CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

Why is the Plume Disappearing Faster than it Should? Mass Loss Investigations at the Orica Botany Site

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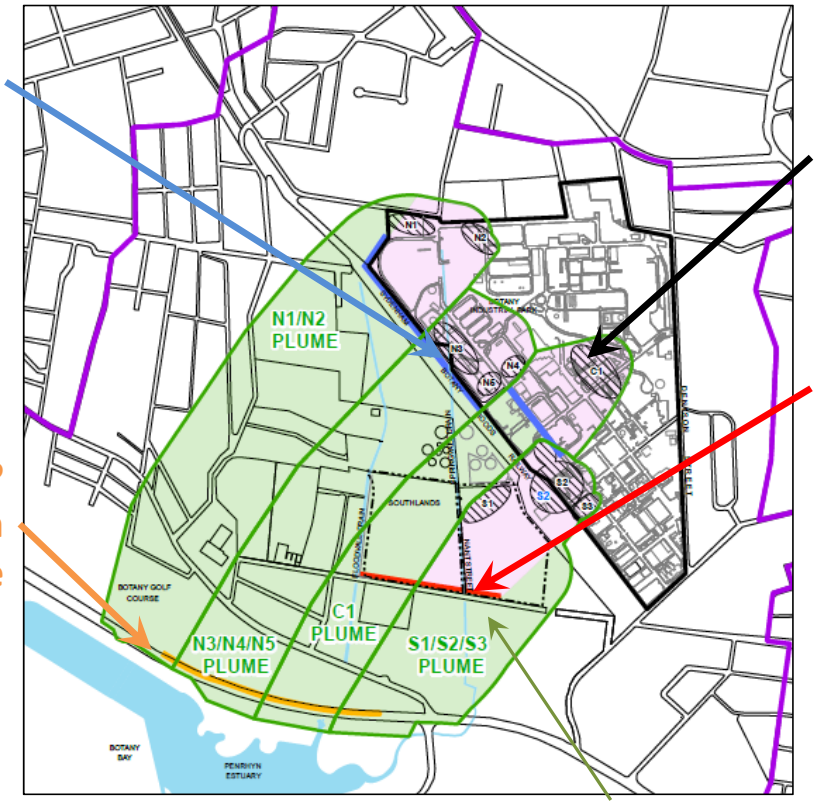
Outline

- The problem and approach
- Bulk attenuation behavior
- Primary and secondary sources of mass
- Biotic and abiotic degradation
- The big picture

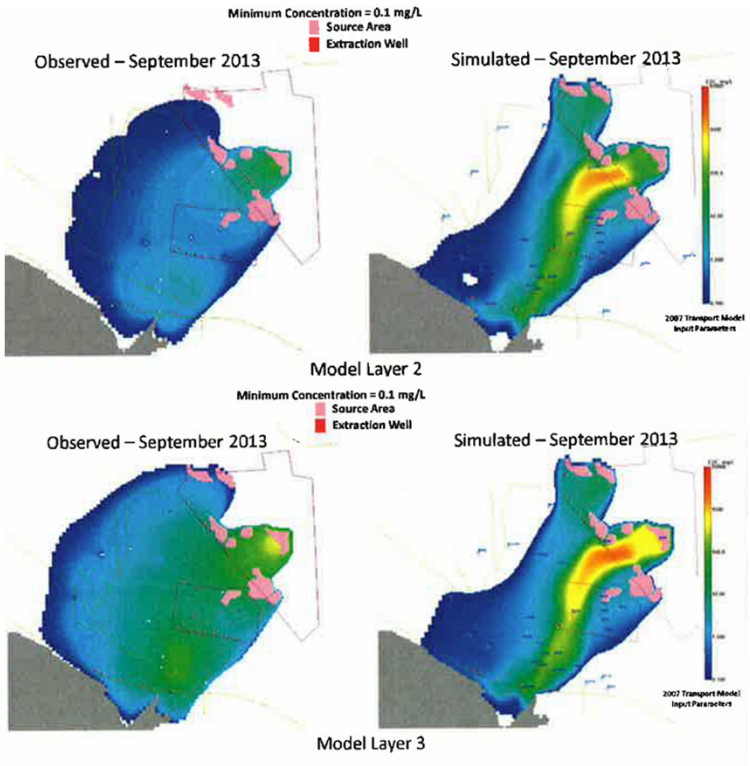
Site Background



- DNAPL sources and large, high concentration plumes
- Multiple chlorinated solvents (EDC, CTC, PCE, TCE, CF, VC…)
- Sand aquifer with many thin peat lenses in aquifer and basal clay layer
- Low pH groundwater
- Groundwater treatment plant (GTP) installed 2006
- P&T since 2004

The Problem

2013 Model Calibration – Laase, 2014

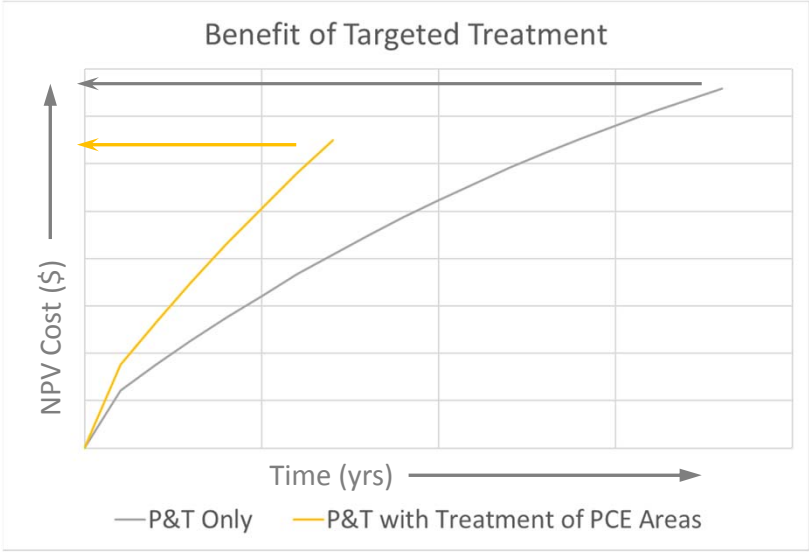


- Contaminant transport model was recalibrated after 10 years of P&T
- Changes in plume simulated by model underpredicted actual changes
- Incorporation of significant attenuation required to calibrate model
  - <180 day biodegradation half-life

Question: Is this behavior real or a model artifact?

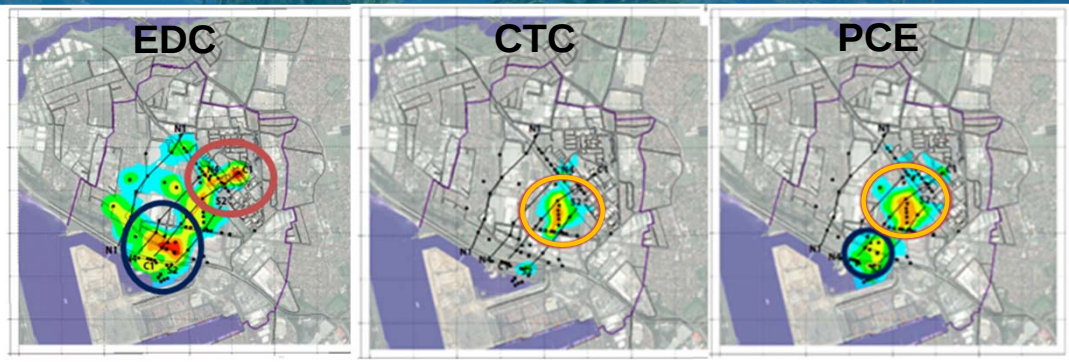
Why is this relevant?

- P&T system costs $10M+ AUD per year to operate, with substantial maintenance requirements upcoming
- Nearly $10M AUD annual cost savings when transition to MNA occurs!
- Understanding attenuation mechanisms can help to develop strategy for reaching this transition point sooner
  - How long will it take for plume to attenuate below aquifer assimilative capacity with P&T?
  - Is it more cost-effective in the long run to spend more money up front to aggressively treat areas of slower bulk attenuation (e.g., PCE sources) and transition to MNA sooner?
  - Is it more cost effective to transition from P&T to alternative forms of containing the southern plume sources?



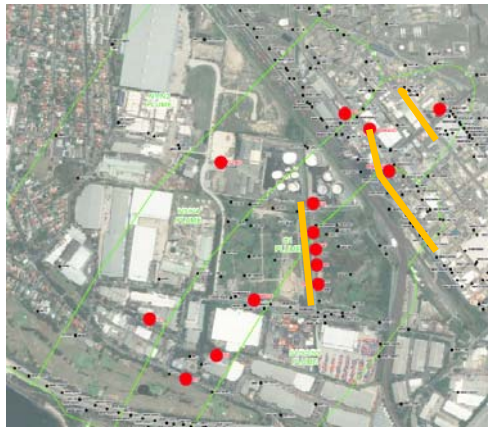
Multiple Lines of Evidence Approach

- Identify locations in plumes and sources where attenuation behavior may differ
- Focus data collection in these areas to assess sorption, diffusion, and abiotic/biotic degradation
- Lines of evidence include:
  - Historical plume statistics
  - Treatability studies - biotic/abiotic degradation
  - Soil detailed profiling - sorption/diffusion
  - Microbial assays - assess potential for inhibition, bioactivity levels
  - CSIA - investigate biotic/abiotic pathways and rates
  - Geochemistry – MNA indicators
  - Source zone mass flux transects – source decay rates (future projections)



Treatability, microbial assays, soil profiling

CSIA, source transects



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Bulk Attenuation Behavior

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Mass Attenuation Mechanisms

- Dissolved mass in equilibrium with source material → indirectly reflects source persistence

Bulk attenuation of dissolved phase $= \sum$ Dissolved mass sinks – dissolved mass sources

- Sink = sorption, diffusion, degradation, volatilization, extraction
- Source = desorption, back-diffusion, DNAPL dissolution

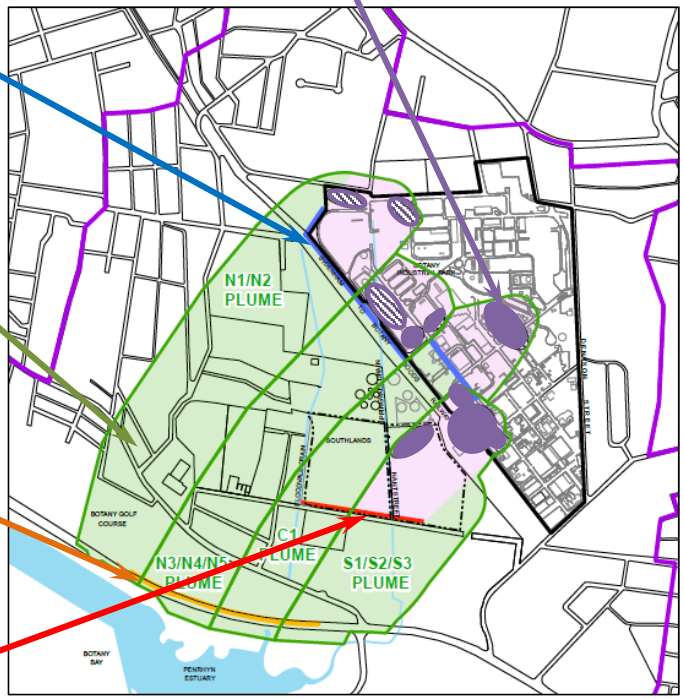
DNAPL SOURCES AND PLUMES:
DNAPL dissolution, sorption/desorption, diffusion/back-diffusion, degradation

GTP:
Dissolved phase extraction

PLUMES:
Sorption/desorption, degradation, diffusion/ back-diffusion

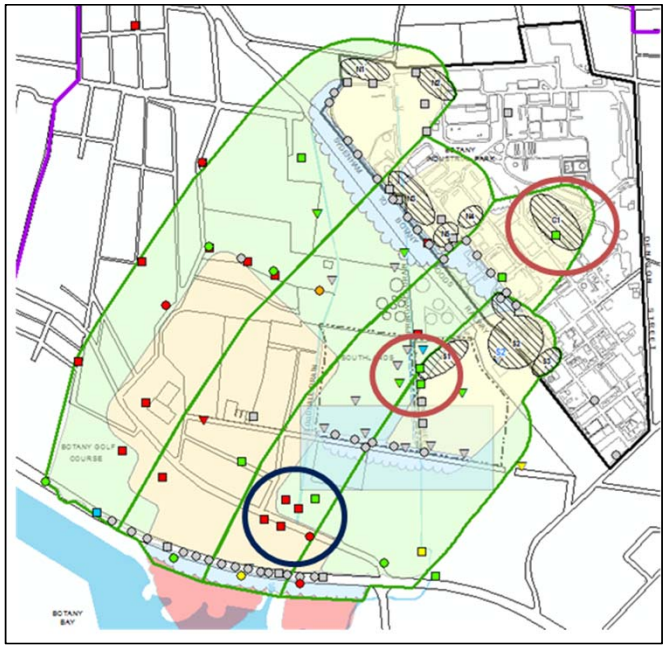
GTP:
Dissolved phase extraction

GTP:
Dissolved phase extraction



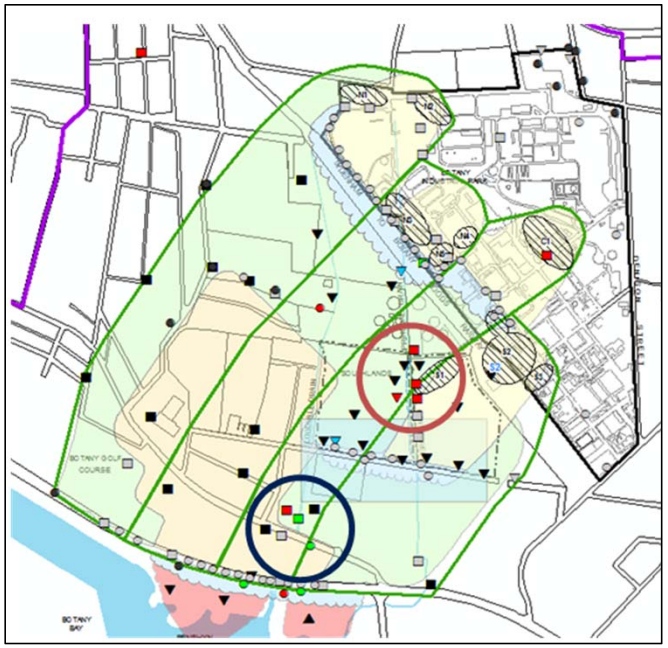
Variability in Bulk Attenuation Behavior

EDC



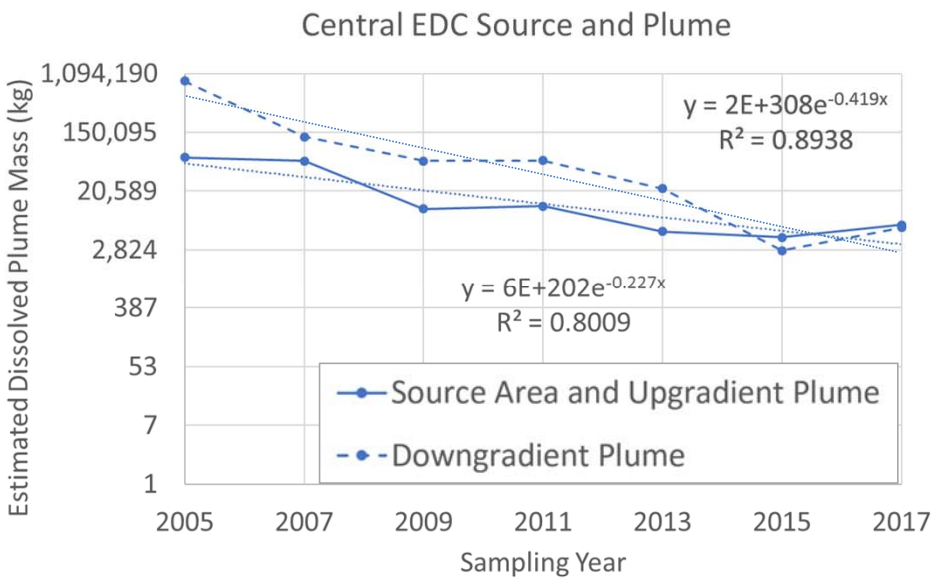
EDC DNAPL attenuating, plume toe persisting

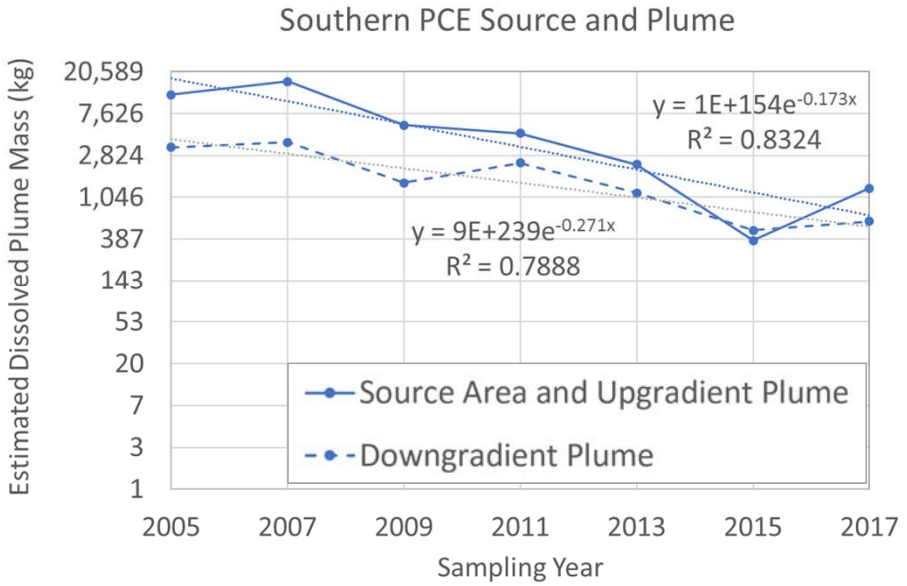
PCE



PCE DNAPL and plume toe persisting

Dissolved Mass Bulk Attenuation and Source Decay Rates





	EDC in Central Source and Plume Half-Life (yrs)	PCE in Southern Sources and Plumes Half-Life (yrs)
Source(s) and Upgradient Plume(s)	1.9 < 3.0 < 7.1	1.6 < 2.6 < 6.3
Downgradient Plume(s)	1.2 < 1.7 < 2.7	2.6 < 4.0 < 8.3

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Primary and Secondary Sources of Mass

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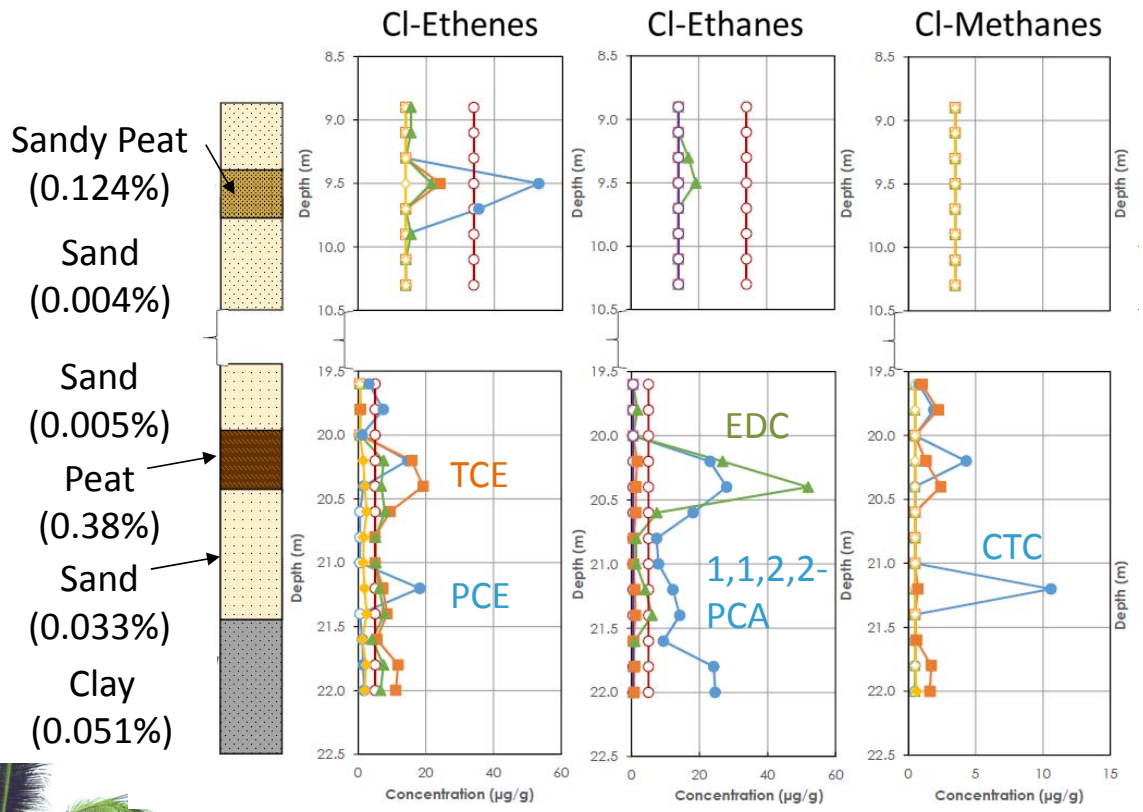
Sorption and Back-Diffusion as Secondary Sources

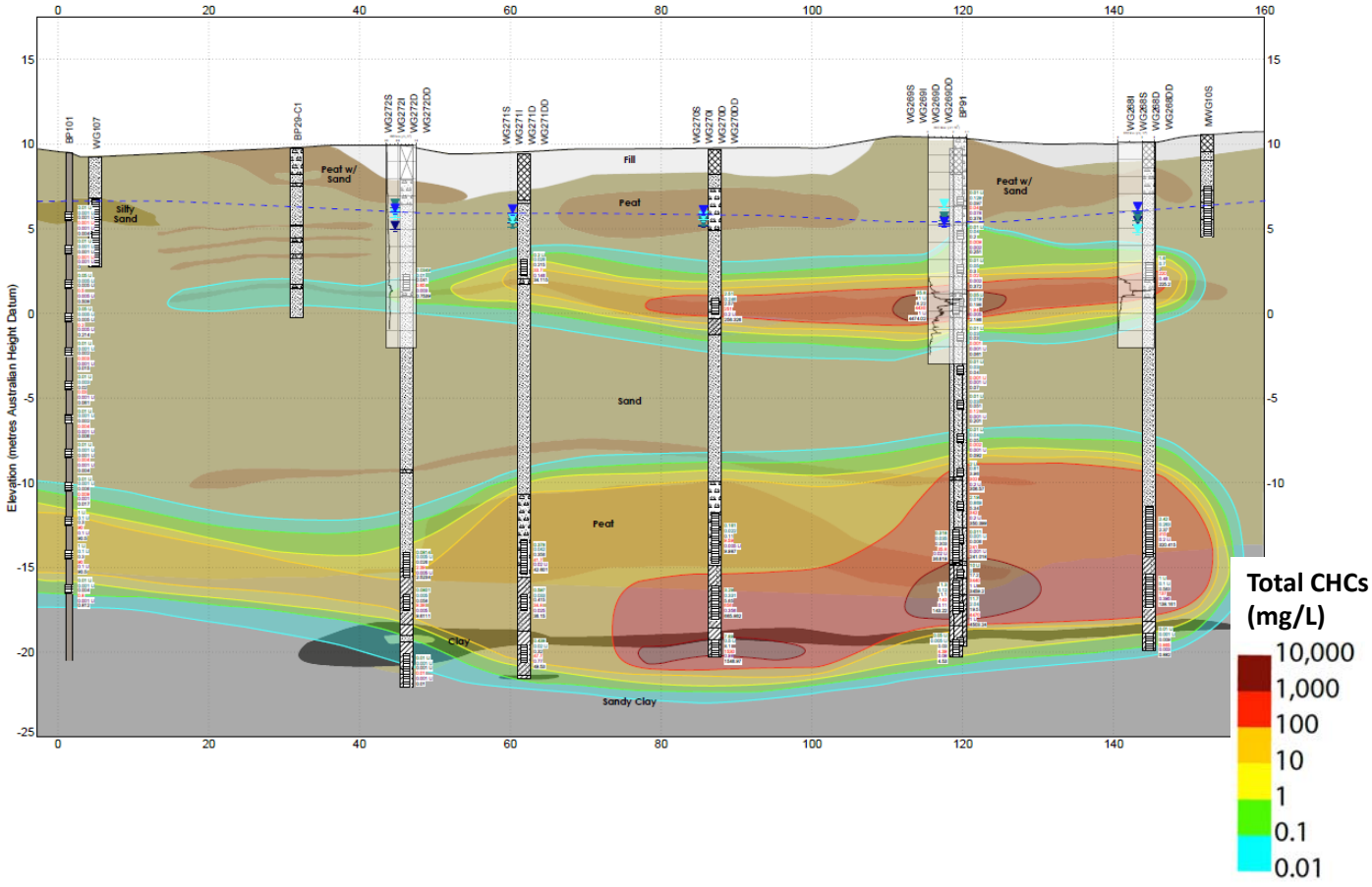


Micro-Profiling of Soil Cores:

- Mass diffused into clay acting as secondary source
- Peat is secondary source (desorption) in some areas, may be bioactive zones in others
- Creating "halos" around peat and clay layers
- Similar behavior observed in:
  - central source area
  - southern source area
  - downgradient plumes

Mass Discharge from DNAPL Sources

- Transects installed downgradient of DNAPL sources
- Again seeing “halo” around peat/clay
- Mass discharge calculated every two years
- Decay of mass discharge from DNAPL sources monitored to assess DNAPL lifespan



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Biotic and Abiotic Degradation

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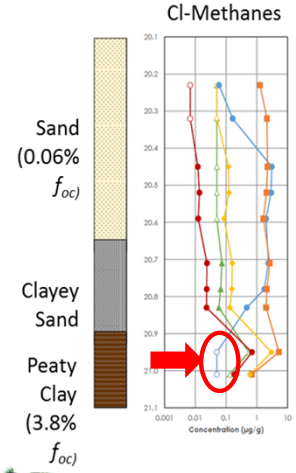
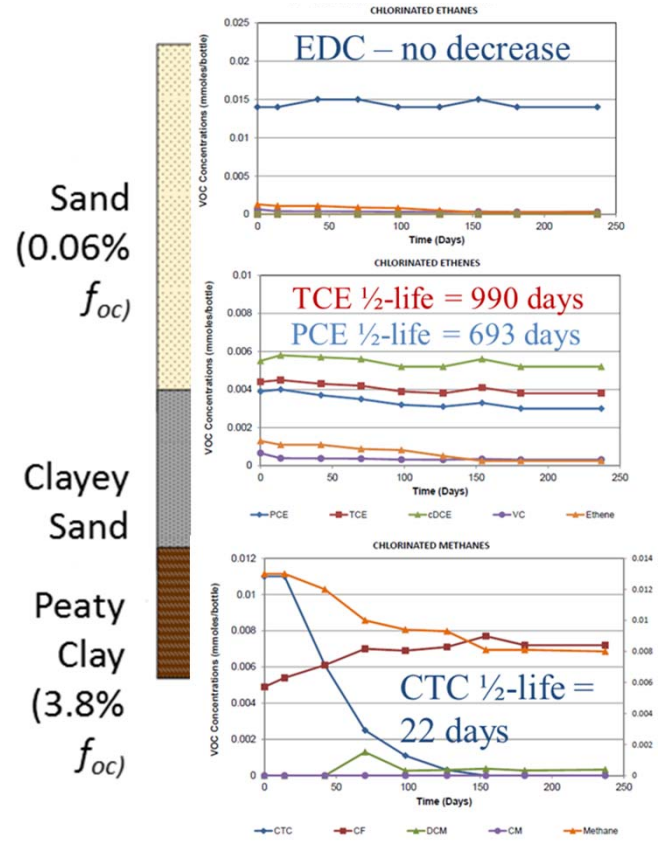
Treatability Studies – Attenuation Pathway Assessment and Quantifying Degradation Using Stable Carbon Isotopes

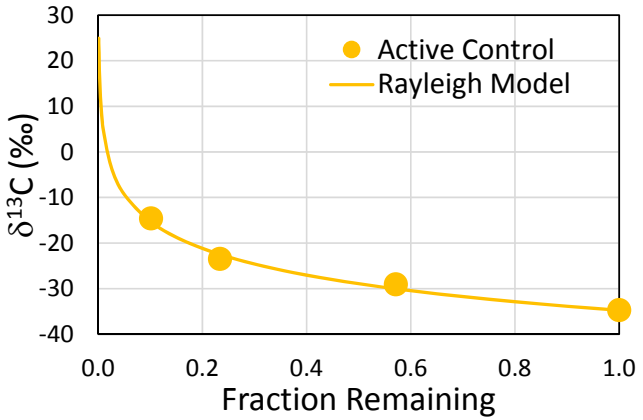
CTC in 2015



Active Control [CHC] Trends

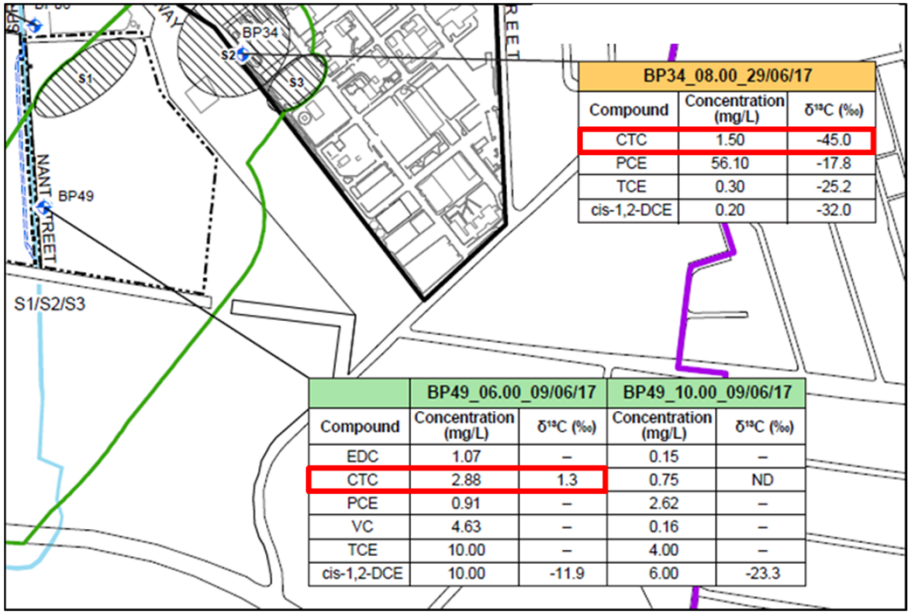


CTC ^{13}C



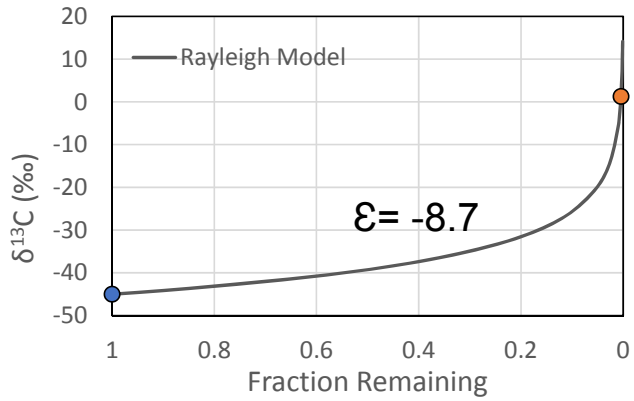
- No abiotic degradation
- Rapid biodegradation of CTC in peat, others slow
- Isotope characterization used to estimate Ɛ = -8.7

Identifying Dominant Bulk Attenuation Processes - CTC



BP34_08.00_29/06/17		
Compound	Concentration (mg/L)	δ¹³C (‰)
CTC	1.50	-45.0
PCE	56.10	-17.8
TCE	0.30	-25.2
cis-1,2-DCE	0.20	-32.0

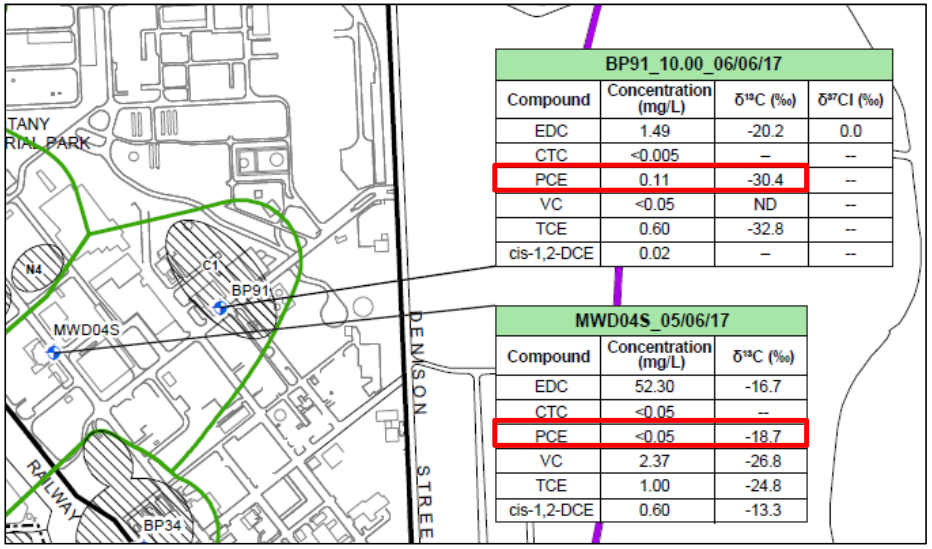
	BP49_06.00_09/06/17		BP49_10.00_09/06/17	
Compound	Concentration (mg/L)	δ¹³C (‰)	Concentration (mg/L)	δ¹³C (‰)
EDC	1.07	–	0.15	–
CTC	2.88	1.3	0.75	ND
PCE	0.91	–	2.62	–
VC	4.63	–	0.16	–
TCE	10.00	–	4.00	–
cis-1,2-DCE	10.00	-11.9	6.00	-23.3



	Rate (k)	Half-Life
Isotope-Derived Degradation	1.73 yr^{-1}	0.40 yr
Spatial Concentration-Derived Bulk Attenuation	N/A	N/A
Temporal Concentration-Derived Bulk Attenuation	1.24 yr^{-1}	0.56 yr

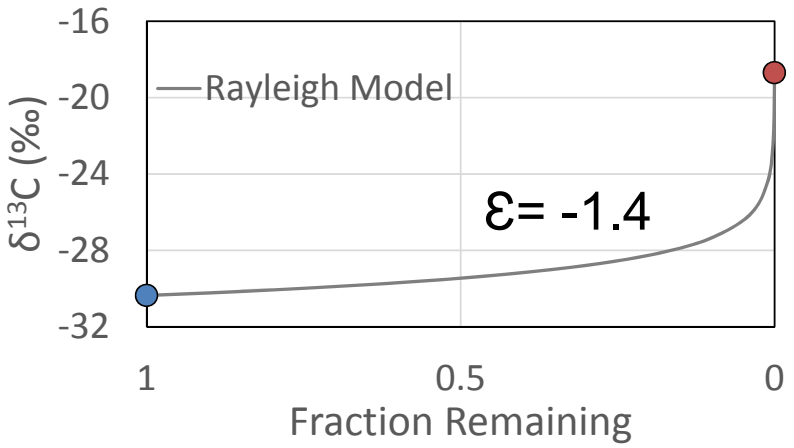
- Significant fractionation between source and downgradient well despite an increase in [CTC]
- Similarity between bulk attenuation rate at BP49 and isotope-derived rate supports biodegradation as dominant bulk attenuation process

Identifying Dominant Bulk Attenuation Processes - PCE



BP91_10.00_06/06/17			
Compound	Concentration (mg/L)	$\delta^{13}C$ (‰)	$\delta^{37}Cl$ (‰)
EDC	1.49	-20.2	0.0
CTC	<0.005	--	--
PCE	0.11	-30.4	--
VC	<0.05	ND	--
TCE	0.60	-32.8	--
cis-1,2-DCE	0.02	--	--

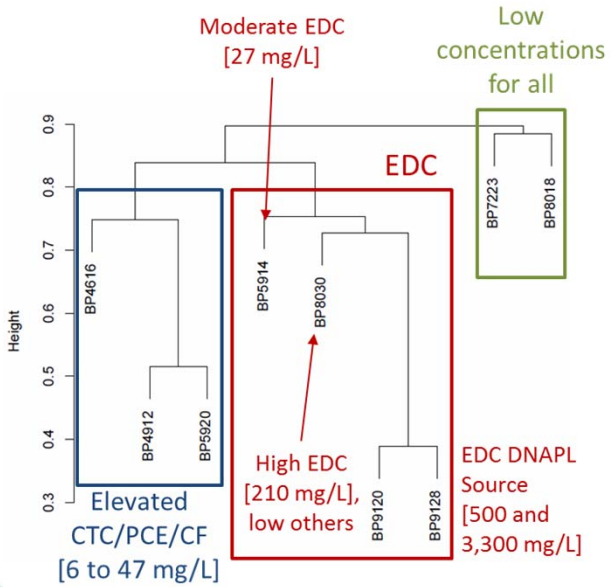
MWD04S_05/06/17		
Compound	Concentration (mg/L)	$\delta^{13}C$ (‰)
EDC	52.30	-16.7
CTC	<0.05	--
PCE	<0.05	-18.7
VC	2.37	-26.8
TCE	1.00	-24.8
cis-1,2-DCE	0.60	-13.3

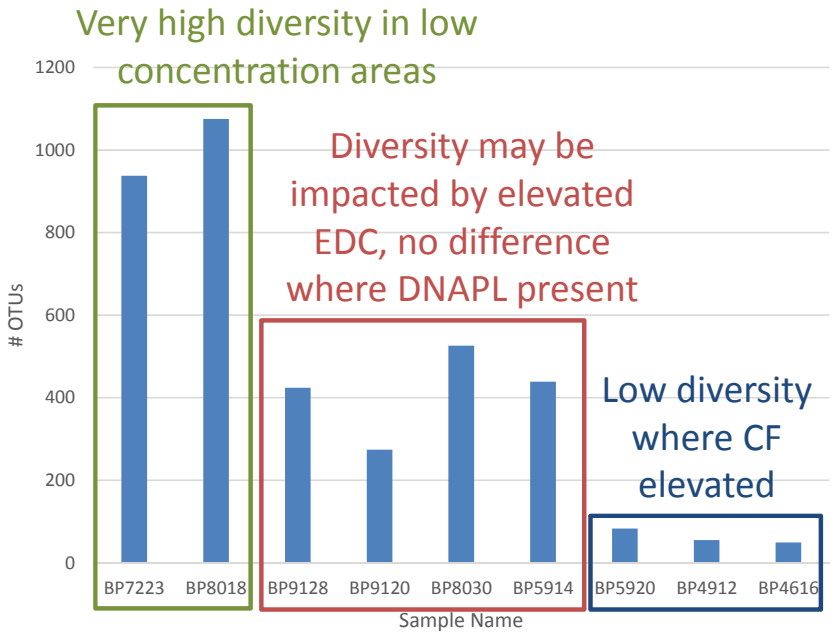


	Rate (k)	Half-Life
Isotope-Derived Degradation	4.36 yr^{-1}	0.15 yr
Spatial Concentration-Derived Bulk Attenuation	0.40 yr^{-1}	1.7 yr
Temporal Concentration-Derived Bulk Attenuation	0.49 yr^{-1}	1.4 yr

- Isotope-derived degradation rate more rapid than bulk attenuation
- Difference between bulk attenuation rate and isotope-derived rate suggests effect of biodegradation is dominated by desorption

Investigating Inhibitory Factors with Next Generation Sequencing





Typically 100s of OTUs at most sites

- Fairly low biomass across the site
- Common dechlorinators inhibited in CTC/CF source areas
- *Dehalococcoides* and *Geobacter* dominant for low [EDC] areas
- Community shifts to sulphate reducers at higher [EDC]

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The Big Picture

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Tying it all Together

- DNAPL sources persist but concentrations are decaying over time and mass flux is in thin layers above peat/clay lenses where pools remain
- Plume concentrations (except CTC) are becoming more dominated by desorption and back-diffusion from peat and clay layers
- Areas of slower bulk attenuation correlate to DNAPL sources and locations/depths with higher peat/clay content
- PCE will drive the long-term plume persistence
- Biological attenuation is variable and complex, and likely changing over time as inhibitory concentrations reduce

Wrap-Up

Acknowledgements:

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  - Al Laase

Questions?

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