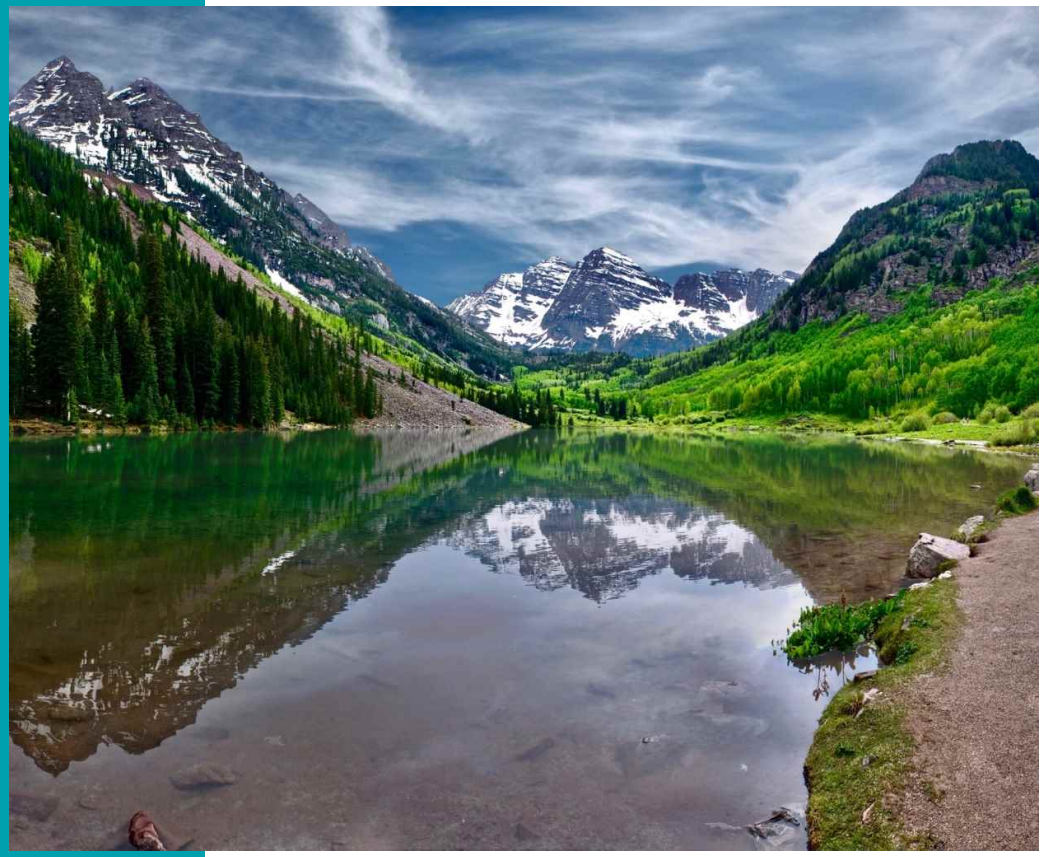
Geosyntec consultants

CREATIVE THINKING
EXCEPTIONAL SOLUTIONS



Advancements in Remedial Performance Assessment at Complex Sites Incorporating Advanced Data Analytics and Innovative Characterization Tools

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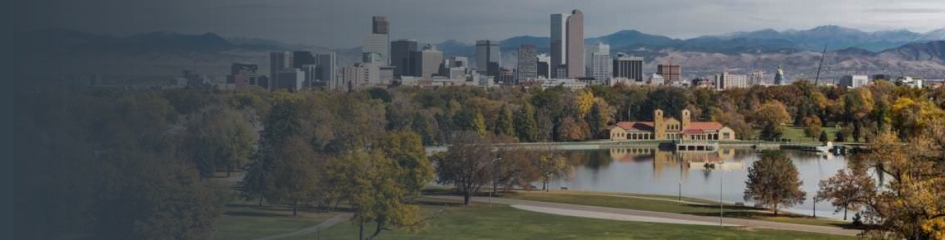
Site Background

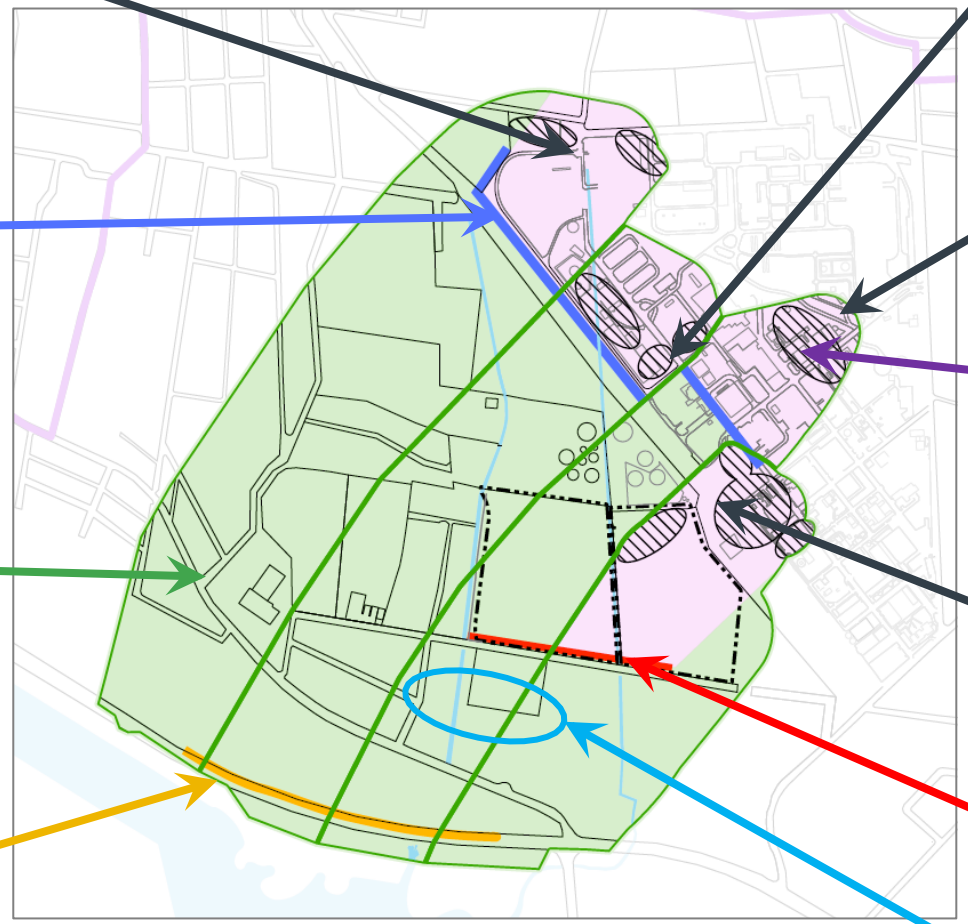


N1/N2 SOURCES
Primarily EDC, likely residual sorbed source

ACTIVE EXTRACTION
1st Pump-and-treat containment line

PLUMES
Dissolved mass of varying chemistries, sorption/desorption, diffusion/back-diffusion, biodegradation

ACTIVE EXTRACTION
3rd containment line



N3/N4/N5 SOURCES
N3 – Primarily EDC, may be sorbed source
N4 – CTC/PCE DNAPL, some EDC
N5 – Primarily EDC

C1 SOURCE
>99% EDC DNAPL, trace others

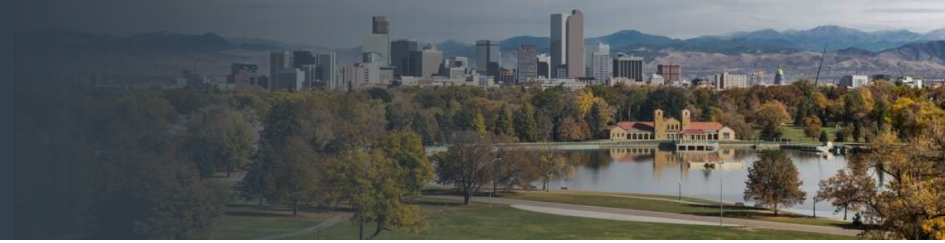
SOURCE AREAS
DNAPL dissolution, desorption, back-diffusion, biodegradation

S1/S2/S3 SOURCES
S1 – CTC and PCE, heavy ends
S2 – CTC and PCE
S3 – TCE and CTC

ACTIVE EXTRACTION
2nd Pump-and-treat containment line

STAGNANT ZONE

Remediation Timeline



1942
Industrial operations and chemical manufacturing began on site

1960s
Larger manufacturing plants were introduced on site making a wider range of chemicals

1970s and 1980-1981
Groundwater contamination was first identified during site development works

1989 through 1990s
Groundwater investigations began and continued through the 1990s

1993-1996
DNAPL sources first identified, and investigations continued through 2000

1999
Zero-valent iron permeable reactive barrier trial completed

2003-2004
Bioremediation trials completed

2005-Present
Construction of the pump-and-treat system (GTP) began in 2005 and operations began in 2006

2006
Total CHCs recovered from groundwater and treated reached 200 tonnes

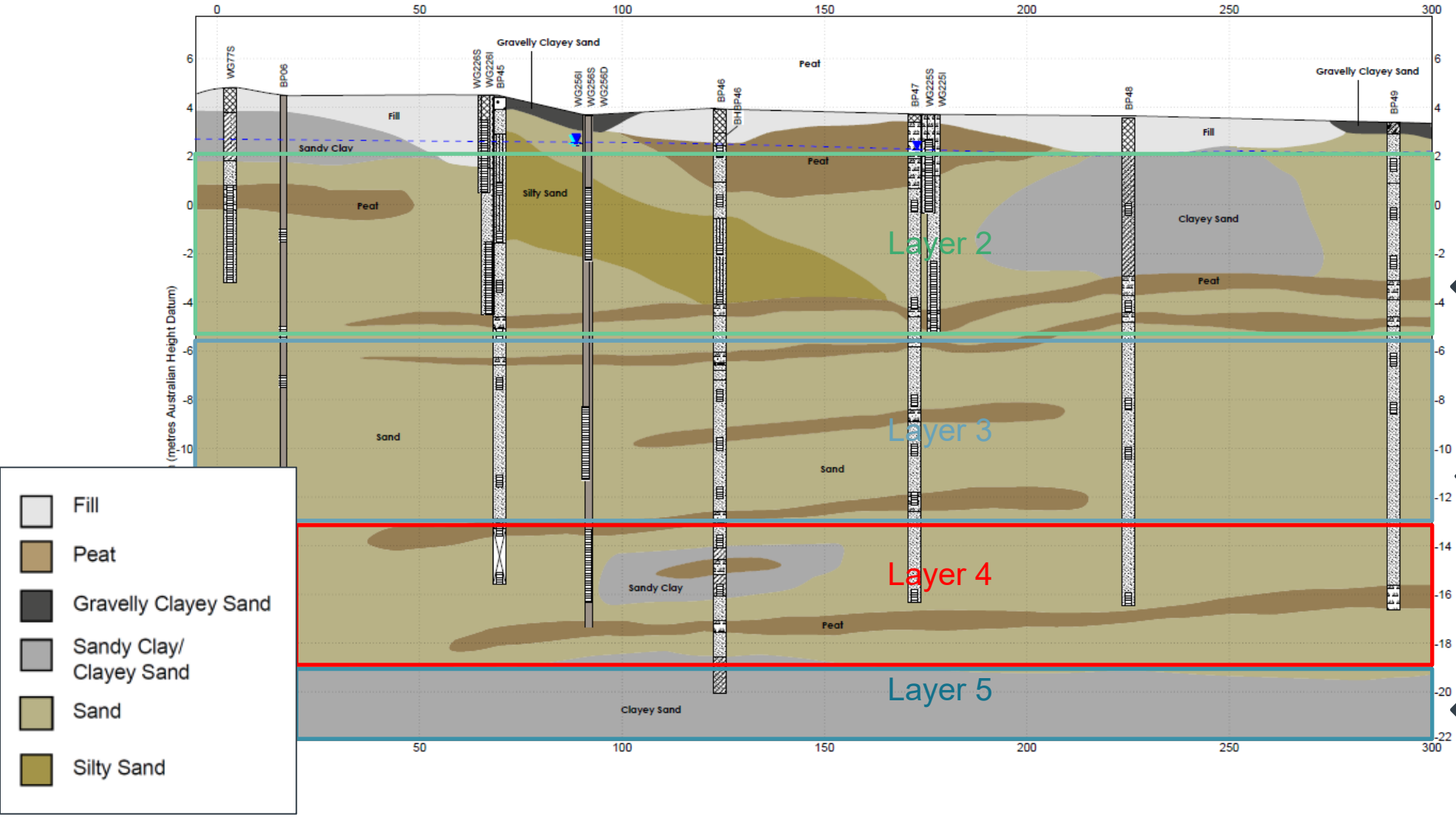
2007
Numerical modeling of GTP performance completed and results indicated GTP may need to operate for >100 years

2014
Updated modeling indicates plumes are disappearing faster than predicted in 2007

2016-Present
Attenuation studies began and continue to present day

2023
GTP has removed ~1,500 tonnes of CHCs

Geological Environment

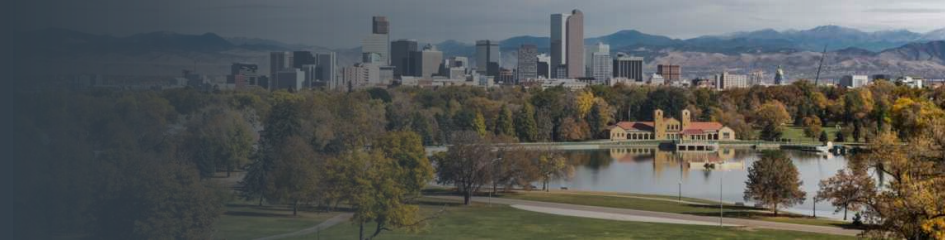


High organic content = sorption/desorption, Low K = confining layers

Transmissive layers, becoming less transmissive with depth

Low permeability = diffusion/back-diffusion, low transmissivity

Contaminant Physical Properties



Constituent	Single-Component Solubility (mg/L)	Octanol-Water Partition Coefficient (log K_{ow}; mL/g)	Henry's Constant (atm-m^3/mole)
1,1,2,2-TeCA	2,900	2.39	3.67e-04
1,1,2-TCA	4,590	1.89	8.24e-04
EDC (1,2-DCA)	8,600	1.48	11.8e-04
TCE	1,280	2.61	98.5e-04
PCE	206	3.40	177e-04
VC	2,700	1.46	278e-04
CTC	793	2.83	276e-04
CF	7,950	1.97	36.7e-04

Legend:	
	DNAPLs dissolve readily, lower retardation (lower sorption/desorption), volatilize readily
	DNAPLs dissolve slower, moderately sorbs/desorbs, moderate volatility
	DNAPLs dissolve slowly, significant retardation/desorption, low volatility

Problem Statement

Large, expensive pump-and-treat system currently operating.

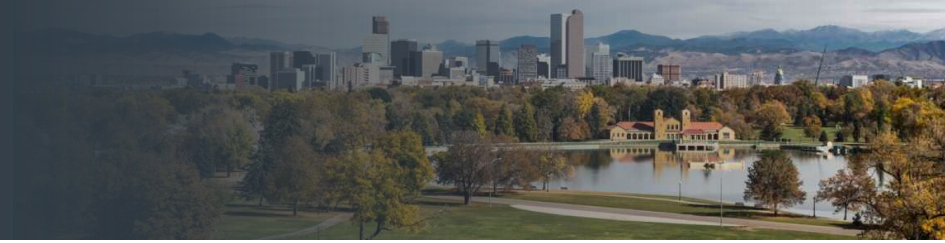
Multiple DNAPL sources still exist on site.

Questions:

- How long will the DNAPL sources persist for?
- How long will the pump-and-treat system have to operate for?
- When can it reasonably be turned off or ramped down while still managing receptor exposure risk?
- What is driving persistence of concentrations in the plume, and is there anything we can do to accelerate attenuation?

Picture from: Botany Groundwater Cleanup Project - Orica

Lines of Evidence Investigated



Initial evaluation included:

- Evaluating the contributions from secondary sources
- Assessing natural attenuation rates and mechanisms
- Conducting mass balances to assess impact of pump-and-treat on dissolved phase mass

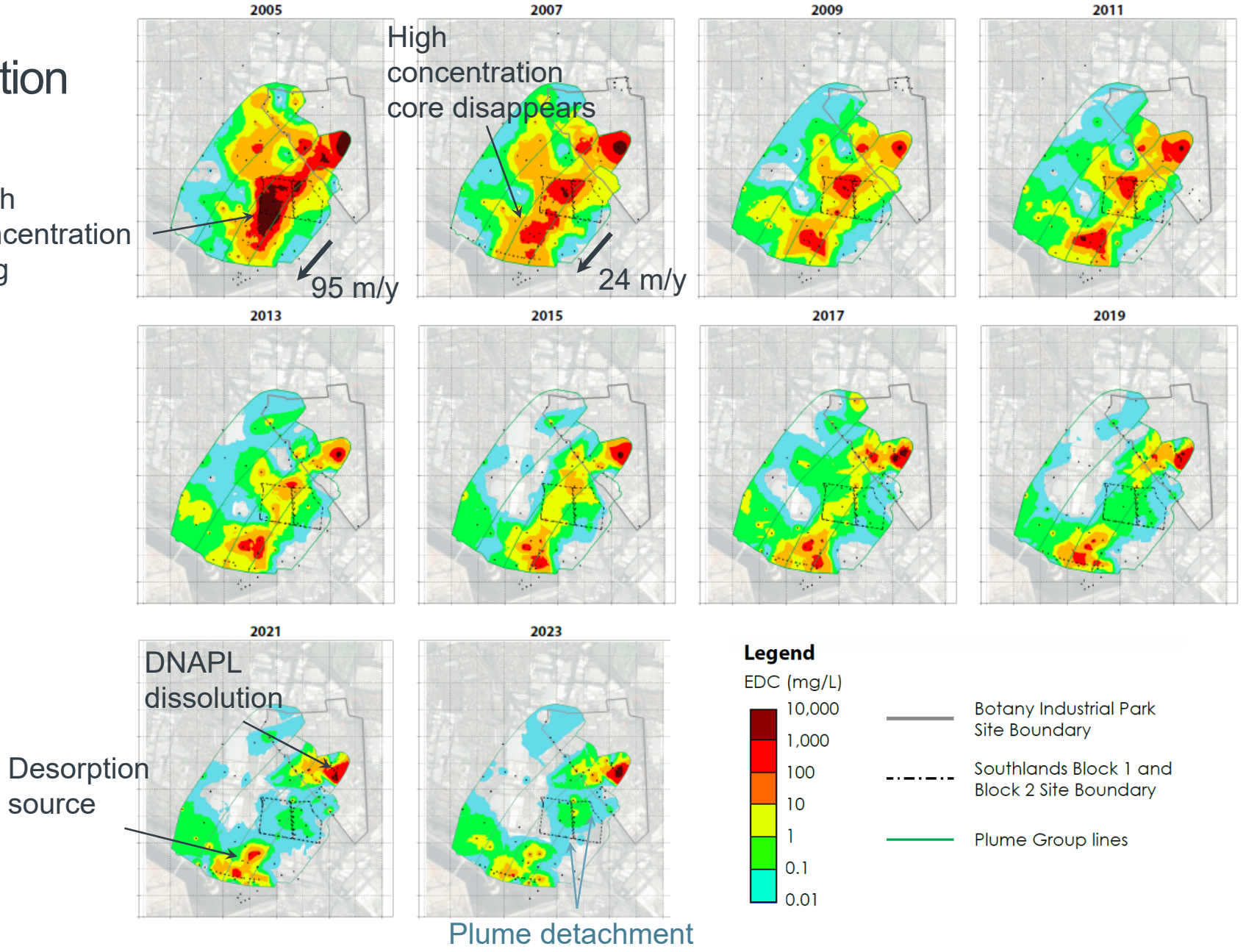
Ongoing assessments (updated every 1-2 years) include:

- Reassessing changes in natural attenuation rates and mechanisms
- Updated assessments of plume attenuation and source mass discharge rates
- Updating mass balances monitoring impact of pump-and-treat system on dissolved phase mass

EDC (1,2-DCA) Plume Evolution

Maximum concentrations at any depth plotted.

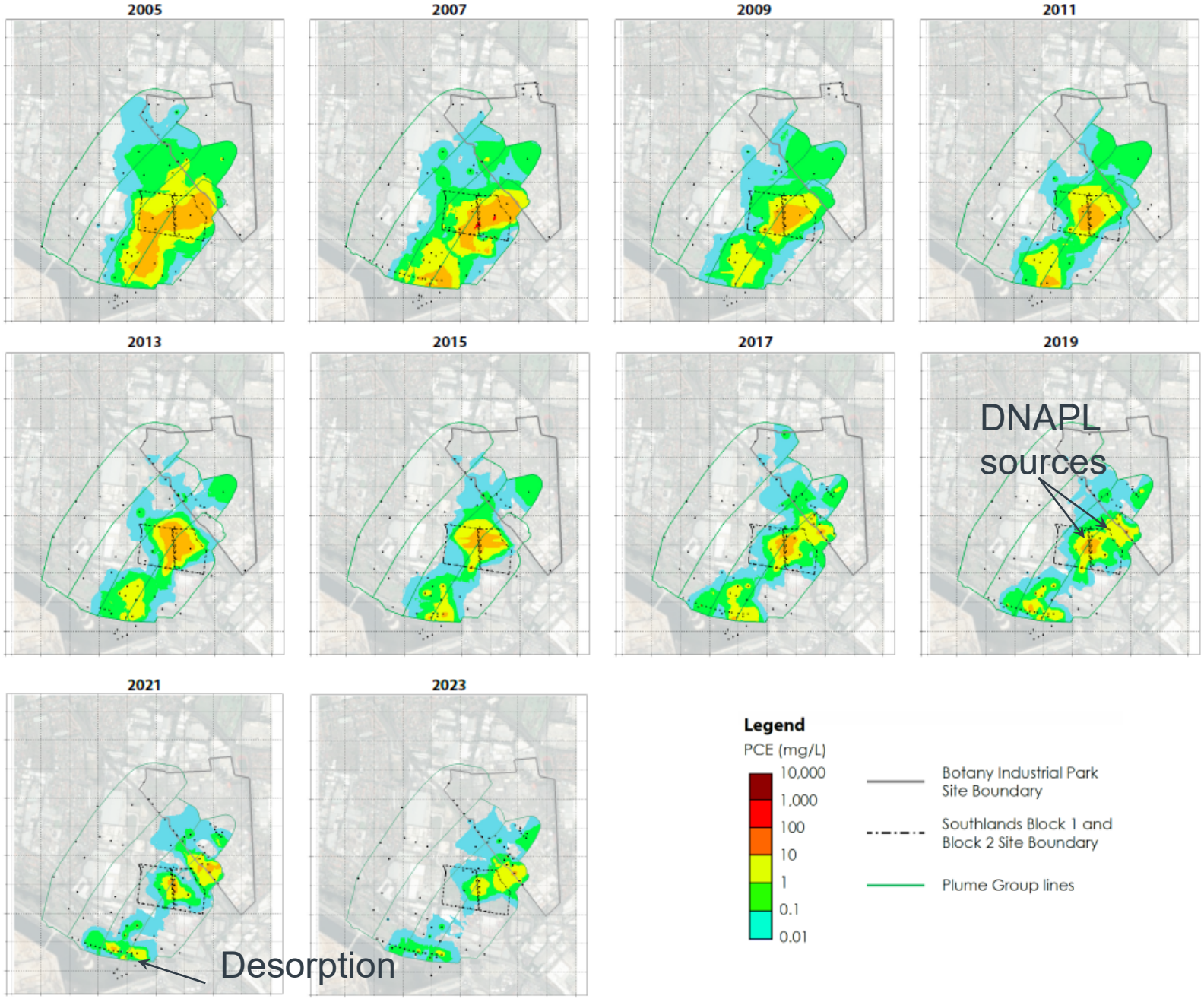
Full-scale GTP operation begins 2006. After 18 years of GTP operation, ~70% of initial mass has been extracted and recovered.



PCE Plume Evolution

After 18 years of GTP operation, <2% of the estimated initial mass of PCE has been extracted and recovered.

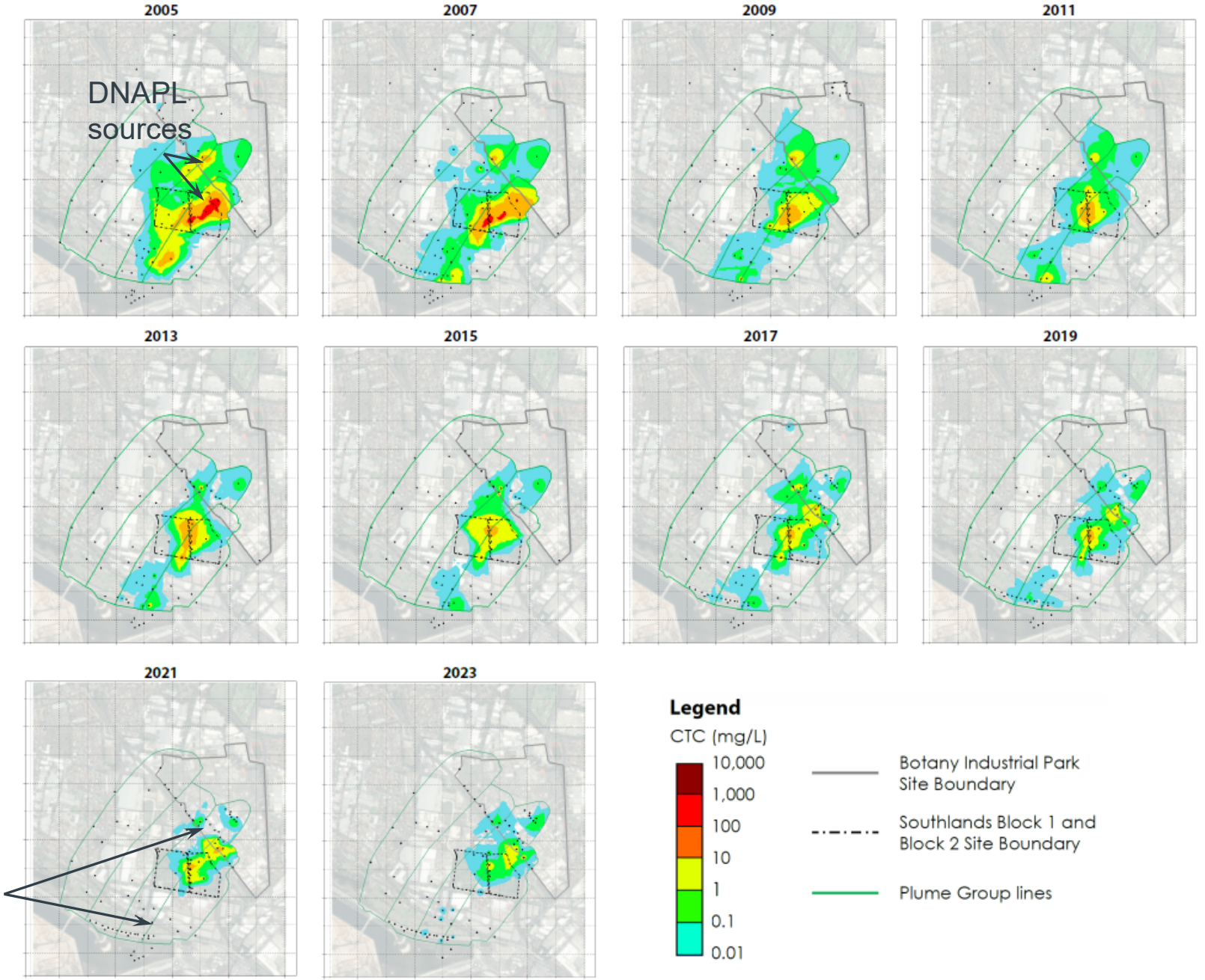
Over the past 18 years of GTP operation, substantial attenuation of the PCE plume has been observed.



CTC Plume Evolution

After 18 years of GTP operation, <3% of the estimated initial mass of CTC has been extracted and recovered.

CTC is disappearing faster than other CHCs – rapidly biodegrading in some areas, abiotically degrading in others.

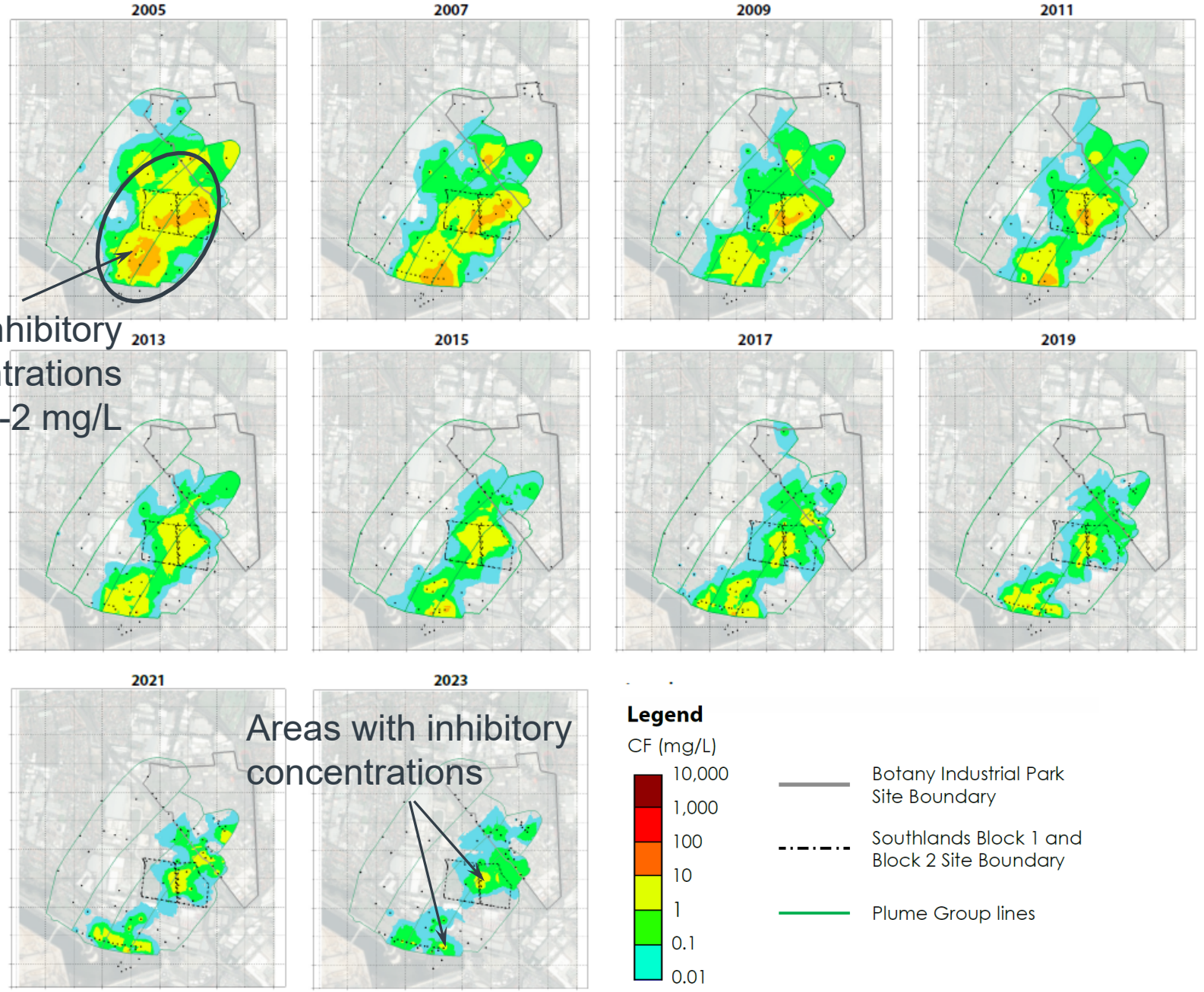


CF Plume Evolution

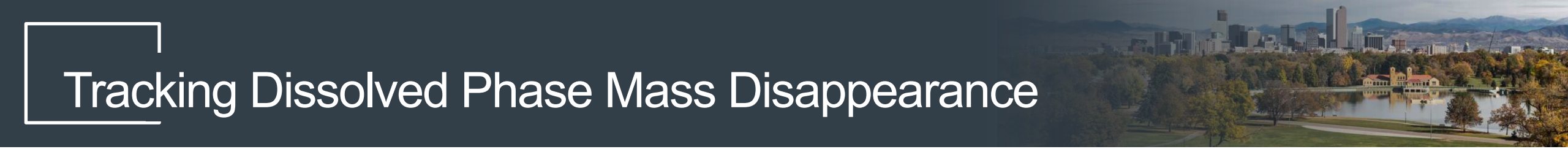
After 18 years of GTP operation, ~1,000% of the estimated initial mass of CF has been extracted and recovered.

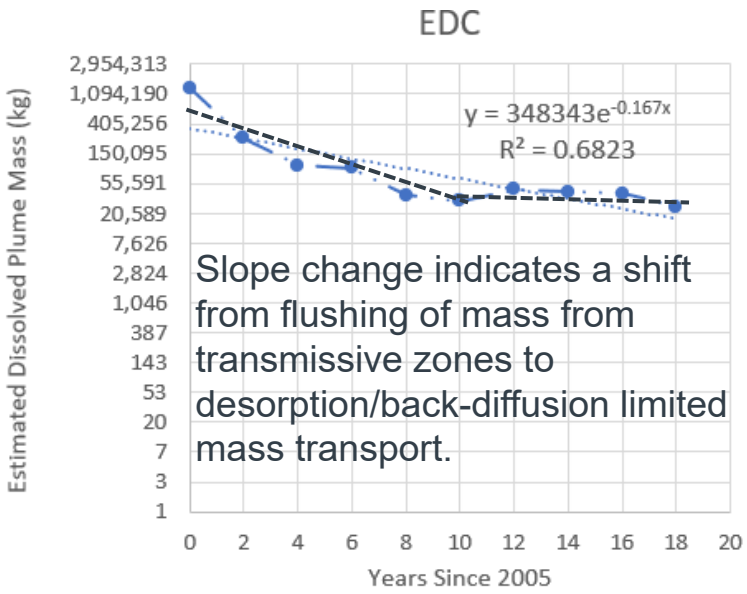
CF distribution mirrors CTC but is more persistent than CTC.

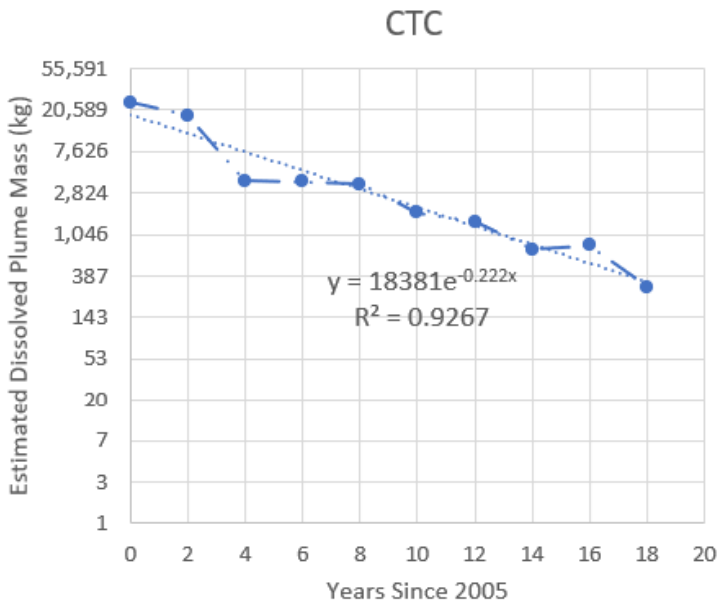
Extent of plume with CF concentrations exceeding inhibitory levels is now much smaller.

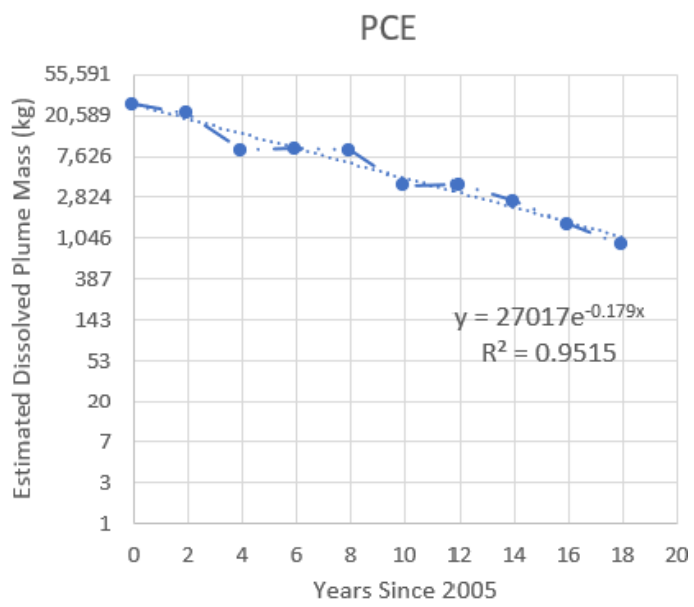


Tracking Dissolved Phase Mass Disappearance



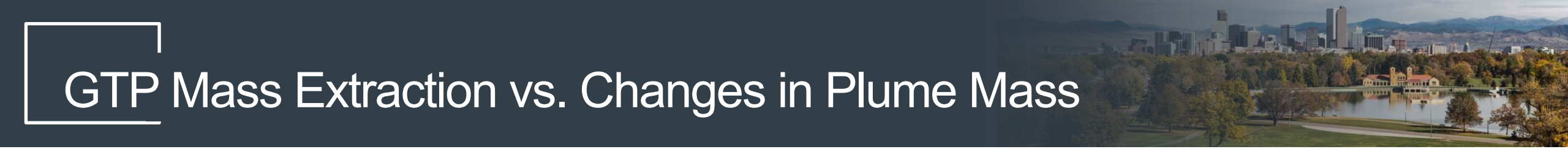


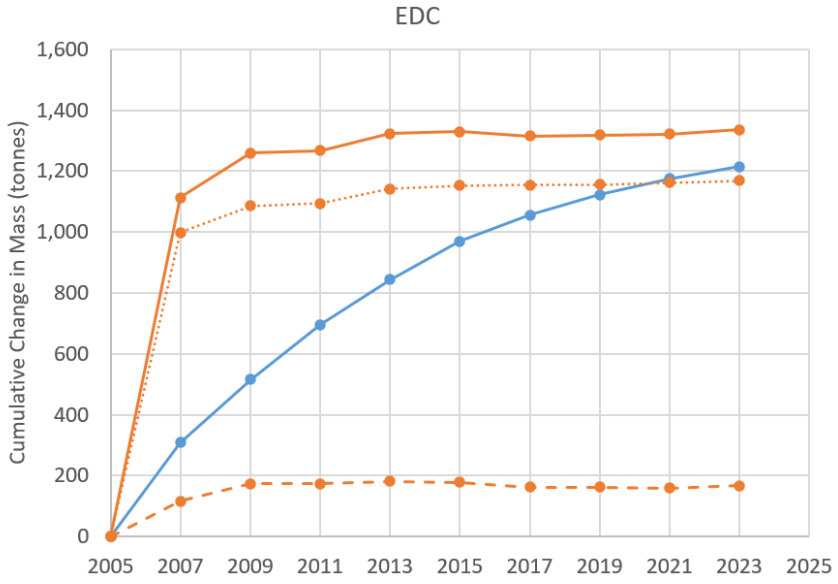


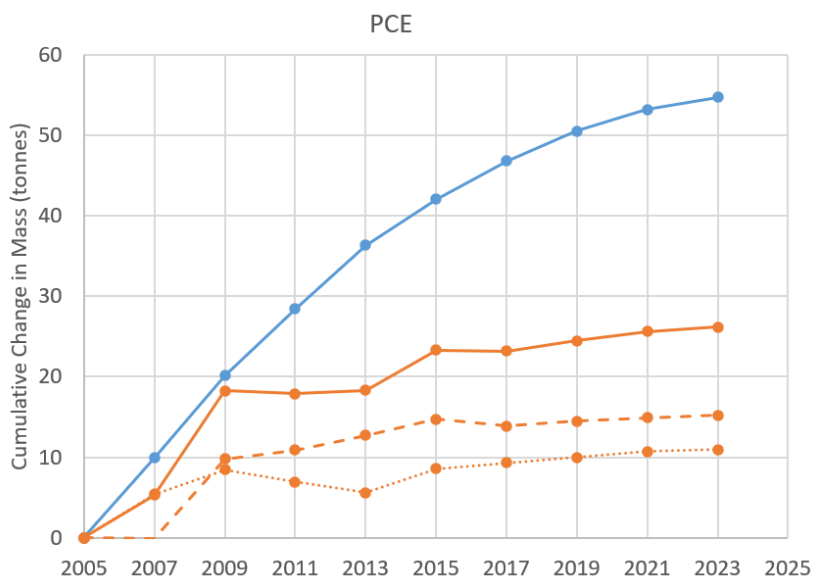


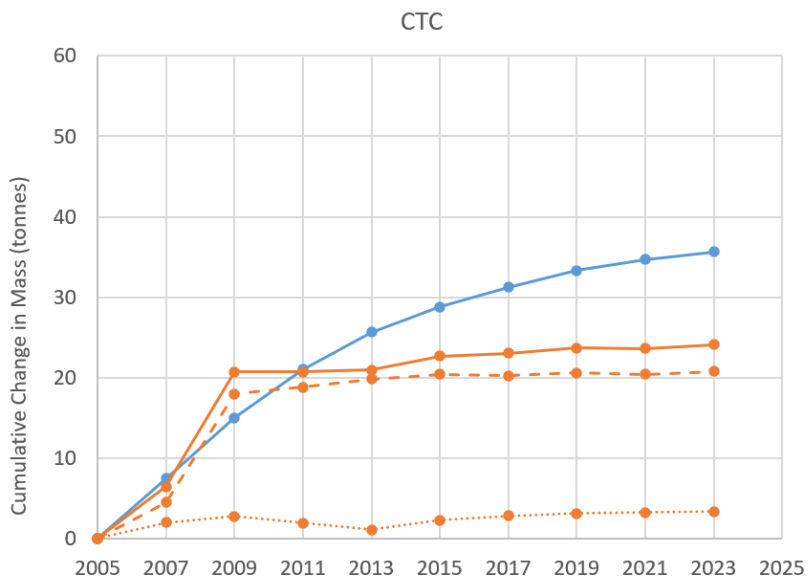
DNAPL Constituent	Average Plume Attenuation Half-Life (years)	Range in 95% UCL/LCL Plume Attenuation Half-Lives (years)
EDC	2.7	1.0 to 12
CTC	3.4	1.3 to 21
PCE	4.1	1.0 to 28

GTP Mass Extraction vs. Changes in Plume Mass





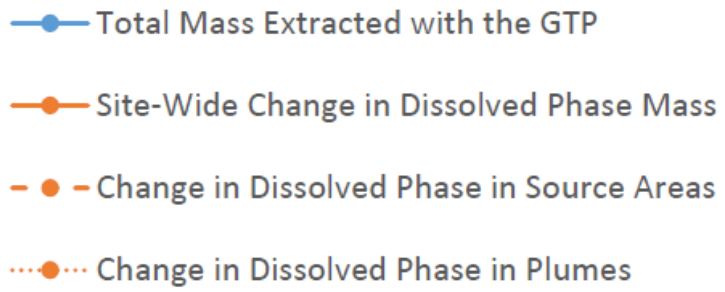




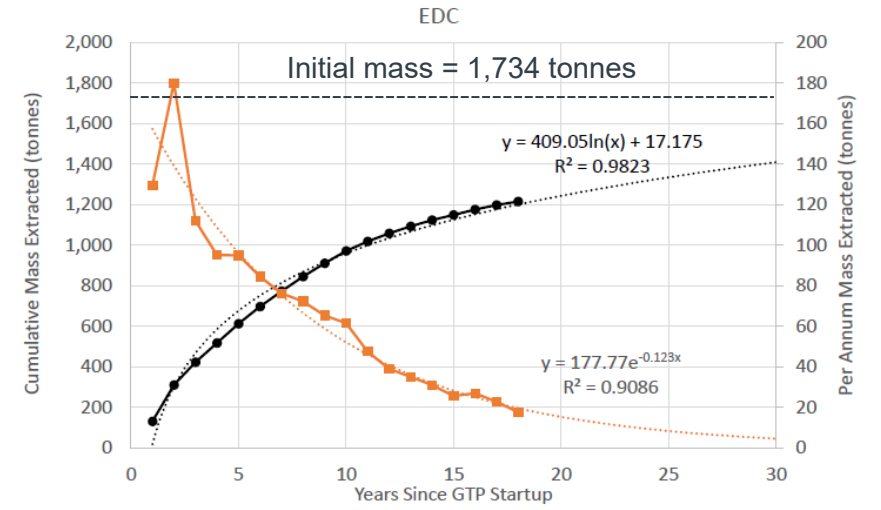
More EDC (1,2-DCA) mass has disappeared from the plume than can be explained by GTP operation, especially in first two years. Expanding EDC plume resulted in early-time plume losses due to sorption.

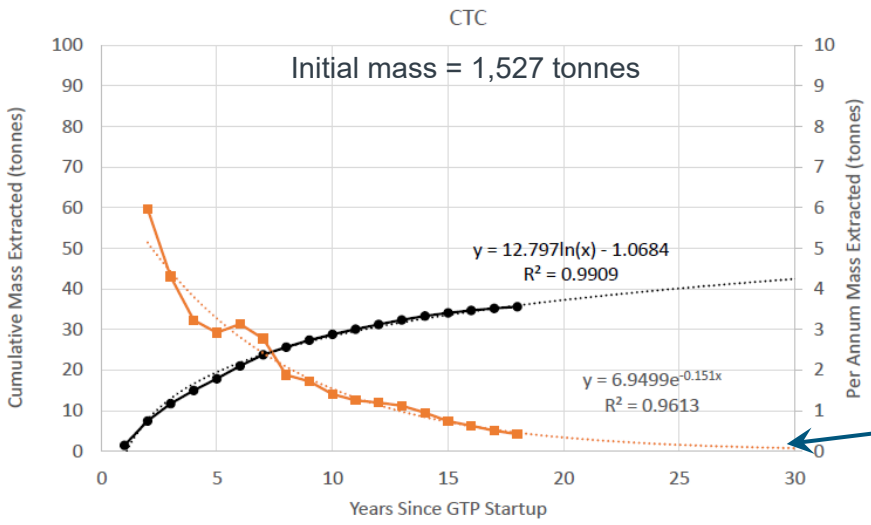
Continuing operation of the GTP is removing some PCE and CTC, but having minimal effect on plume mass.

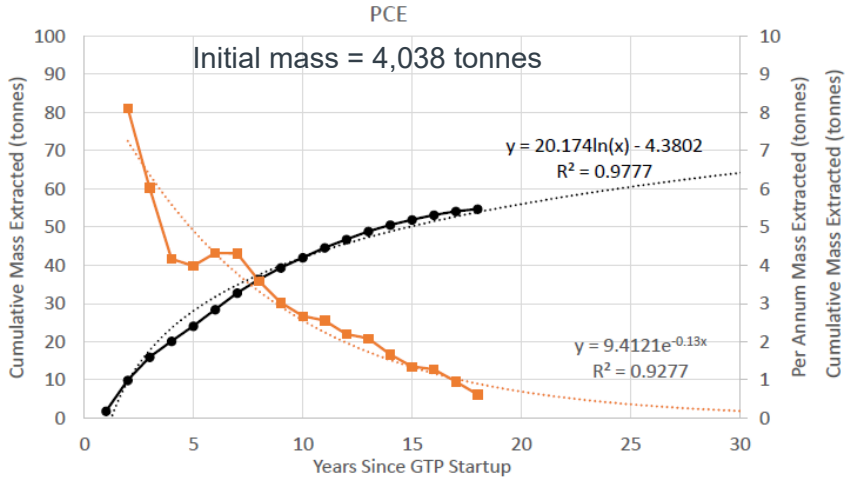
Rates of mass removal are slowing down.

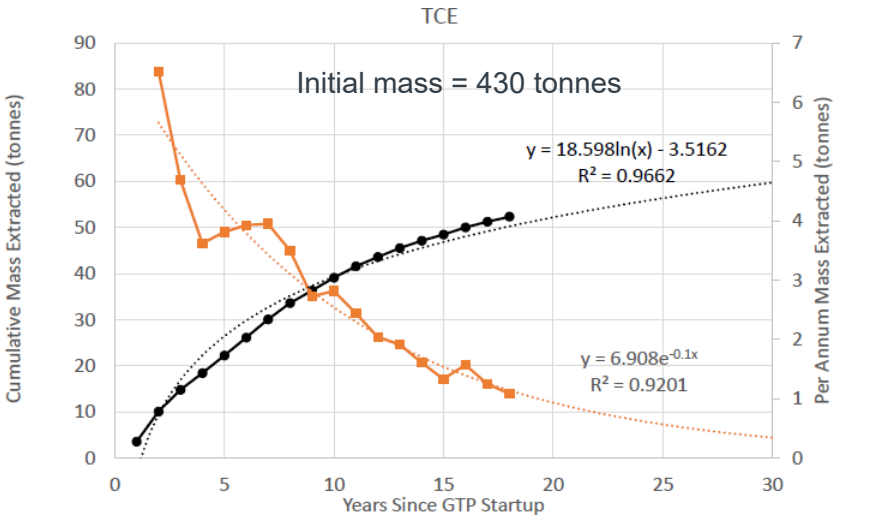


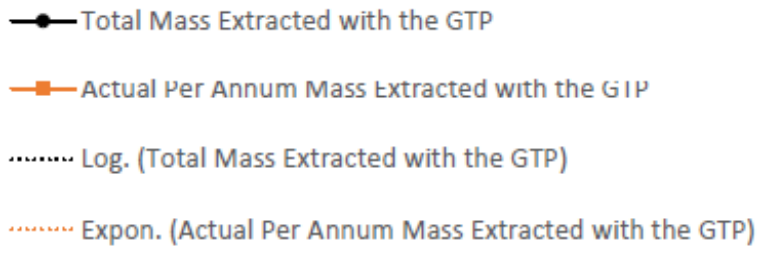
Forward Projections of Total Mass Extracted with the GTP







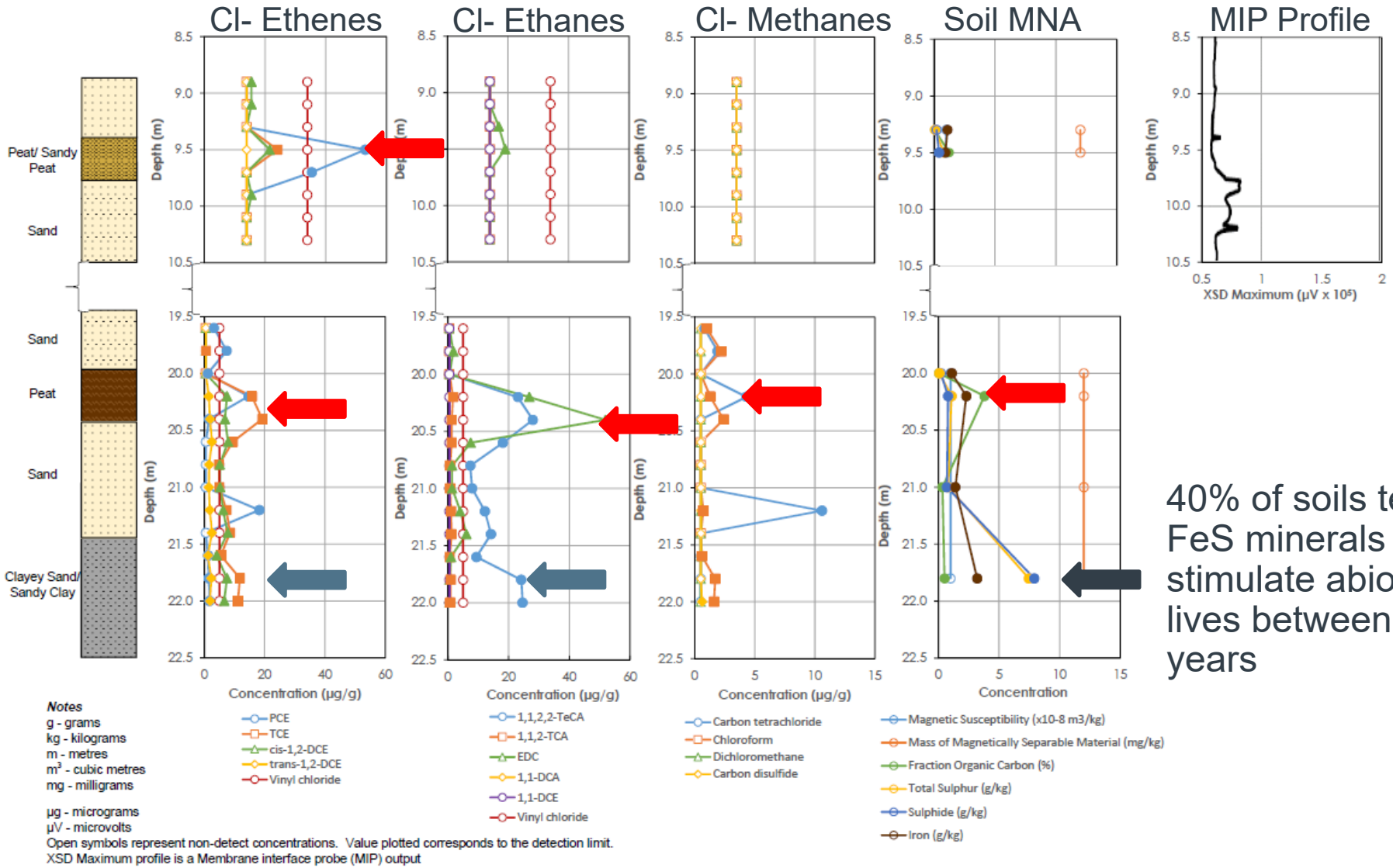




Diminishing returns over time

Constituent	30-Year Flushing "Efficiency" (% of total initial mass)
EDC	81% (~1,400 tonnes)
CTC	2.8% (~42 tonnes)
PCE	1.6% (~63 tonnes)
TCE	14% (~60 tonnes)

Sorption and Diffusion as Secondary Sources

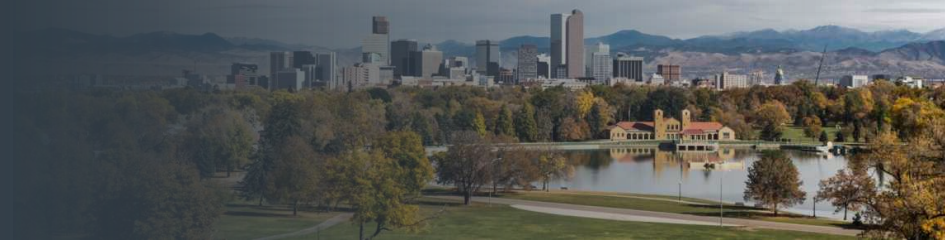


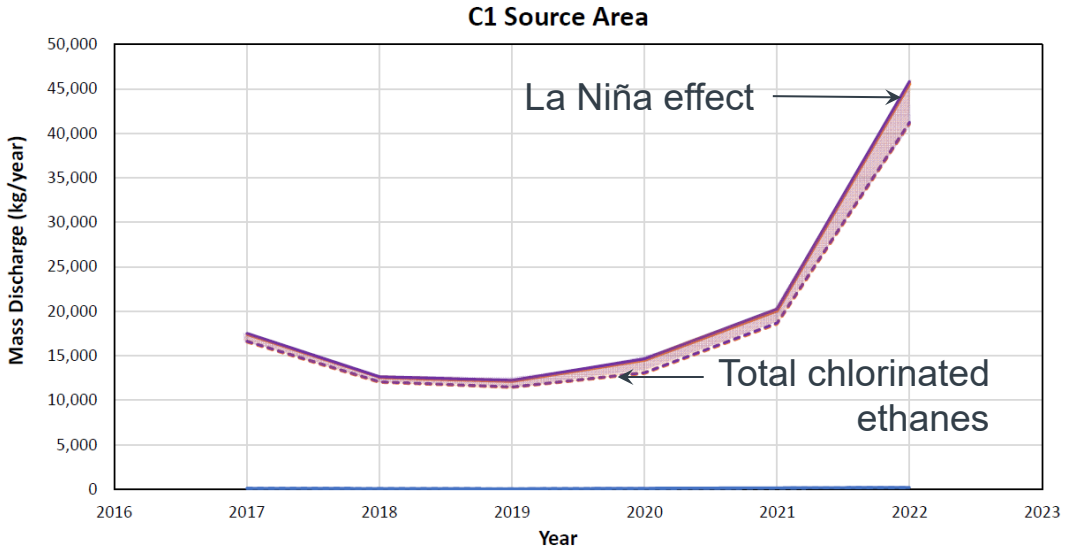
Notes
g - grams
kg - kilograms
m - metres
m^3 - cubic metres
mg - milligrams

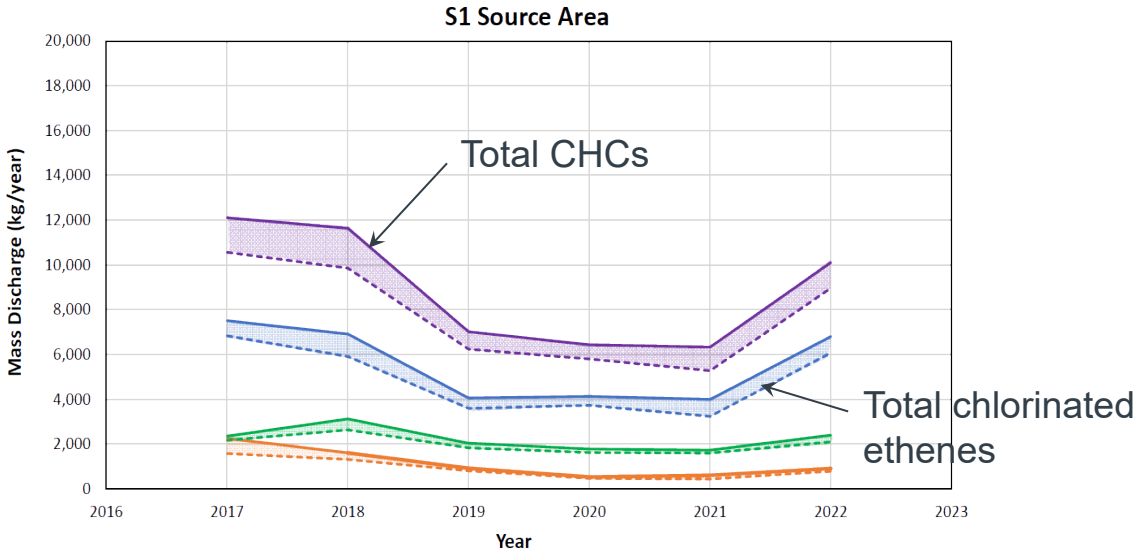
µg - micrograms
µV - microvolts
Open symbols represent non-detect concentrations. Value plotted corresponds to the detection limit.
XSD Maximum profile is a Membrane interface probe (MIP) output

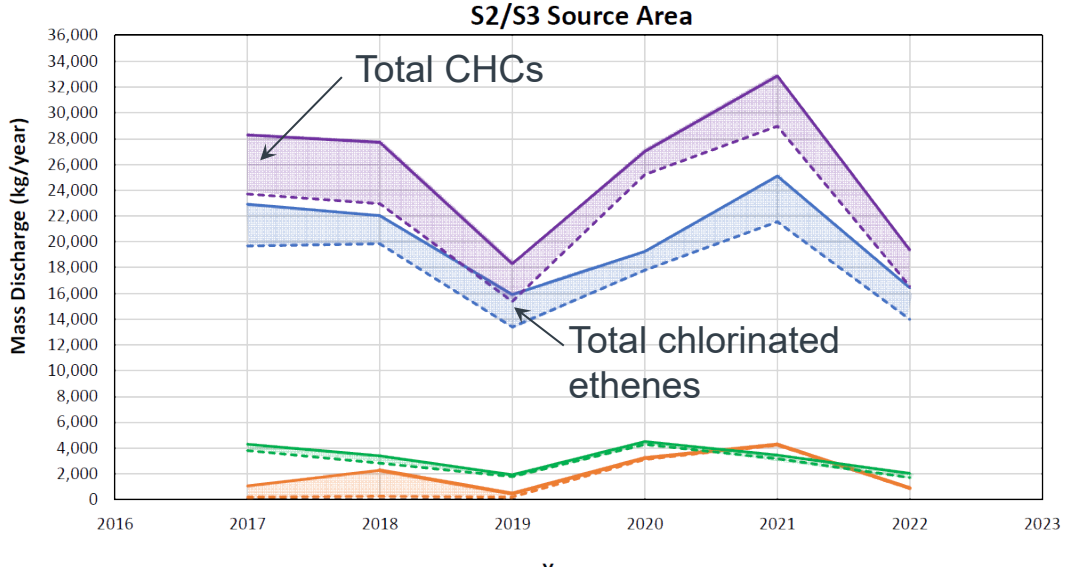
40% of soils tested had FeS minerals sufficient to stimulate abiotic half-lives between 1 to 5 years

Temporal Trends in Source Mass Discharge



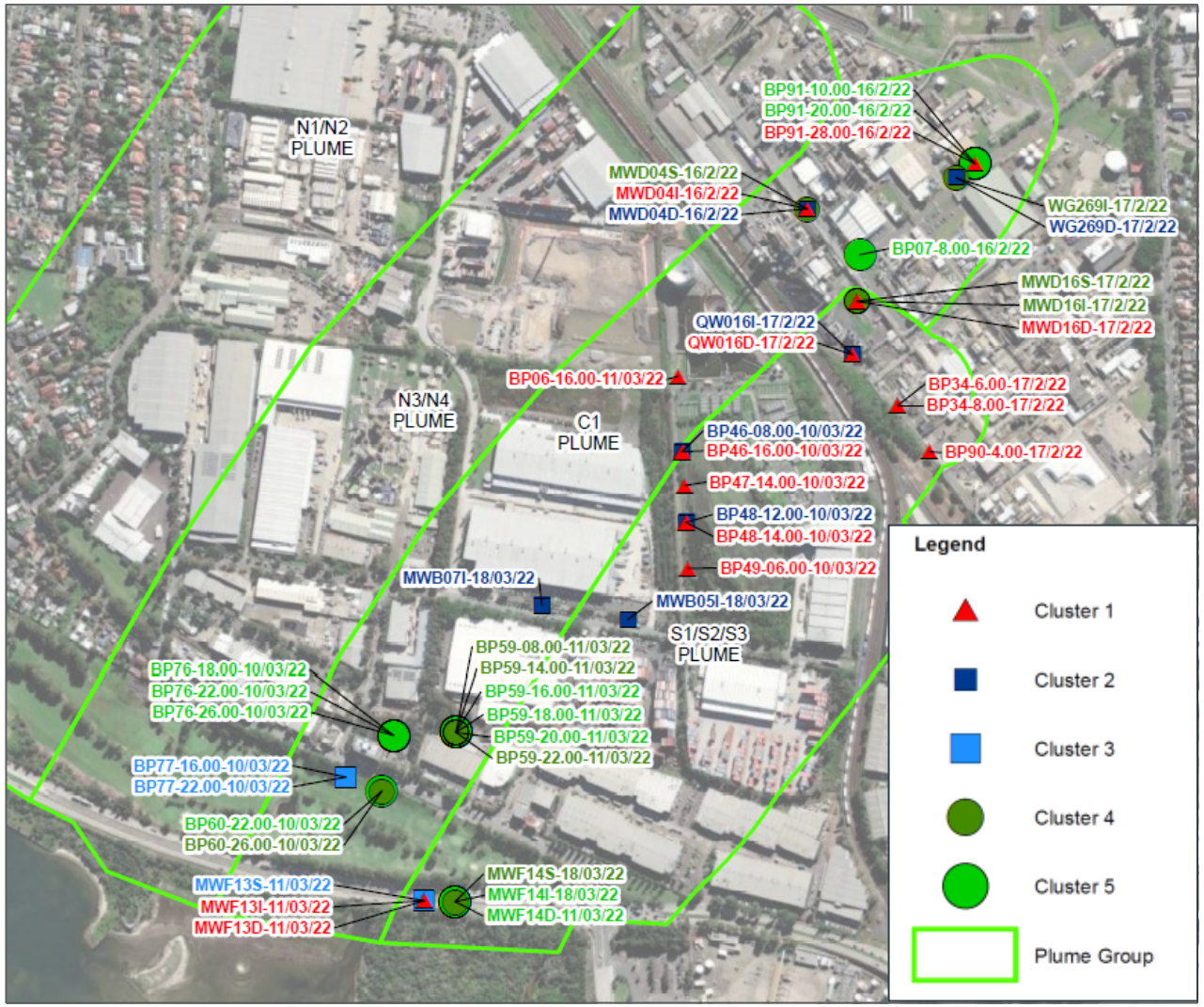






Source Area	Trend and Change in Total Mass Discharge (%)	
	2017-2021	2022
C1	Stable	Increasing (+200%)
S1	Decreasing (-49%)	Increasing (+65%)
S2/S3	Stable	Stable

Spatial Variability in Microbial Activity Can Be Significant



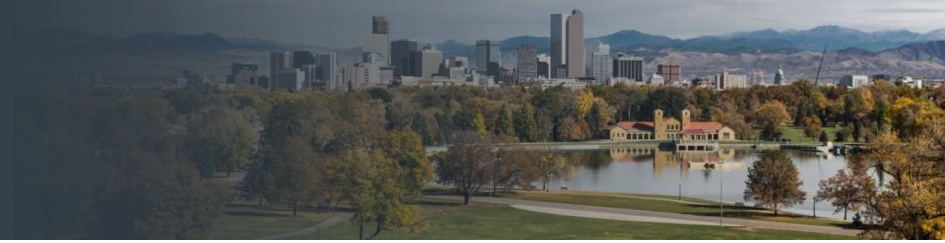
Cluster	Dominant Functional Activity	Average [EDC] (Range; mg/L)	Average [CF] (Range; mg/L)
1	Aerobic chemoheterotrophy	176 (0.008 – 2,350)	3.7 (<1 – 10.6)
2	Respiration of sulphur compounds	183 (0.05 – 1,140)	2.8 (<0.1 – 7.4)
3	Methanogenesis	0.30 (0.002 – 0.61)	0.030 (0.025 – 0.036)
4	Reductive dechlorination	119 (<0.02 – 802)	0.39 (<0.2 – 1.5)
5	Respiration of sulphur compounds and fermentation	95 (0.27-273)	2.6 (<0.1 – 7.2)

Lowest ORB populations observed where EDC > 2,000 mg/L and CF > 1 mg/L.

Methanogens dominate where CHC concentrations are low.

Obligate ORBs dominate when EDC < 1,000 mg/L and CF < 2 mg/L.

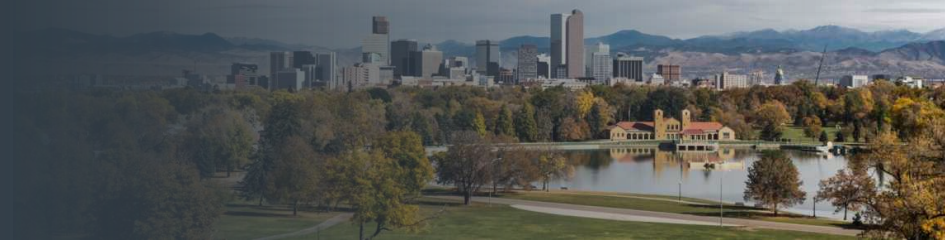
Assessment of Attenuation Rates



DNAPL Constituent	Location-Specific Point Attenuation Half-Lives (years)	Site-Wide Dissolved Phase Attenuation Half-Life (years)	CSIA-Estimated Half-Lives (years)
EDC	0.2 ≤ 2.1 ≤ 33	1.4 ≤ 2.6 ≤ 7.9	0.9 ≤ 2.0 ≤ 4.3
CTC	0.1 ≤ 1.8 ≤ 44	1.3 ≤ 3.4 ≤ 11	0.6 ≤ 1.9 ≤ 3.2
PCE	0.2 ≤ 2.4 ≤ 52	1.0 ≤ 4.7 ≤ 25	2.4 ≤ 3.5 ≤ 4.5
TCE	0.2 ≤ 2.4 ≤ 127	--	--

Note that these rates reflect extended periods of CF inhibition. In many areas, degradation rates have accelerated since CF concentrations reduced below 1 mg/L.

Overall Picture



Bulk mass attenuation behaviour is a complex balance of competing attenuation and inhibition mechanisms.

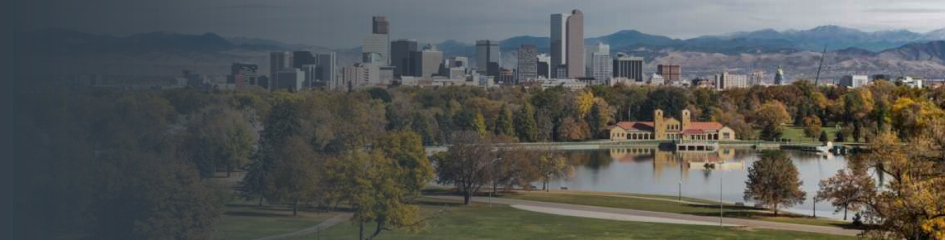
Flushing and GTP operation alone will not likely achieve end goals.

- GTP has greater impact on EDC removal than other DNAPL constituents

In situ degradation is an important mechanism contributing to faster decay of the plumes and sources.

- Abiotic degradation is slow but is occurring
- Biologically-mediated degradation is rapid with CTC, contributing to its faster disappearance, slower with other constituents but still substantial
- Elevated CF is inhibiting bioactivity in some areas of the site, but that volume of aquifer is getting smaller every year

What does the future look like?



- Slowing mass removal with the GTP, but recovery continues to be substantial (10s tonnes/year)
- Desorption/back-diffusion may drive long-term persistence of plumes
- CTC will disappear first
- As CF concentrations reduce below inhibitory levels, microbial populations will likely increase, enhancing rate of mass removal *in situ*
- PCE may be long-term driver for site cleanup

Questions?

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