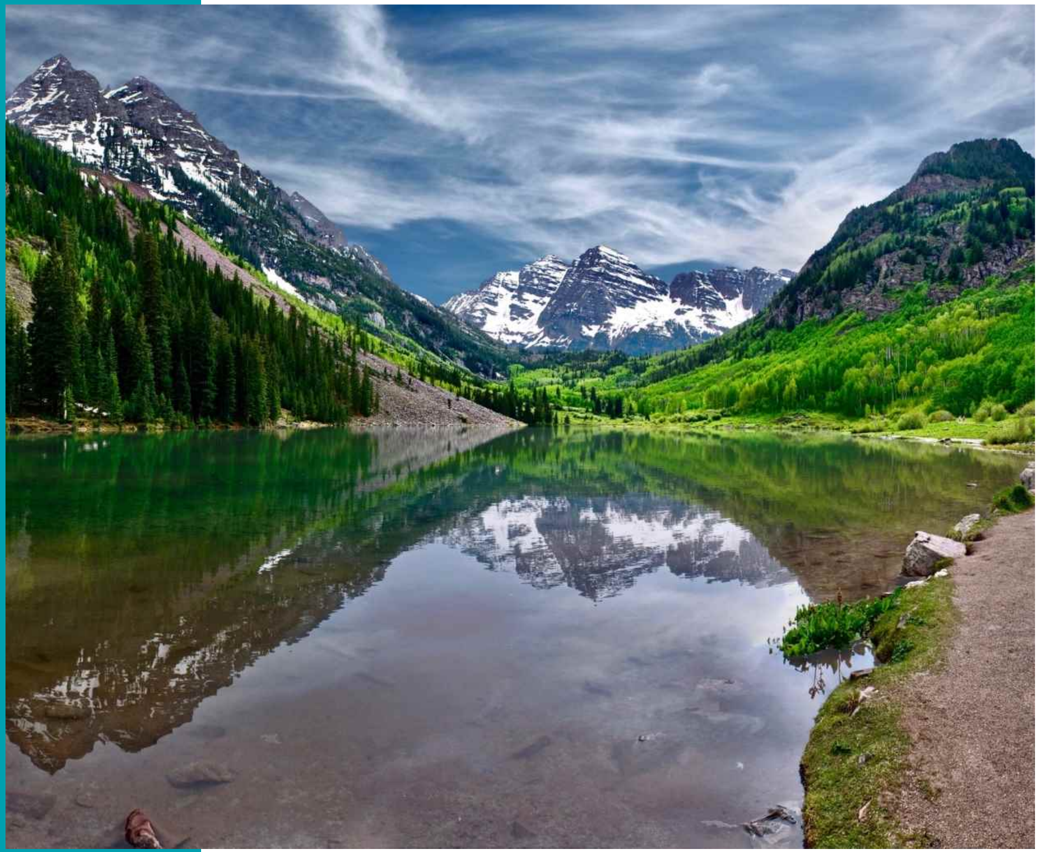
CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

A Biogeochemical Model for Enhanced Bioremediation of Chloro-, Nitro- and Amino-substituted Aromatics using Advanced Tools and Methods



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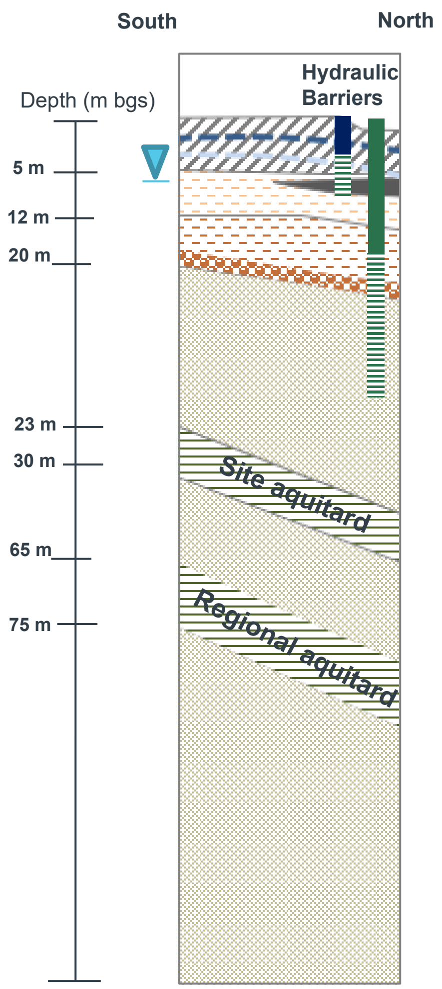
J. Henderson, P. Carvalho, E. E. Mack (Corteva Agriscience)

Site Background and Complexities



Matrix: highly heterogeneous

Sources: multiple and non-unique

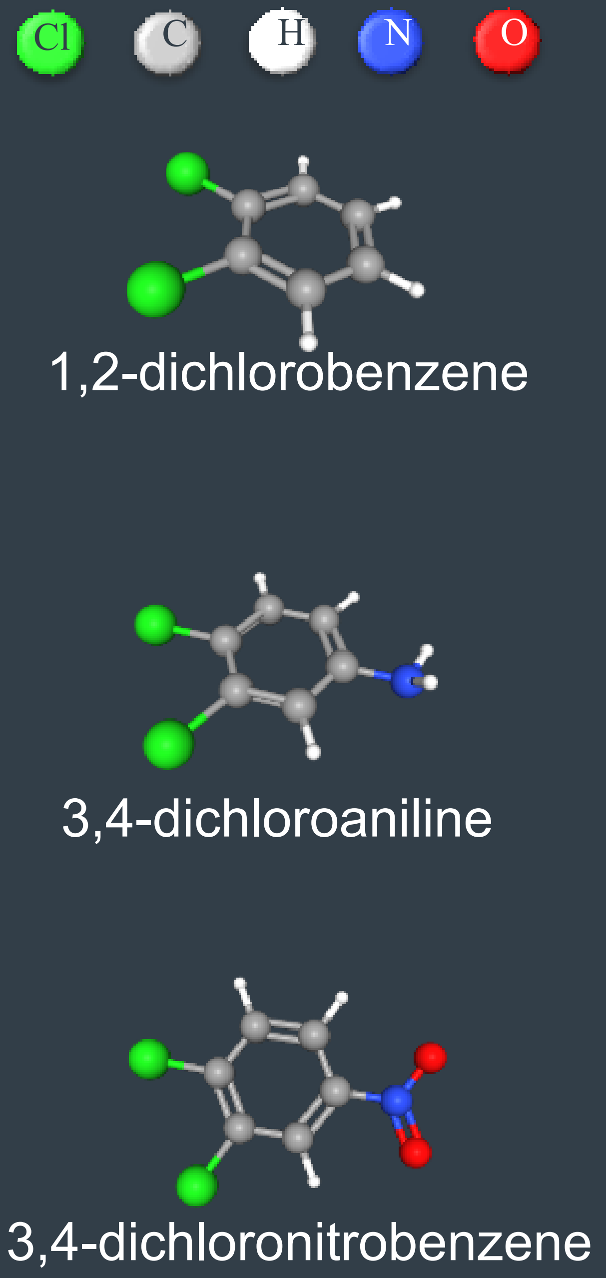
Contaminant mixture: VOCs + SVOCs; products and degradation products

Non-aqueous phase: liquids and solids

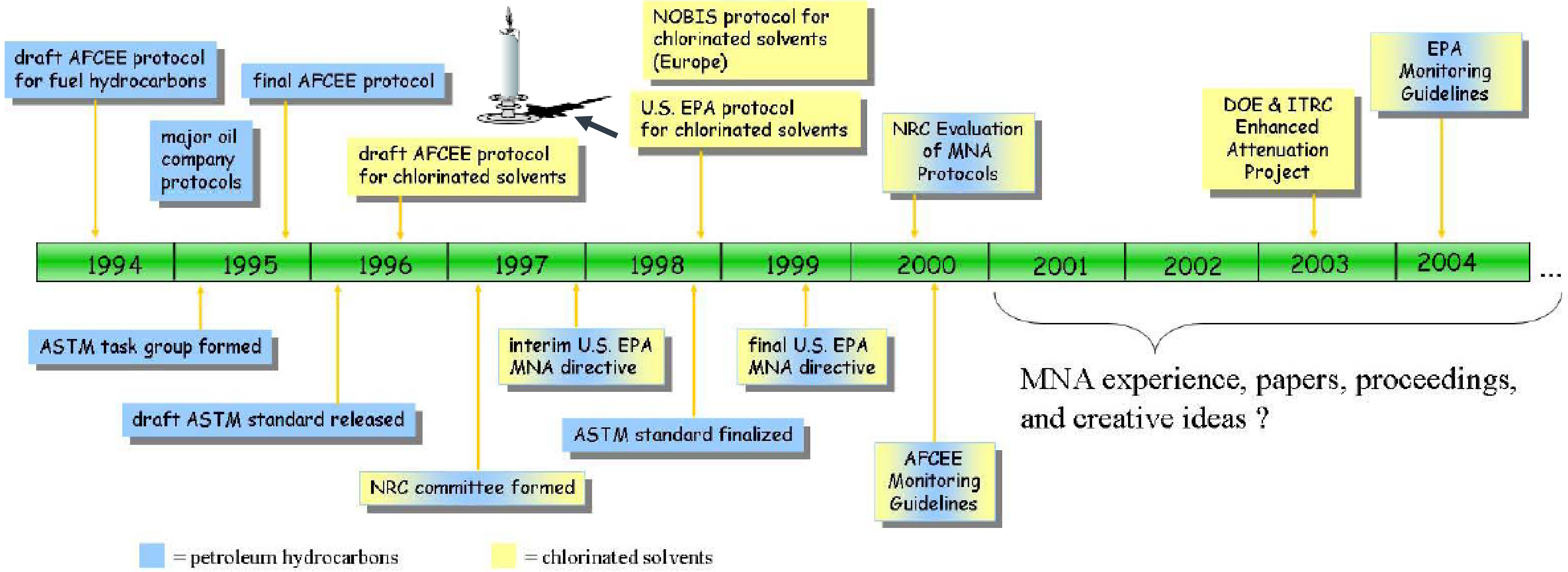
Microorganisms: ongoing research to identify and quantify microbial community

Bioavailability of nutrients and inhibitory factors

CSIA: enrichment factors partially known



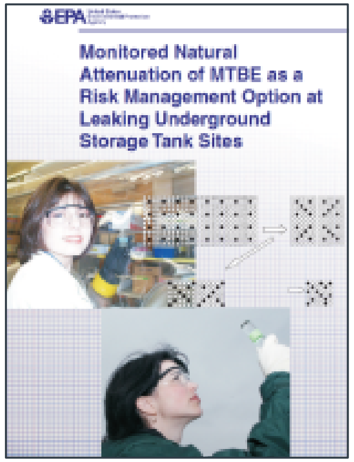
Conventional Methods and Protocols



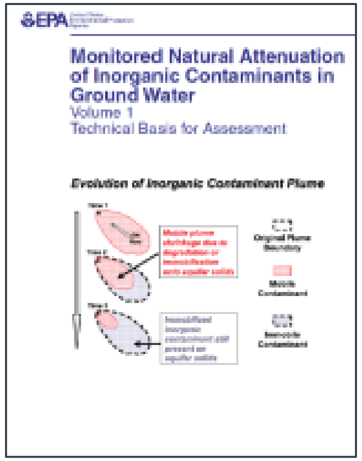
Modified from chart provided by Todd Wiedemeier (2000)

Fonte: ITRC (2008)

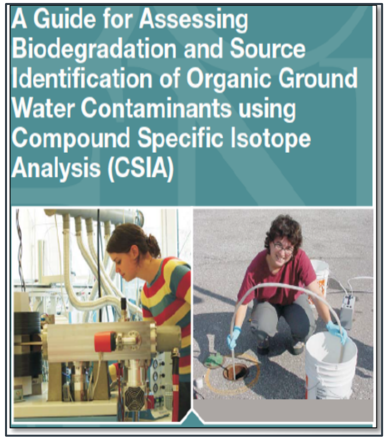
Biogeochemical Modelling and Remedy Selection



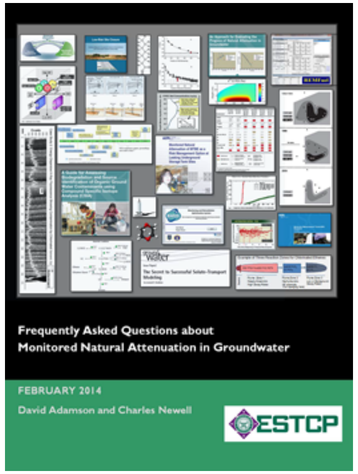
U.S.EPA (Ford et al. 2005)



U.S.EPA (Wilson et al. 2007)

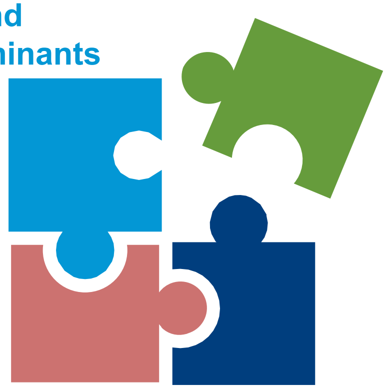


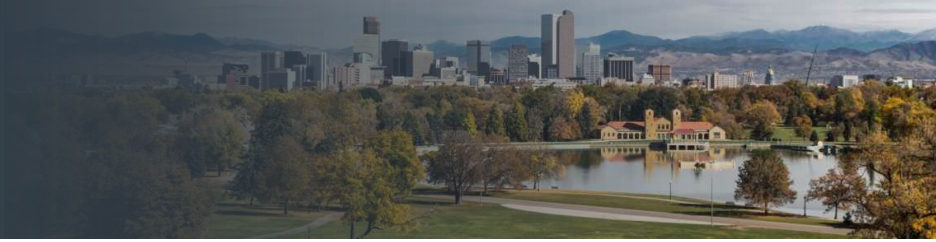
U.S.EPA (Hunkeler et al. 2009)



ESTCP (Adamson and Newel 2014)

- Existing guidance and molecular biological tools are mostly limited to
  - Inorganics
  - chlorinated solvents
  - hydrocarbons
- Conventional tools and methods can be insufficient for complex sites
- Need for a comprehensive biogeochemical model to support
  - field data interpretation
  - current conditions assessment
  - remedy selection





Compounds of Interest | VOCs

Compound	Solubility in water (mg/L) / at "x" °C	log P (octanol-water)	Vapor Pressure (mmHg) / at "xx" °C	Henry's Law (atm-m3/mole) / at "xx" °C	Density (g/cm^3) / at "xx" °C	K_{oc} (Soil Adsorption Coefficient) - L/Kg
1,2,3-Trichlorobenzene	18 / 25	4.05	2.1×10^{-1} / 25	1.25×10^{-3} / 25	1.4533 / 25	2140
1,2,4-Trichlorobenzene	49 / 25	4.02	4.6×10^{-1} / 25	1.42×10^{-3} / 25	1.459 / 20	1260
1,2-Dichlorobenzene	156 / 25	3.43	1.36 / 25	1.15×10^{-3} / 20	1.3059 / 20	363
1,3-Dichlorobenzene	125 / 25	3.53	2.15 / 25	2.83×10^{-3} / 25	1.2884 / 20	380
1,4-Dichlorobenzene	81.3 / 25	3.44	1.74 / 25	2.41×10^{-3} / 25	1.2475 / 25	447
Chlorobenzene	499 / 25	2.84	12 / 25	3.11×10^{-3} / 25	1.1058 / 20	141
Nitrobenzene	2090 / 25	1.85	0.24 / 25	2.4×10^{-5} / 25	1.199 / 25	87.1
1,2-Dichloroethane	8600 / 25	1.48	78.9 / 25	1.18×10^{-3} / 25	1.2454 / 25	33.1
Benzene	1790 / 25	2.13	94.8 / 25	5.56×10^{-3} / 25	0.8756 / 20	56.2
Ethylbenzene	170 / 25	3.15	9.6 / 25	7.88×10^{-3} / 25	0.8626 / 25	170
O-Xylene	208 / 25	3.12	6.61 / 25	5.18×10^{-3} / 25	0.878 / 20	178
P-Xylene	162 / 25	3.15	8.84 / 25	6.90×10^{-3} / 25	0.86104 / 20	257
Toluene	526 / 25	2.73	28.4 / 25	6.64×10^{-3} / 25	0.8623 / 20	140
Vinyl Chloride	8800 / 25	1.46	2.980×10^{3} / 25	2.78×10^{-2} / 25	0.9106 / 20	20.4

Environmental Fate Summary

Mobility in Soil: K_{oc}

Low to no mobility

High mobility

Partitioning water/soil - air: Henry's Law / Vapor Pressure

Low partitioning to air/ volatilization

High partitioning to air/volatilization

Mobility in Water: Log K_{ow} / solubility

Low to no mobility

High mobility

If it occurs multiphase flow in water

DNAPL

LNAPL

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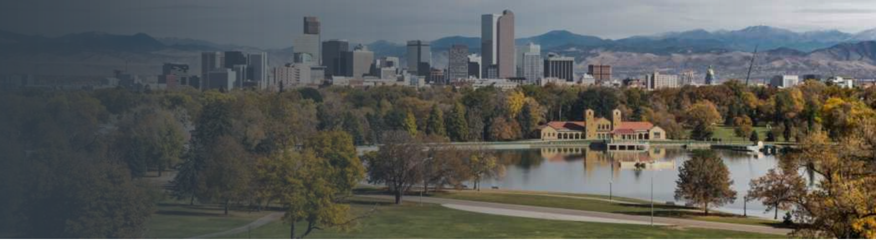
Compounds of Interest | SVOCs



Compound	Solubility in water (mg/L) / at "x" °C	log P (octanol-water)	Vapor Pressure (mmHg) / at "xx" °C	Henry's Law (atm-m3/mole) / at "xx" °C	Density (g/cm^3) / at "xx" °C	Koc (Soil Adsorption Coefficient) - L/Kg
Phenol	82800 / 25	1.46	0.35 / 25	3.33×10^{-7} / 25	1.071 / 25	26.9
2-Chloroaniline (2-CA)	8165 / 25	1.9	0.204 / 25	5.39×10^{-6} / 25	1.2114 / 22	155
3-Chloroaniline (3-CA)	5400 / 20	1.88	0.066 / 25	1.00×10^{-6} / 25	1.2150 / 22	135
4-Chloroaniline (4-CA)	3900 / 25	1.83	0.071 / 25	3.10×10^{-6} / 25	1.43 / 19	91.2
2,3-Dichloroaniline (2,3-DCA)	436 / 25	2.78	0.02 / 25	5.01×10^{-7} / 25	1.383 / 25	891
2,5-Dichloroaniline (2,5-DCA)	504 / 25	2.92	0.0148 / 25	1.86×10^{-7} / 25	1.54 / 25	347
3,4-Dichloroaniline (3,4-DCA)	92 / 20	2.69	6.32×10^{-3} / 25	7.74×10^{-7} / 25	1.57 / 25	269
3,4-Dichloronitrobenzene (3,4-DCNB)	121 / 20	3.12	0.0103 / 25	8.07×10^{-6} / 25	1.56 / 15	339
2-Methylphenol (o-cresol)	25900 / 25	1.95	0.18 / 25	1.20×10^{-6} / 25	1.047 / 20	123
3-Methylphenol (m-Cresol)	22700 / 25	1.96	0.11 / 25	8.60×10^{-7} / 25	1.034 / 20	120
4-Methylphenol (p-Cresol)	21500 / 25	1.94	0.11 / 25	1.00×10^{-6} / 25	1.034 / 20	501
2,4-Dinitrotoluene (2,4-DNT)	200 / 25	1.98	1.47×10^{-4} / 22	5.40×10^{-8} / 25	1.521 / 15	347
2,6-Dinitrotoluene (2,6-DNT)	204 / 25	2.1	5.67×10^{-4}/ 25	1.17×10^{-7} / 25	1.41 / 25	363
2-Nitrotoluene	609 / 20	2.3	0.185 / 25	1.25×10^{-5} / 25	1.1622 / 19	72.4
3-Nitrotoluene	450 / 20	2.45	0.107 / 25	9.30×10^{-6} / 25	1.163 / 20	70.8
4-Nitrotoluene	361 / 25	2.37	0.0157 / 25	5.63×10^{-6} / 25	1.286 / 20	79.4
Ethofumesate	50 / 25	2.7	4.9×10^{-6} / 25	1.26×10^{-6} / 25	1.29 / 20	339
Propanil	150 / 25	3.07	9.08×10^{-7} / 25	1.86×10^{-9}/ 25	1.25 / 25	148
Hexachlorobenzene	0.0047 / 25	5.73	1.72×10^{-5} / 25	5.80×10^{-4} / 25	2.044 / 23	5500
p-Nitrocumene	249 / 25	3.33	4.76×10^{-2} / 25	9.33×10^{-6} / 25	1.11 / 25	2240
Bis(2-ethylhexyl) phthalate	0.27 / 25	7.6	1.42×10^{-7} / 25	2.63×10^{-7} / 25	0.981 / 25	87100

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DNAPL

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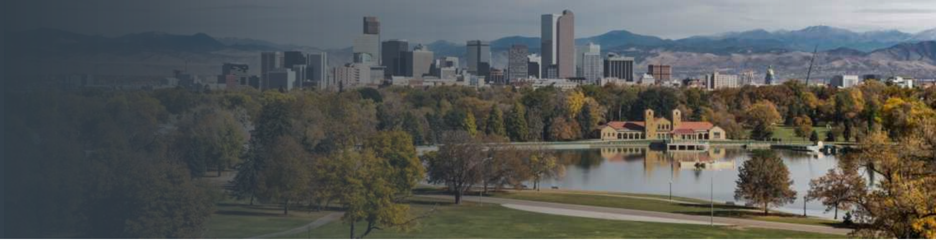
Advanced Methods



Data Gap		Solution
Site Heterogeneity and inconsistent historical data	Integrated database for spatial / temporal trend analysis and multivariate statistics	
Unknown COI mixtures and fingerprints	Advanced tools / methods (CSIA, NMR, 16S sequencing, qPCR)	
Unknown COI degradation pathways	Comprehensive Research Program	

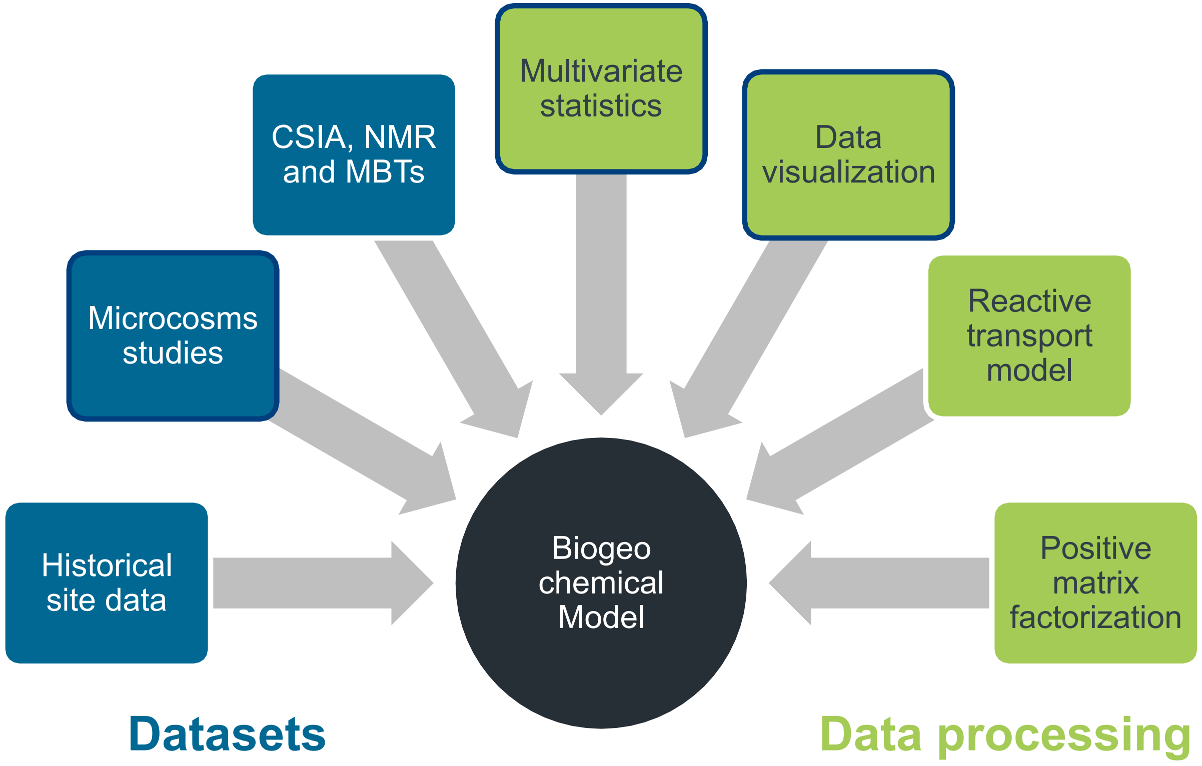
University of Toronto | University of Guelph | Clemson University | University of West Florida | UFPE | UFBA Universidade Federal da Bahia | SiREM Leading Science · Lasting Solutions | Isodetect Environmental Monitoring

Lines of Evidence for Natural Attenuation of Contaminants

	USEPA Guidance	Micro- & Mesocosms	Site-wide Evaluation
Decreasing Concentrations LOE 1	Decreasing trend of contaminant mass and/or concentration over time at appropriate monitoring or sampling points.	Decreasing trend downgradient biosparging and gravel bed pilot systems.	Plume stability analysis. Groundwater Flow Modeling.
Indirect Evidence LOE 2	Hydrogeochemistry to demonstrate active natural attenuation processes	Increased DO and decreased pH in biosparging pilot. Increased Cl- in gravel bed effluent.	Site geochemistry (radial plots). Correlation with COI. Statistical analyses.
Direct Evidence (process-specific) LOE 3	Direct demonstration of a particular NA process (e.g., biological degradation)	• Lab microcosms & field pilots • CSIA & DNA analyses from cultures to confirm presence of active degrading bacteria • Evaluation of plant uptake • NMR to indicate metabolites	• CSIA & DNA analyses from cultures to confirm presence of active degrading bacteria • NMR source fingerprints and to indicate metabolites

Biogeochemical Model – Use of Advanced Tools

Reverse approach: academic work and literature evaluation and further statistics to confirm LOEs 1, 2, 3



Dataset Preparation

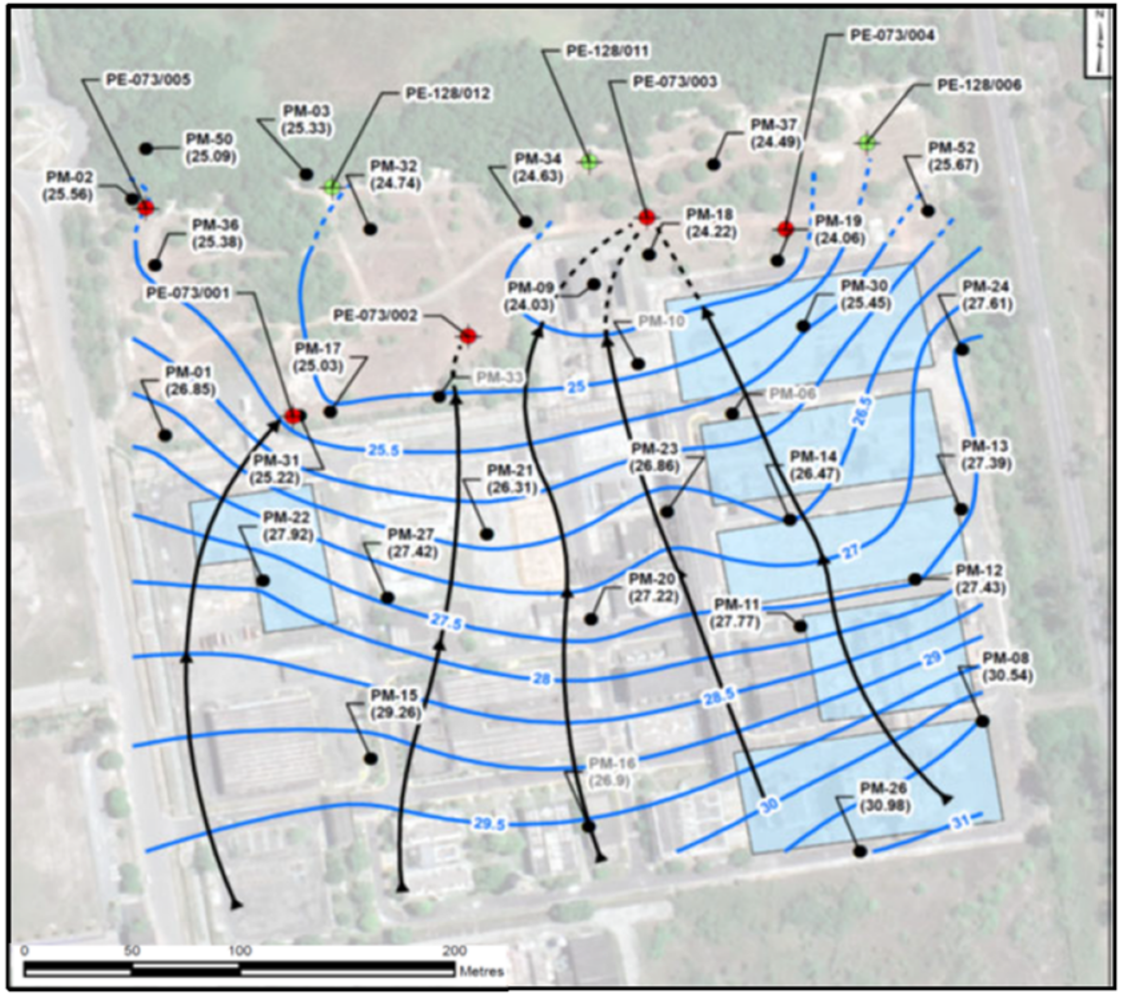
Consistency
- Spatial and temporal
- Locations and analytes
- Detection frequency >50%

Noise reduction
- Annual average
- Check data percentiles and NDs
- Data normalized

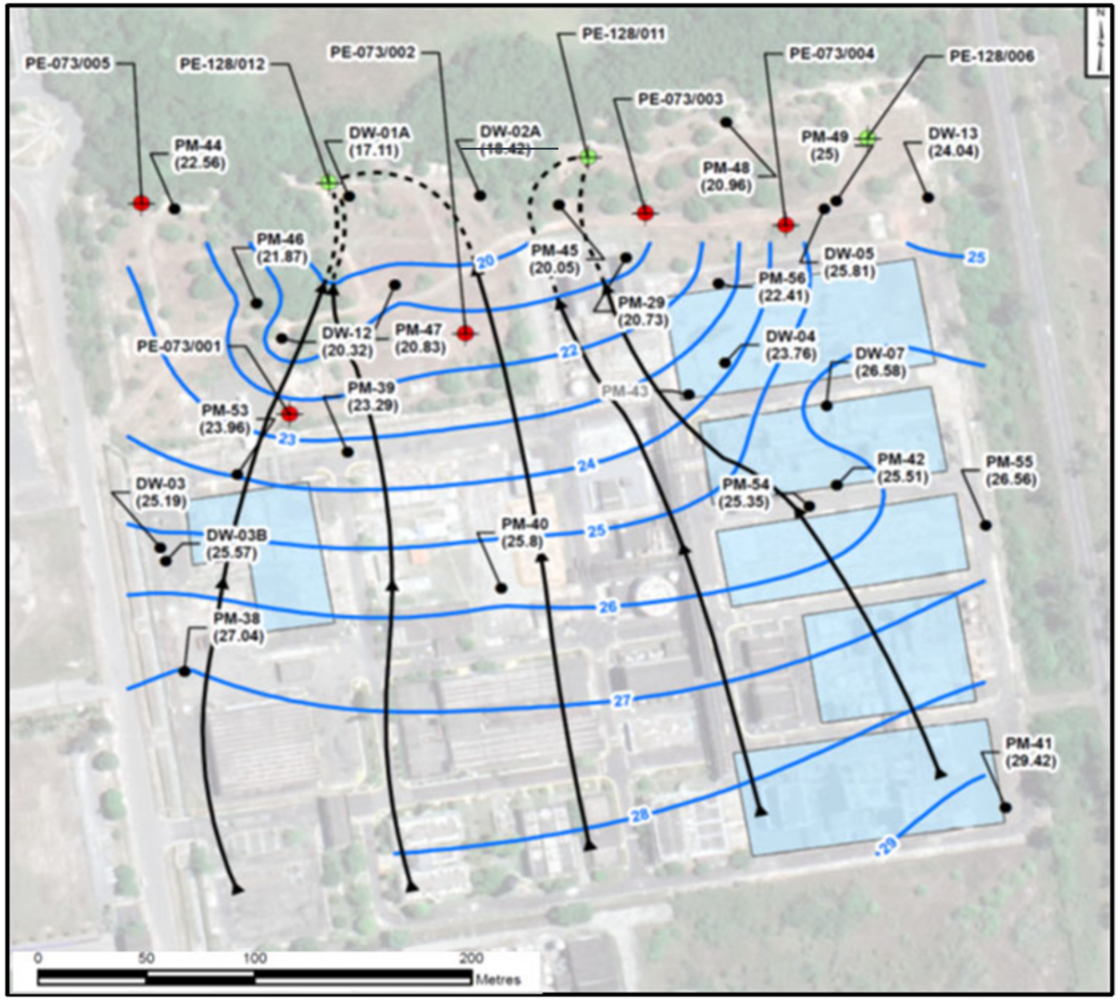
Analysis dataset
- 22 parameters
- 33 wells
- 2011 to 2021
- Upper and Lower Site Aquifer

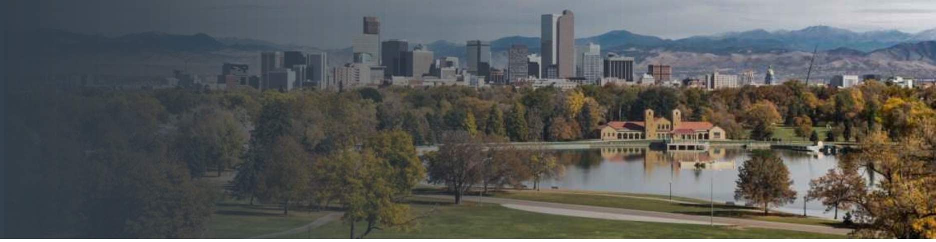
Site Hydrogeology

Upper Site Aquifer (<20 mBGS)

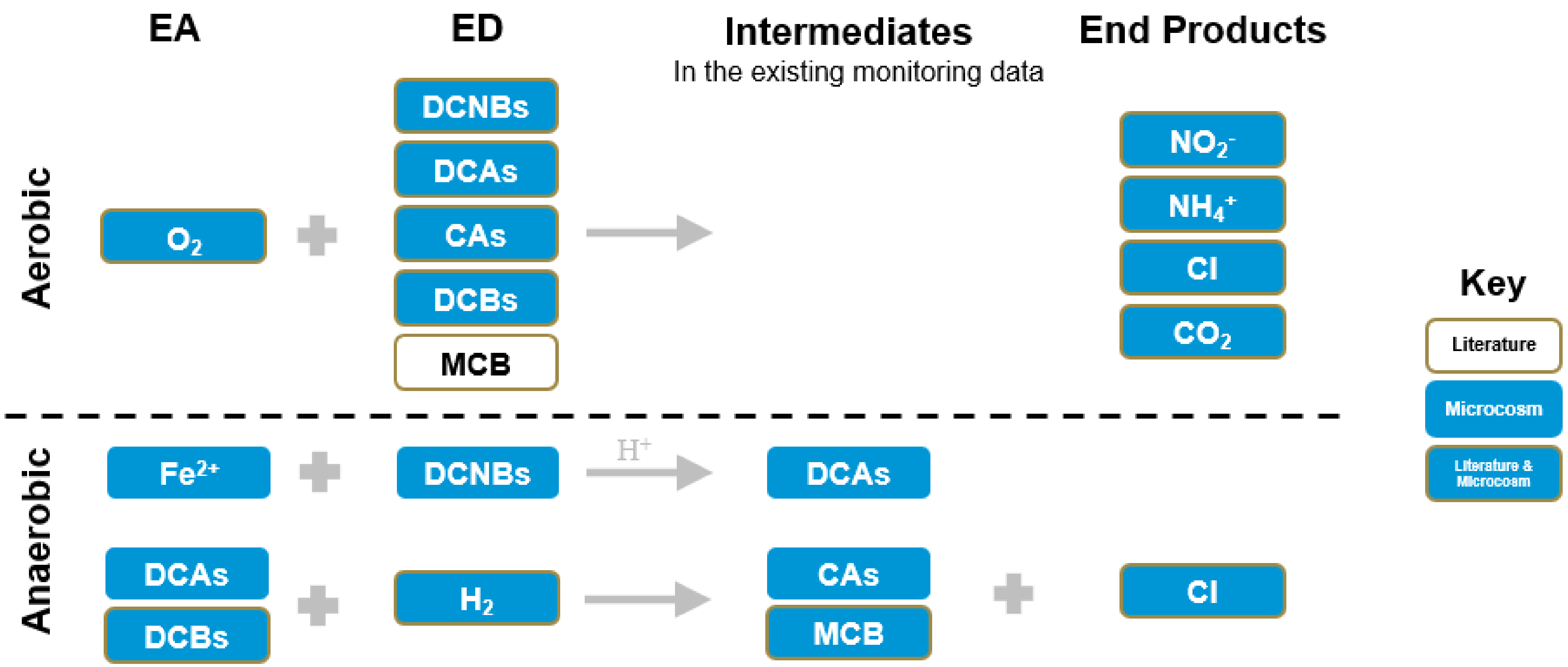


Lower Site Aquifer (>20 mBGS)



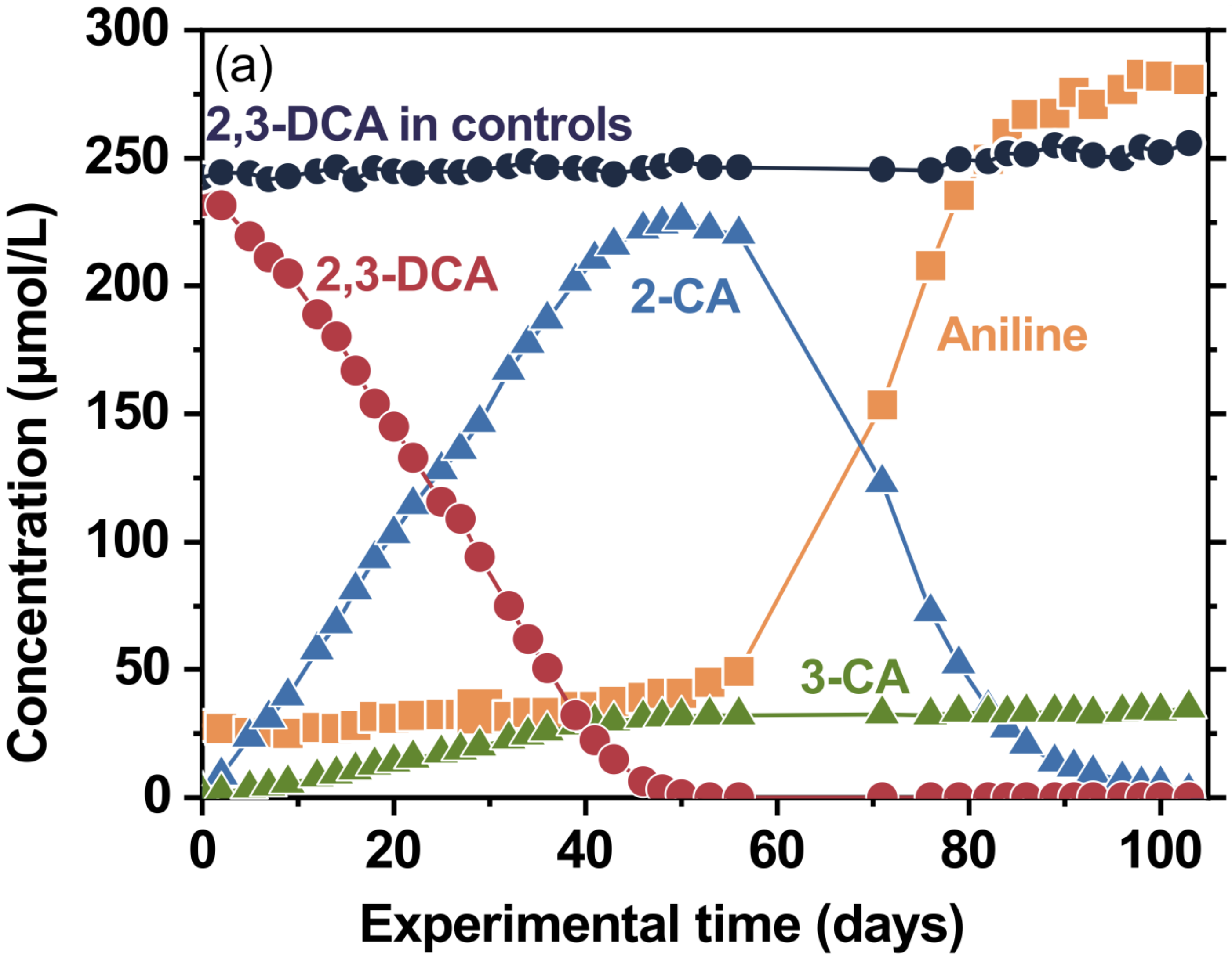


Microcosms Studies and Literature



(D)CA – (Di)chloroaniline
(D)CB – (Di)chlorobenzene
(D)CNB – (Di)chloronitrobenzene

2,3-Dichloroaniline dechlorinates to Aniline



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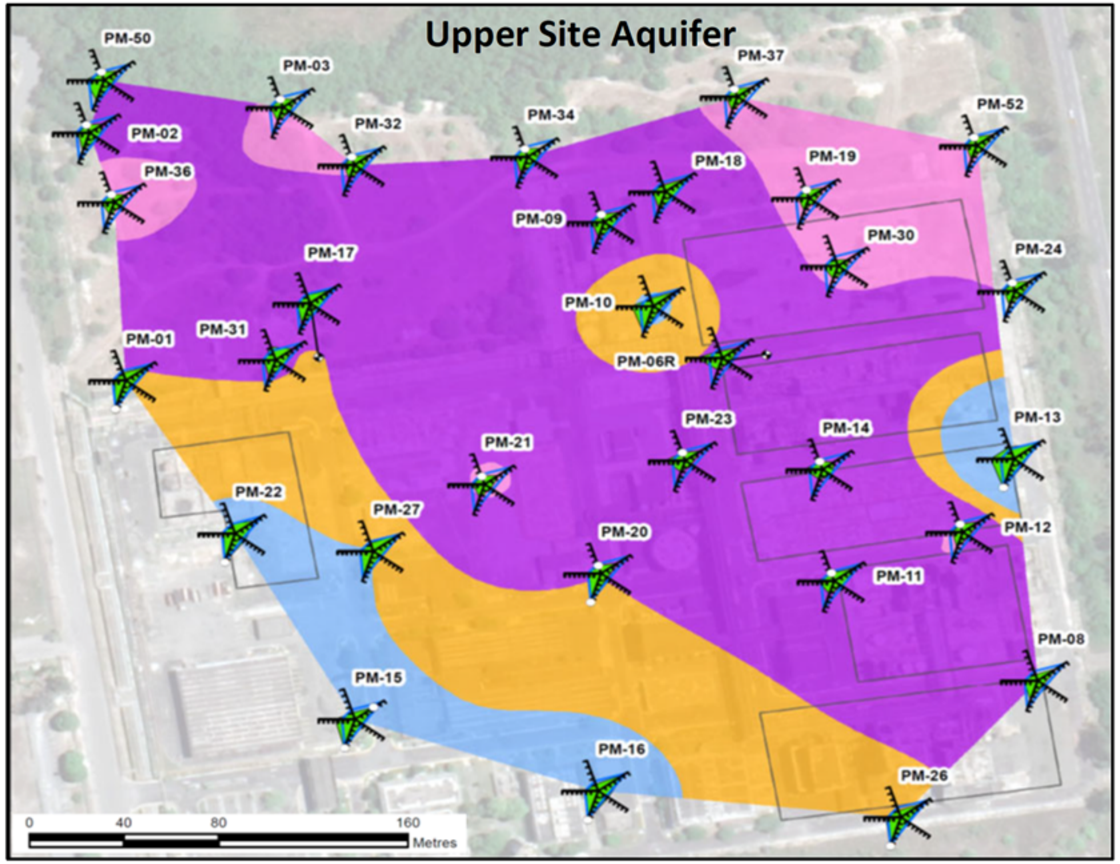
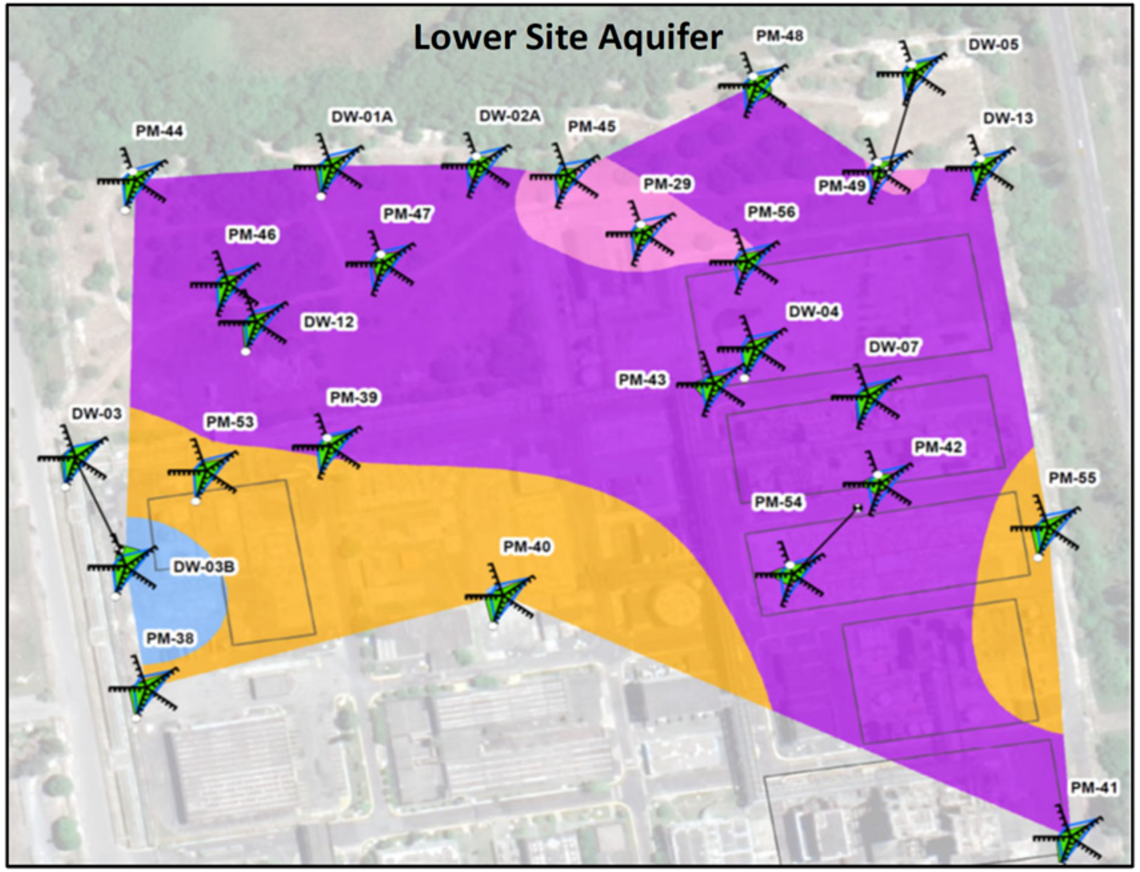
Wang S., Passeport, E.

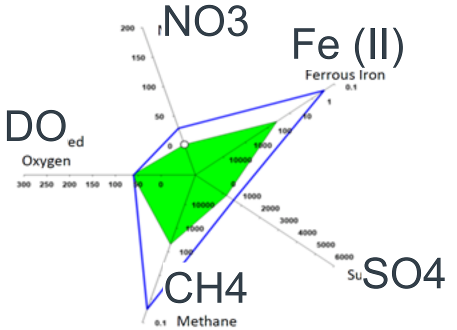
Radial Plots for Multiparameter Evaluation of Site Geochemistry

Terminal Electron Accepting Processes polygon area indicating differences against local background





(Oct-Nov 2020)



Legend

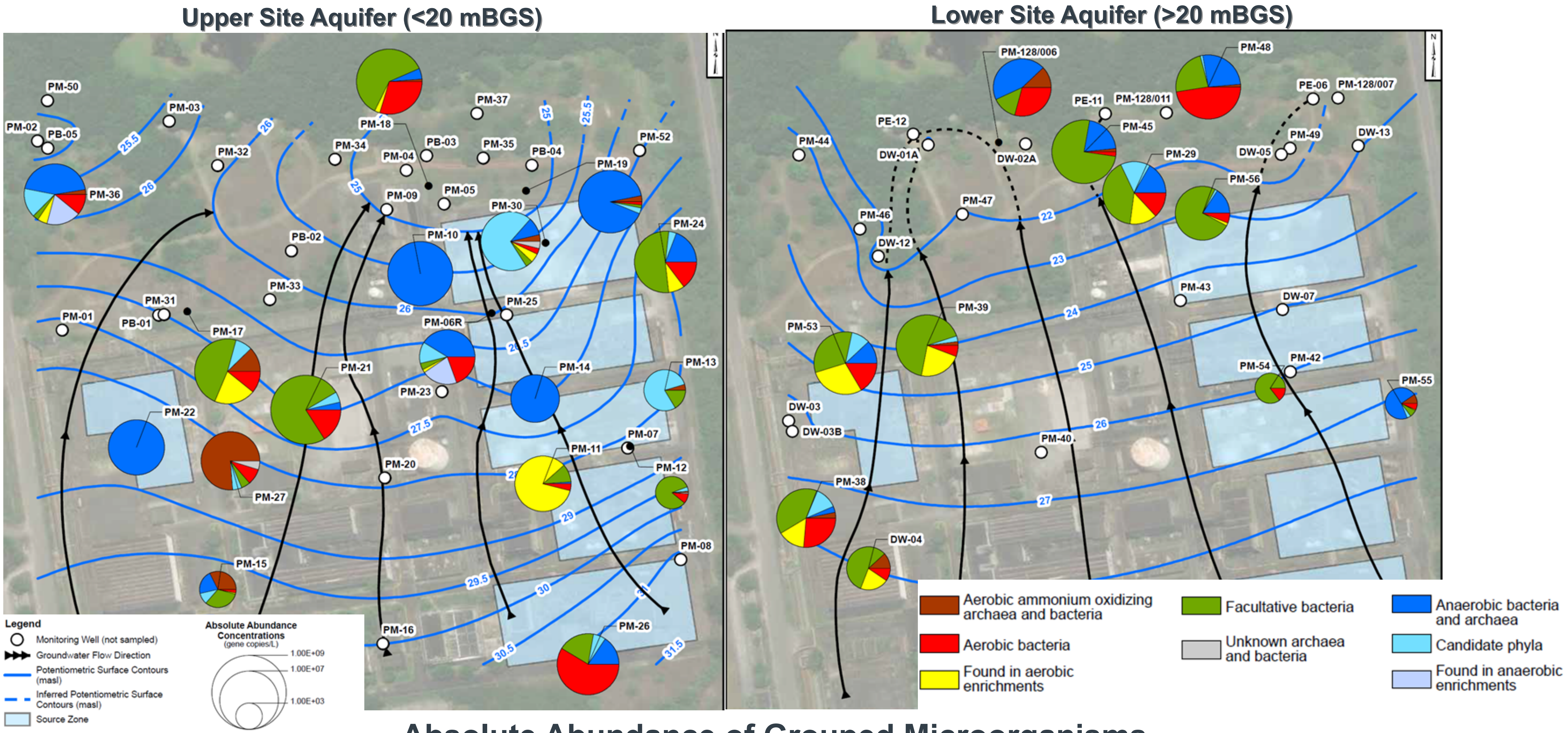
- Local background TEAP polygon[1]
- Well-specific TEAP polygon
- Non-detect
- Source zone

TEAP Polygon % Difference from Local Background

- ≤10%
- >10% - 25%
- >25% - 50%
- >50%

Geos

Molecular Tools – DNA sequencing | Spatial Distribution



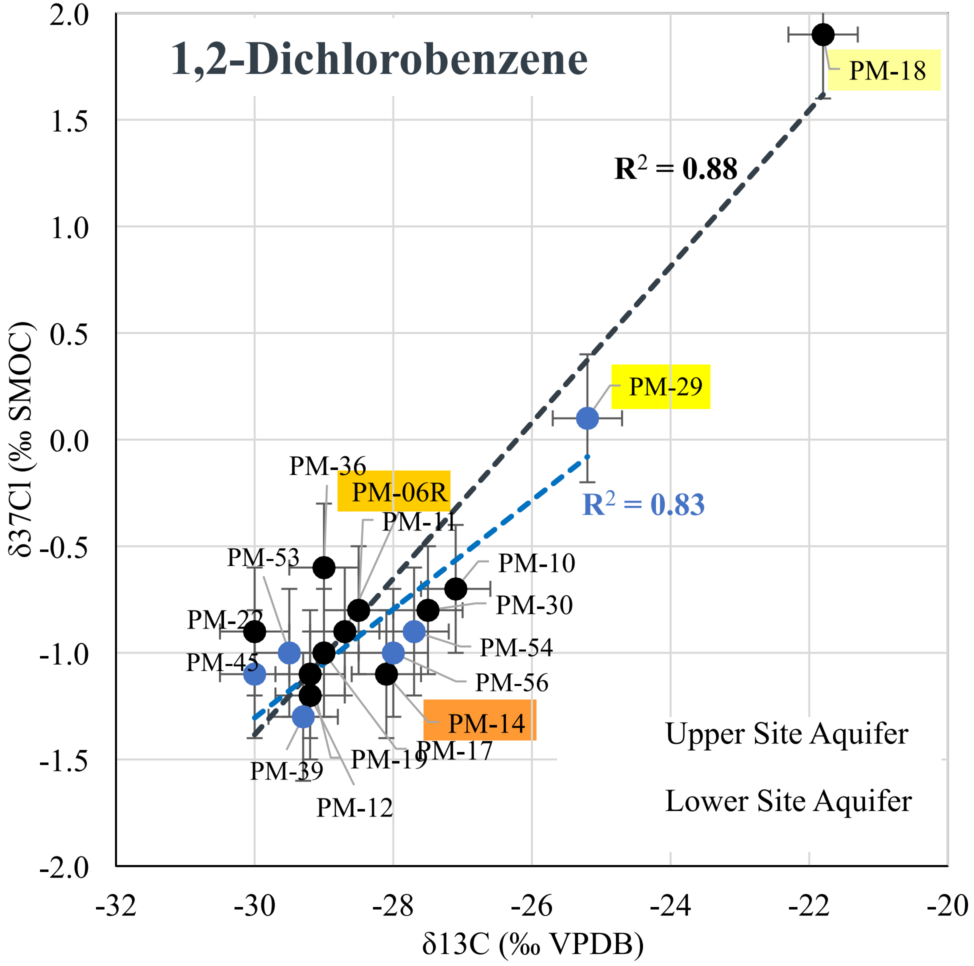
Absolute Abundance of Grouped Microorganisms

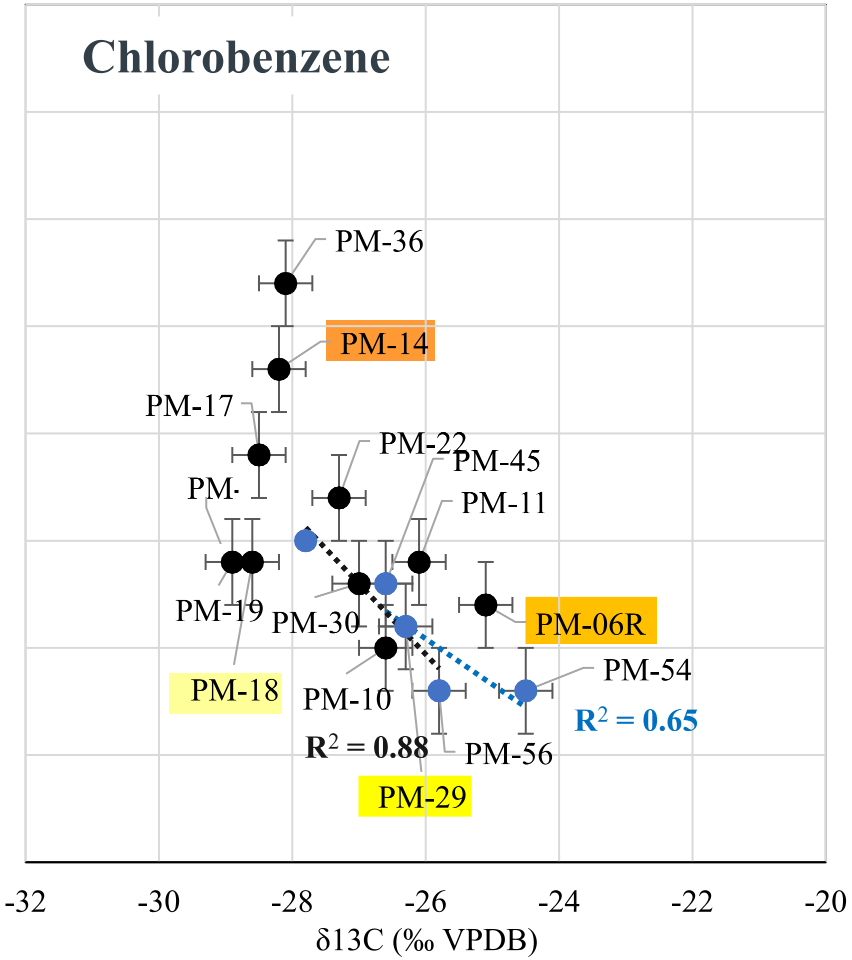
Isotope Enrichment Factors for Site-Compounds

Database of ε (‰)	AEROBIC	ANAEROBIC	ABIOTIC
(di)chloronitrobenzenes		3,4-DCNB	ε_C = -3.9 and -4.8 (OH°) ε_C = -0.65 (Fe(II)) ε_H = -28.0 to -41.9 (Fe(II))
(di)chloroanilines	ε_C = 0 ε_H = 0 ε_N = +6.2 to +7.9 2,3-DCA	2,3-DCA	ε_C = -0.5 to -2.7 (DP), -0.2, -1.0 (IP) ε_N = -2.7 to -9.1 (DP), -1.7, -3.5 (IP) ε_N = -1.9 (MnO_2)
Nitrobenzene	ε_C = -0.6 to -3.9 ε_H = -3.4 to -6.3 ε_N = -0.8 to -1.0 (diox), -26.6 (red)		ε_C = -3.9 (OH°) ε_H = 11.7 (OH°)
Chlorobenzenes	ε_C = -0.1 to -0.4	ε_C = -0.8 to -6.3	ε_C = -0.9 to -1.8 (OH°)
Nitrotoluenes	ε_C = -0.1 to -1.3 ε_H = -2.6 to -5.9 (diox) ε_H = -9.9 (red) ε_N = -1.6 (diox), -25.3 (red)		ε_N = -31.3 to -43.3 (Fe(II))

Hofstetter et al. 2008, Pati et al. 2012, 2014, 2016, Wijker et al. 2013, Hartenbach et al. 2006, 2008, Tobler et al. 2007, Zhang et al. 2016, Passeport et al. 2018, Skarpeli-Liati et al. 2011, Ratti et al. 2015, Kaschl et al. 2005, Liang et al. 2011, 2014, Griebler et al. 2004

Molecular Tools – Compound-Specific Isotope Analysis (CSIA)





upgradient

source zone

plume fringe

downgradient

Fractionation observed along flow path, particularly towards PM-18 downgradient

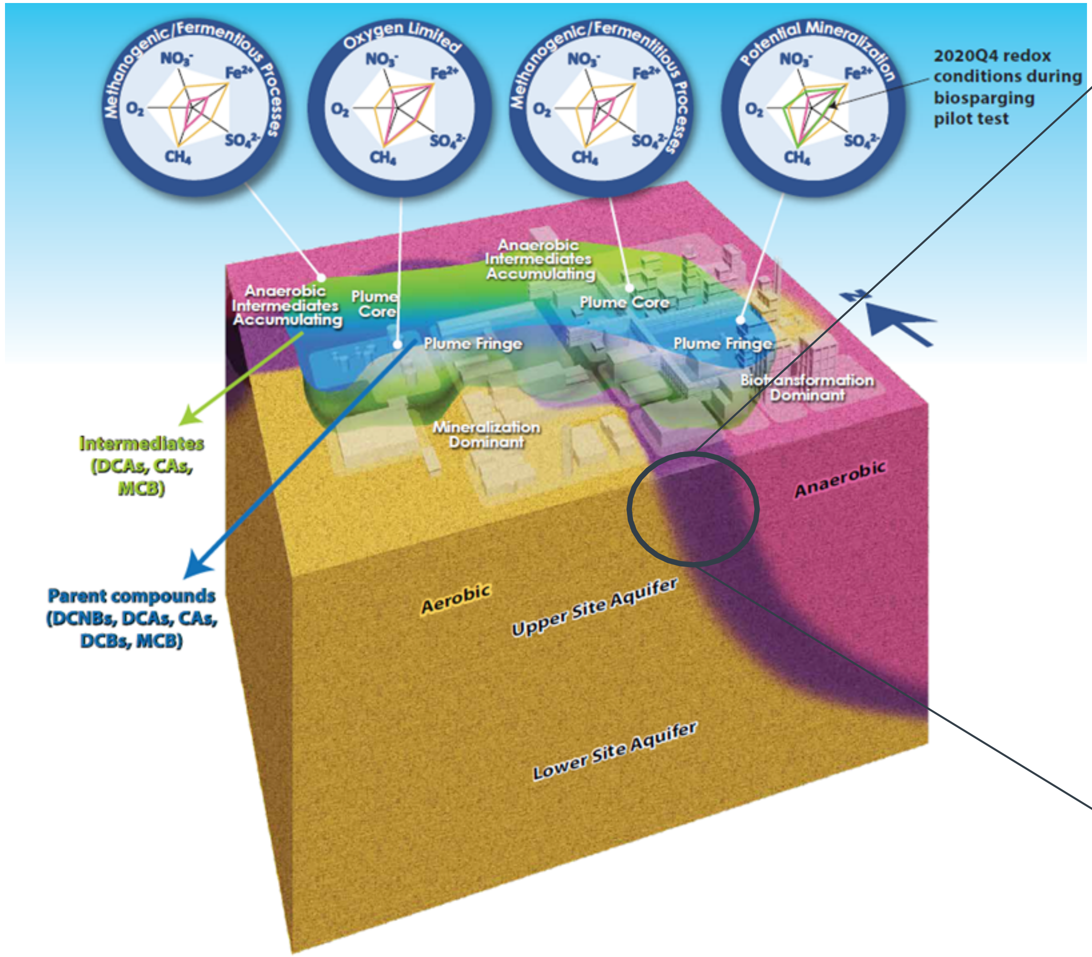
Potential for inverse ^{37}Cl fractionation towards upgradient wells

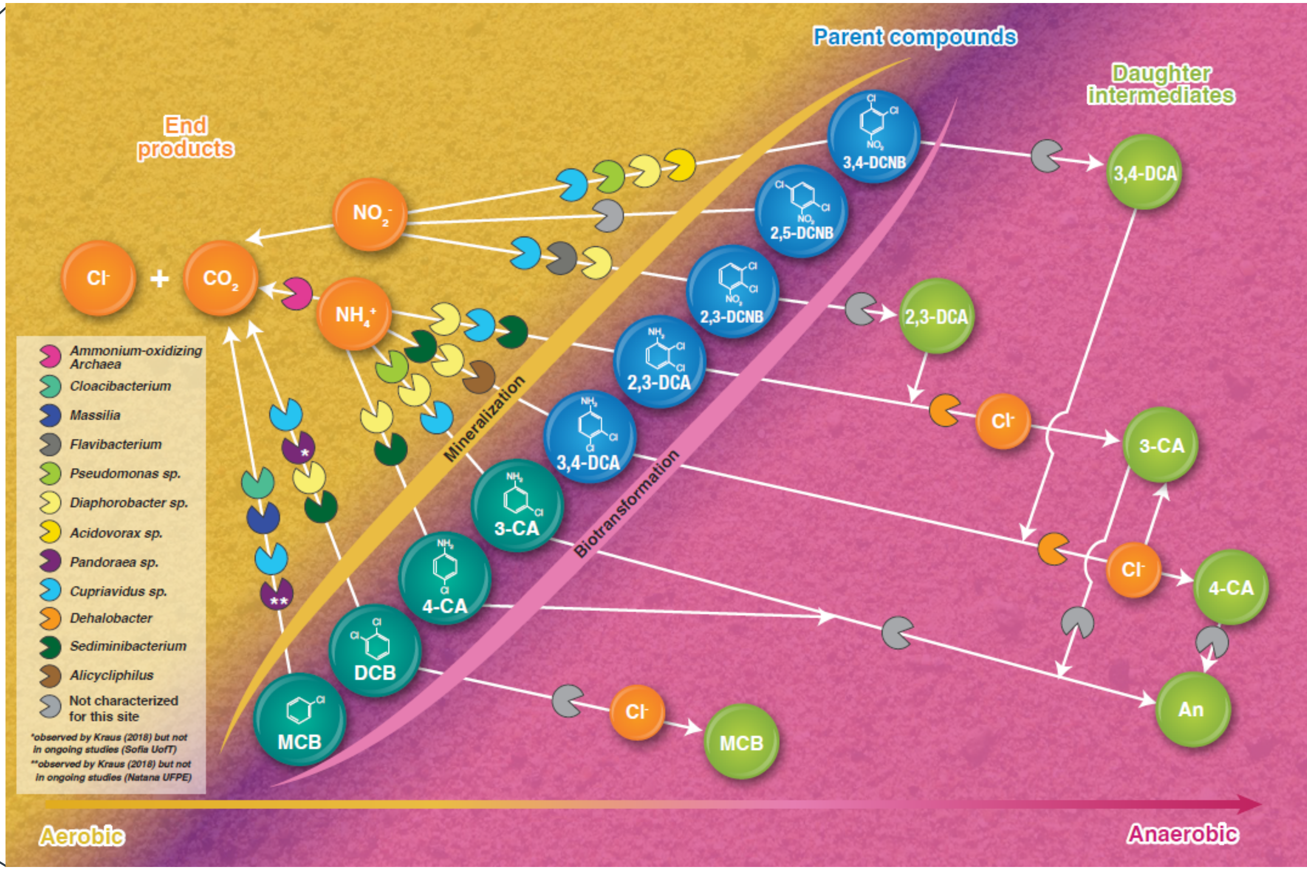
Aquifer Mineralization Capacity

HSU	COI Transformation Product	Average Plume Concentration (µg/l)	Stoichiometric Ratio COI : O_2 (µmol : µmol)	Estimated Mineralization Capacity (%)
Upper Site Aquifer	MCB	3,100	0.14	7%
	3- and 4-CA	14,864	0.15	
Lower Site Aquifer	MCB	2,454	0.14	18%
	3- and 4-CA	6,435	0.15	

Note: 1,2-, 1,3- and 1,4-DCBs and 2,3- and 3,4-DCAs assumed to be anaerobically transformed to their corresponding intermediates (i.e., MCB and 3- and 4-CA) and conservative plume thresholds (Federal Guidelines – Investigation Level) to calculate plume average concentrations using Ricker's approach (Ricker 2008).

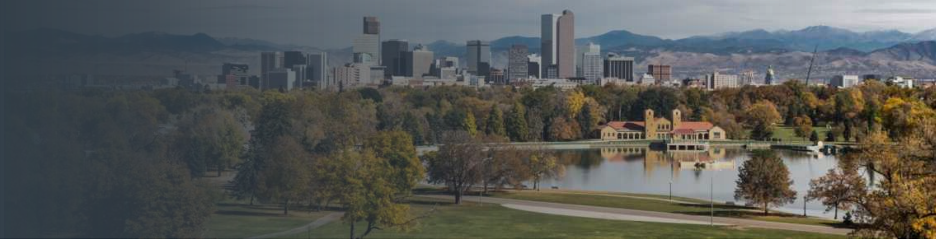
The Biogeochemical Model





The Toolbox – Site Specific Summary

Lines of Evidence	Approach	Findings
LOE 3	Direct evidence of degradation (controlled conditions)	Current site condition: predominantly incomplete biotransformation (i.e., accumulation of intermediates); mineralization under controlled conditions.
LOE 1	Concentration Trends Maps Statistics	Relatively stable temporal trends Inconclusive spatial trends (missing off-site control points) Data consistency for target COIs >2011
LOE 2	Parameter correlation Data variances (PCA) Indirect evidence of degradation (site conditions)	Redox zoning. Mapping terminal electron accepting processes (TEAP) to identify target remedy locations End-products: chloride and nitrate (non-unique reactions) Mineralization capacity



Take away

Biogeochemical models provide valuable insight for:

- Site and remedy selection
- Adapting extant natural attenuation guidance to site-specific compounds

Use of advanced tools / methods can be beneficial to complex sites

- Reverse approach: starting with LOE3

Comprehensive conceptual site model assist on remediation selection, performance monitoring and optimization

Biosparging Pilot

Constructed Wetlands Pilot

Thank you!

Questions?

Contact
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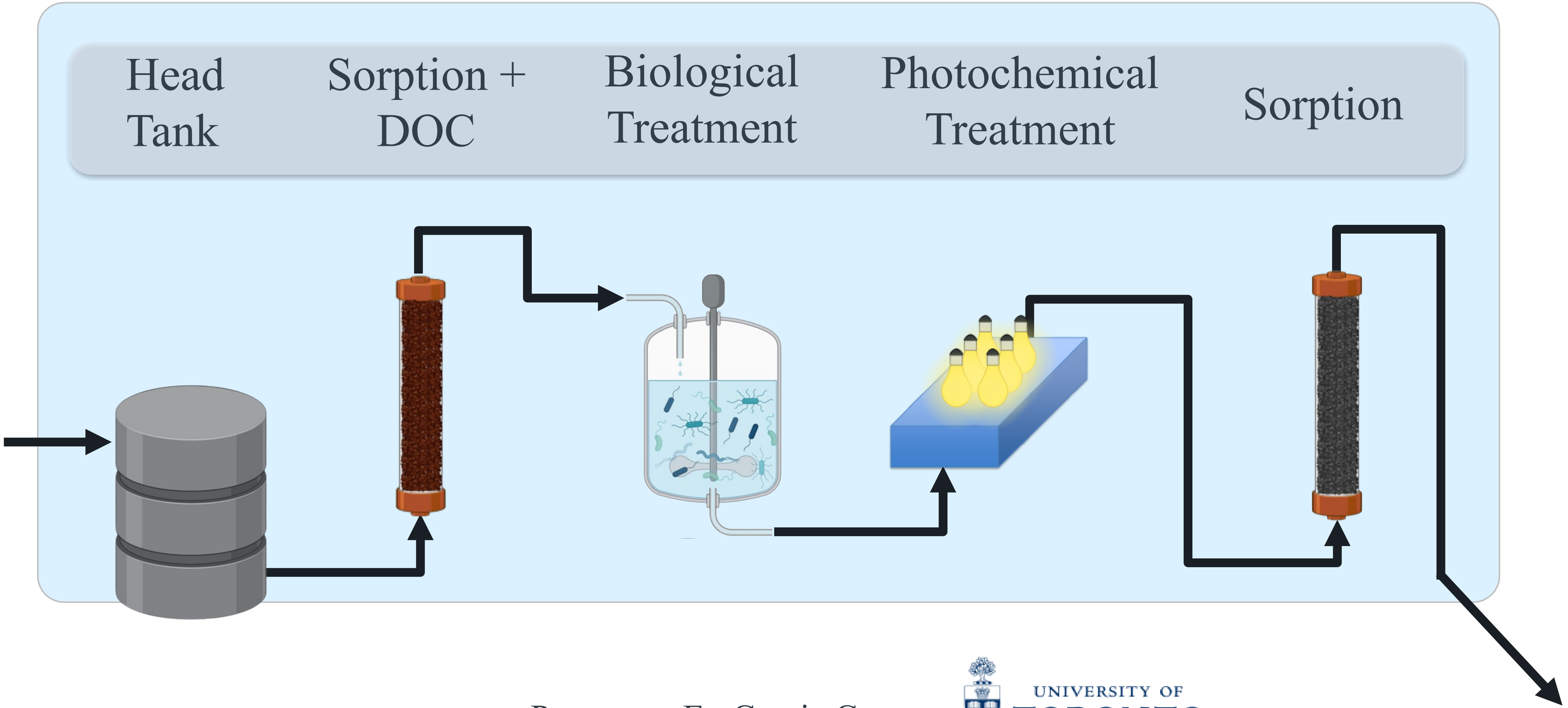
Water treatment system – Working concept



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