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Carbon Amendments for Chlorinated Solvent Remediation: Analytical Challenges and Solutions

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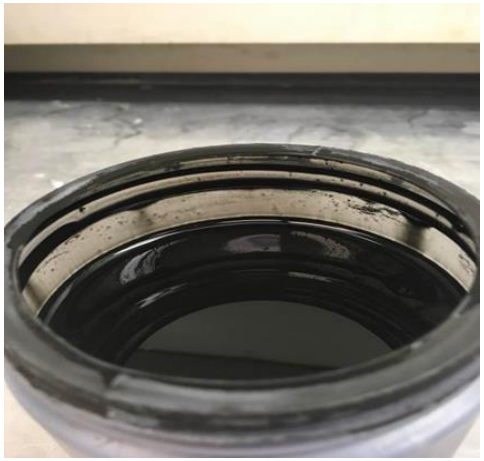
Activated Carbon-based Remedial Approaches

Overview:

- In-situ application of carbon-based amendments for chlorinated solvent remediation has emerged in the last decade.
- Two stage approach:
  - Adsorption: used since the 1950's for ex situ remediation
  - Degradation: ~ two decades of in situ use
- Considered as more effective than subsurface degradation alone due to the added retardation of contaminant migration



Available Activated Carbon Amendments

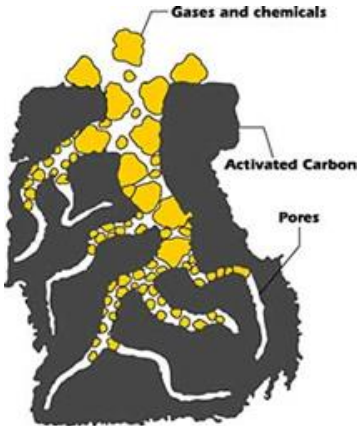
Activated carbon–based products that have been used for in-situ remediation*

Product	Size	Manufacturer	Additive	Target CoCs	Degradation
BOS-100	granular	Calgon	zero valent iron	cVOC	Abiotic reductive dechlorination
BOS-200	powdered	Calgon	electron acceptors, P, N, $CaSO_4$, bacteria	PHC	Aerobic (short-term) and anaerobic (long-term) bioaugmentation
COGAC	granular or powdered	Remington	calcium peroxide, sodium persulfate	cVOC and PHC	Chemical Oxidation, aerobic and anaerobic biostimulation
PlumeStop	colloidal	Regenesis	polymer, H_2 and O_2 releasing compounds, bacteria	cVOC or PHC	cVOC: anaerobic biodegradation; PHC aerobic biodegradation
carbon-iron	colloidal	non-commercial	colloid stabilizer, zero valent iron	cVOC	Abiotic reductive dechlorination

* Adapted from: Fan, D. et al. 2017 Journal of Environmental Management

Typical Application Process

- **Investigation**: Pre-injection subsurface characterization.
- **Select Loading Rate**: Provide sufficient contact between amendment and contaminant.
- **Injection**:
  - Powdered and Granular: low permeability formations, direct push injection and formation fracturing
  - Colloidal: high permeability formations: direct push or injection wells
- **Characterize** distribution post-injection by soil coring – if necessary



contaminant adsorption on activated carbon

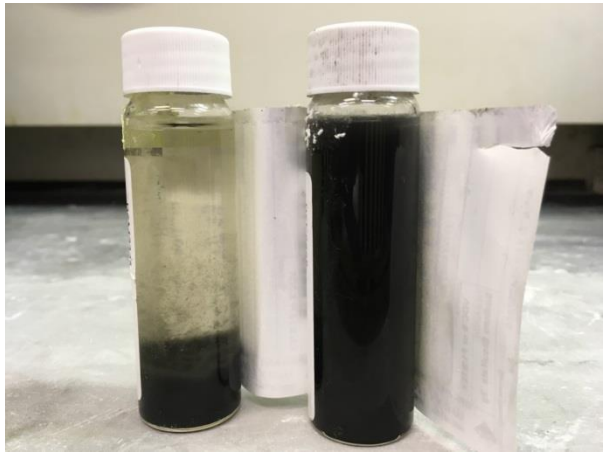
Chemical Assessment of Remedial Performance

Field

- Monitor contaminant concentrations in separate monitoring wells.
- Amendment may appear in monitoring wells.

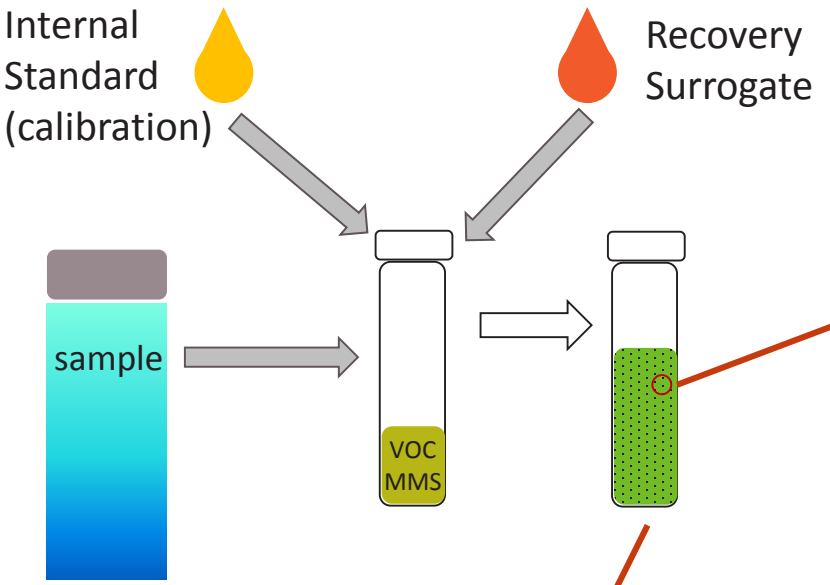
Lab

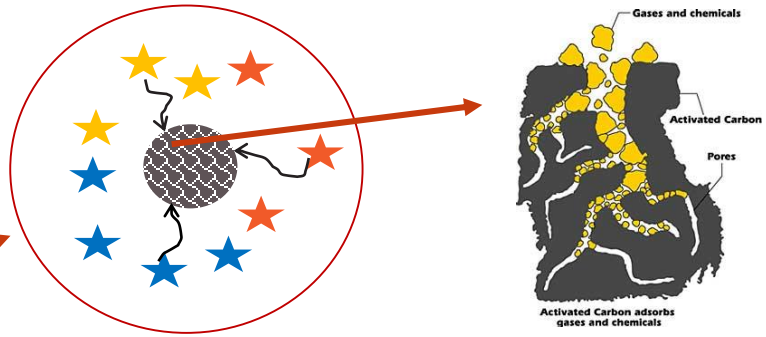
- Allow carbon to settle prior to analysis.
- Complete settling not always possible within required hold times.
- If material does not settle, analytical complications are possible.



Right vial did not settle

Lab Processes





Residual activated carbon in samples may adsorb both contaminants and lab QC spikes.

cVOC measured from vial headspace

- At high carbon loadings, laboratory QC fails
  - Internal standards / recovery surrogates
- Samples must be diluted to pass QC.
- Dilution may cause DL increase above guideline limit.

Site 1 Overview

Low Concentration cVOC, Low Carbon Injected

- Vinyl Chloride (VC) was the remnant contaminant of concern following a 15 year effort including air sparging, pump & treat, vapour extraction
  - < 10 µg/L VC on site
- VC has a low Site Condition Standard of 1.7 µg/L
- Concentration polished at last stage using colloidal carbon
  - 230 kg injected
- Monitoring started 1 month after injection
  - Low flow sampling

Site 2 Overview

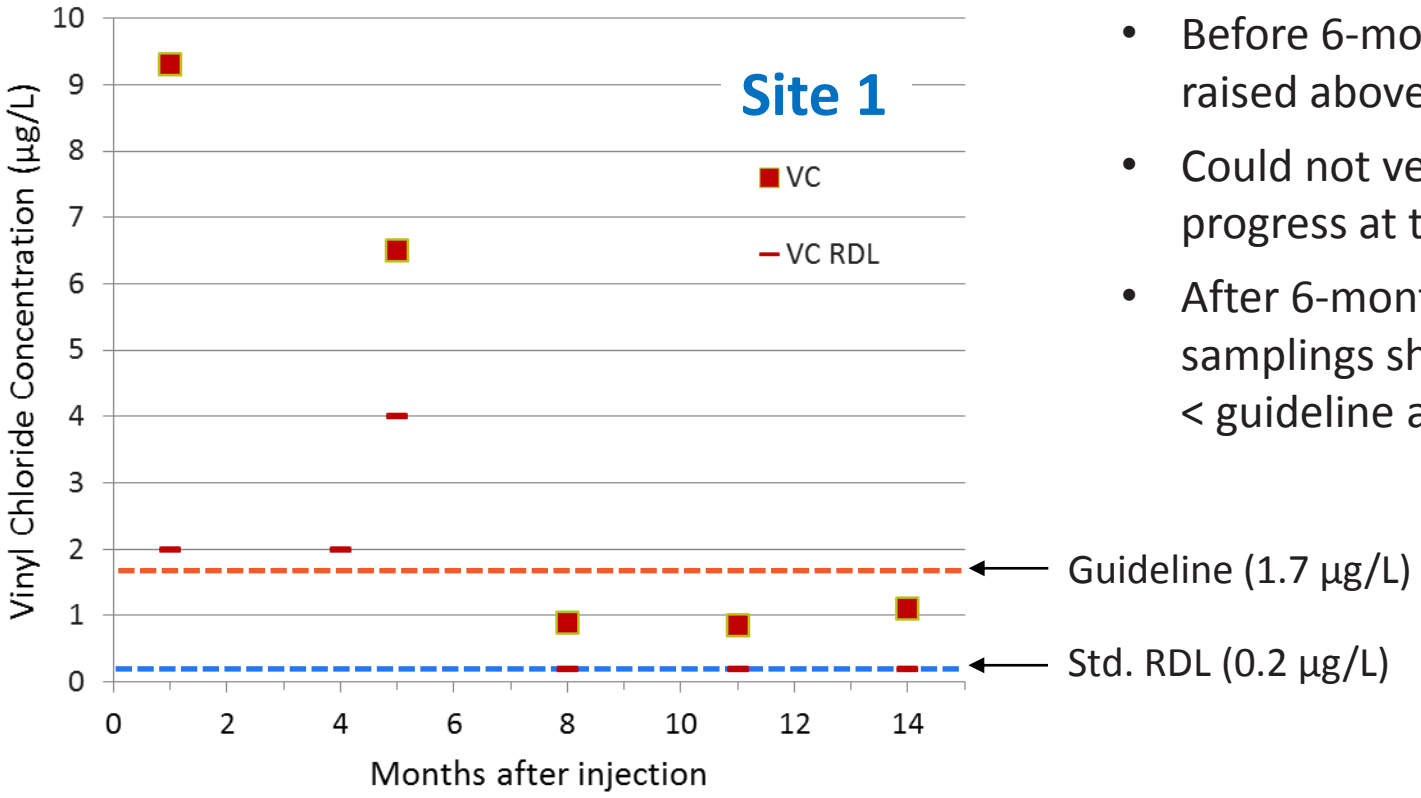
High Concentration cVOC, High Carbon Injected

- Up to 6,000 µg/L vinyl chloride (VC) on site
- Site Condition Standard for VC @ 1.7 µg/L is again the target
- Colloidal carbon used as first line of treatment:
  - 2,500 kg injected
- At 3 months post injection LAC concentration too high in many cases to permit direct analysis of cVOC.
- Passive Diffusion Bag monitoring pre- and post-injection

Site 1 – Low Flow Sampling Results

Vinyl Chloride in monitoring well post-injection

- prior to injection VC was @ 5 µg/L



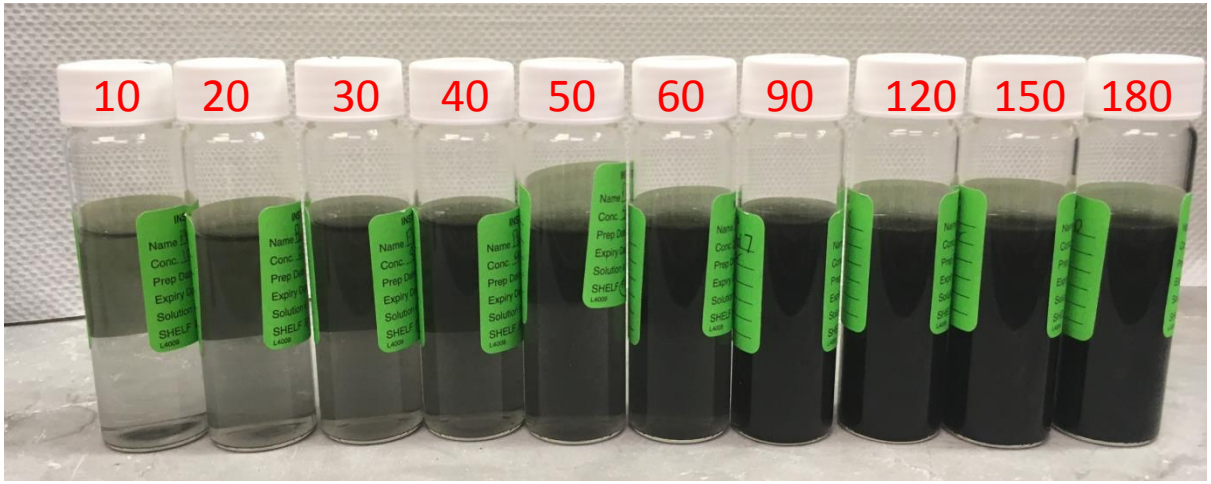
All sampling by low-flow

- Before 6-months, RDLs raised above guideline
- Could not verify remedial progress at this stage
- After 6-months repeated samplings showed total VC < guideline and good RDL

How much carbon causes QC to fail?

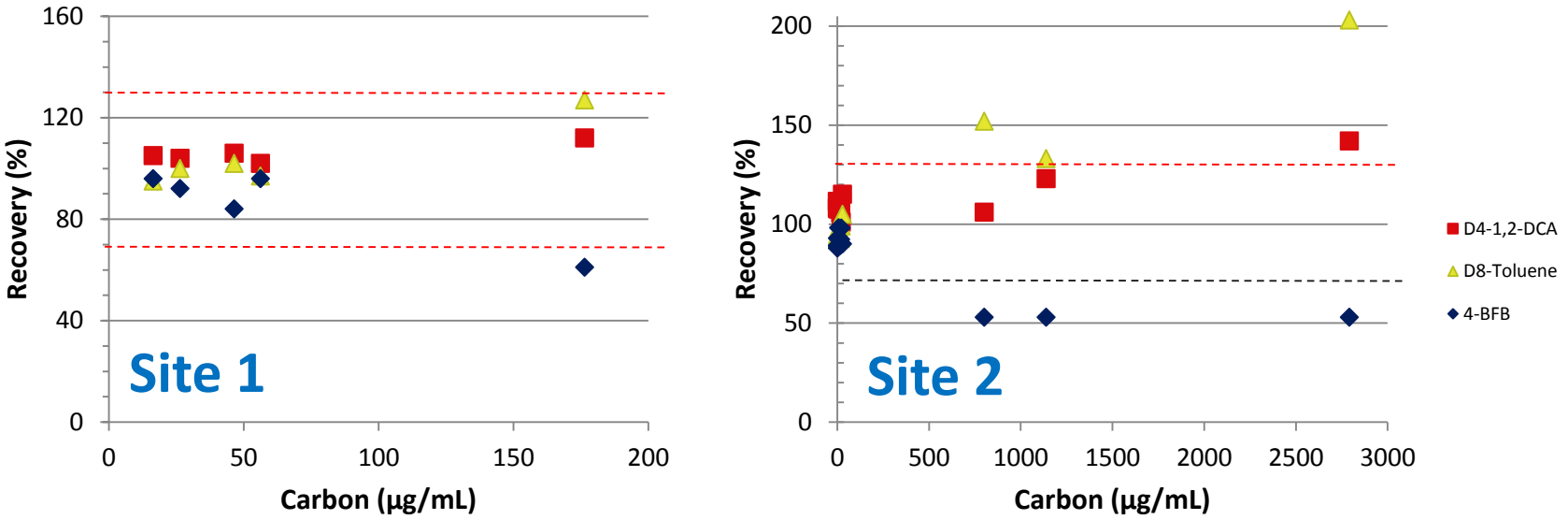
Measurement of carbon amendment concentration

- Measured by UV-Vis spectrophotometer.
- Provides guidance for loadings likely to cause QC failures and elevated DL



Recovery Surrogate Results – no dilution

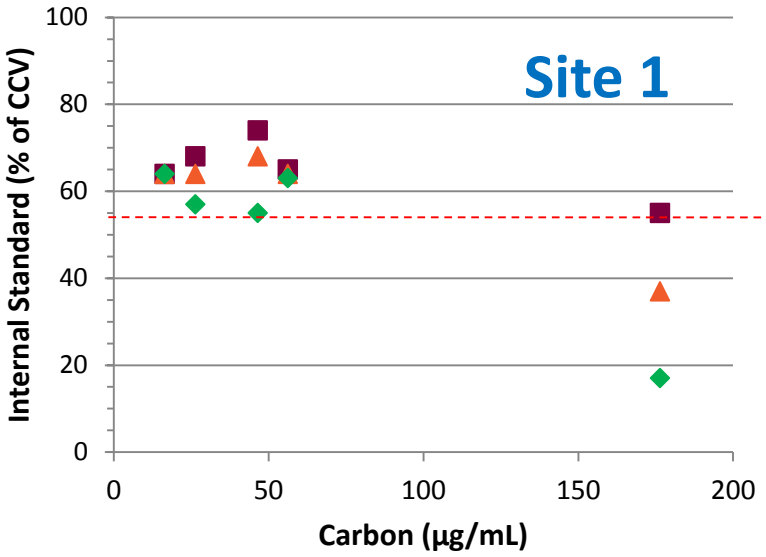
Surrogate QC failures seen at suspended carbon concentrations >100 mg/L

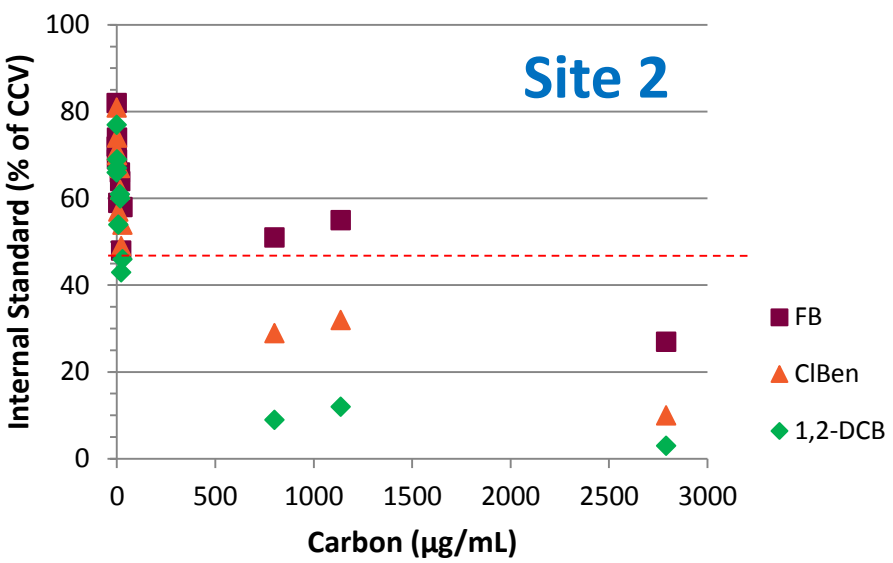


- Surrogate recovery acceptance criteria 70-130% recovery
- Surrogates: d_4-1,2-Dichloroethane; d_8- Toluene; 4-Bromofluorobenzene

Internal Standard Results – no dilution

Internal Standard QC failures also seen at suspended carbon concentrations >100 mg/L





- IS acceptance criteria – above dotted line
- Internal standards: Fluorobenzene; d_5-Chlorobenzene; d_4-Dichlorobenzene

Solutions / Sampling Alternatives

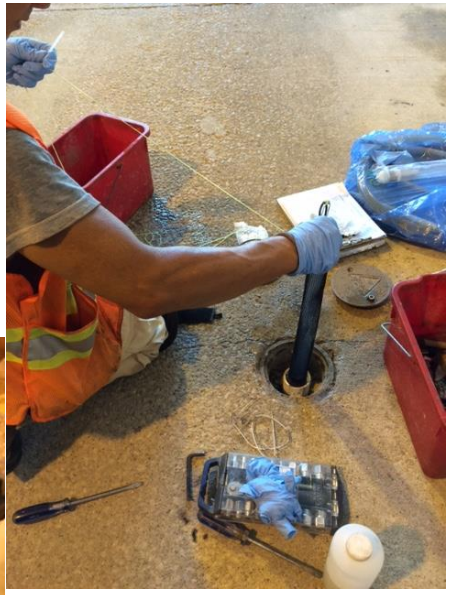
1. **External Standard Calibration:**
   - Contaminant response compared directly to calibration curve
     - disregard failing internal standard responses and surrogate recoveries
   - Not a validated/accredited method
   - Reports free COC concentration
2. **Passive Diffusion Bag Sampling:**
   - Standard analyses, no carbon in samples, no problems with QC, 0.2 µg/L RDL achievable
   - Reports free COC concentration

Overview: Passive Diffusion Bags (PDB)

Example COCs: BTEX, naphthalenes, chlorinated volatiles

Equilibration Sampling in Groundwater

- Low Density Polyethylene tube filled with distilled water
- Deploy in monitoring well
- Equilibrates within 7-14 days
- Once equilibrated:
  - water concentration in PDB = well
- Transfer water from PDB to VOC vials and submit to lab for standard VOC analysis.



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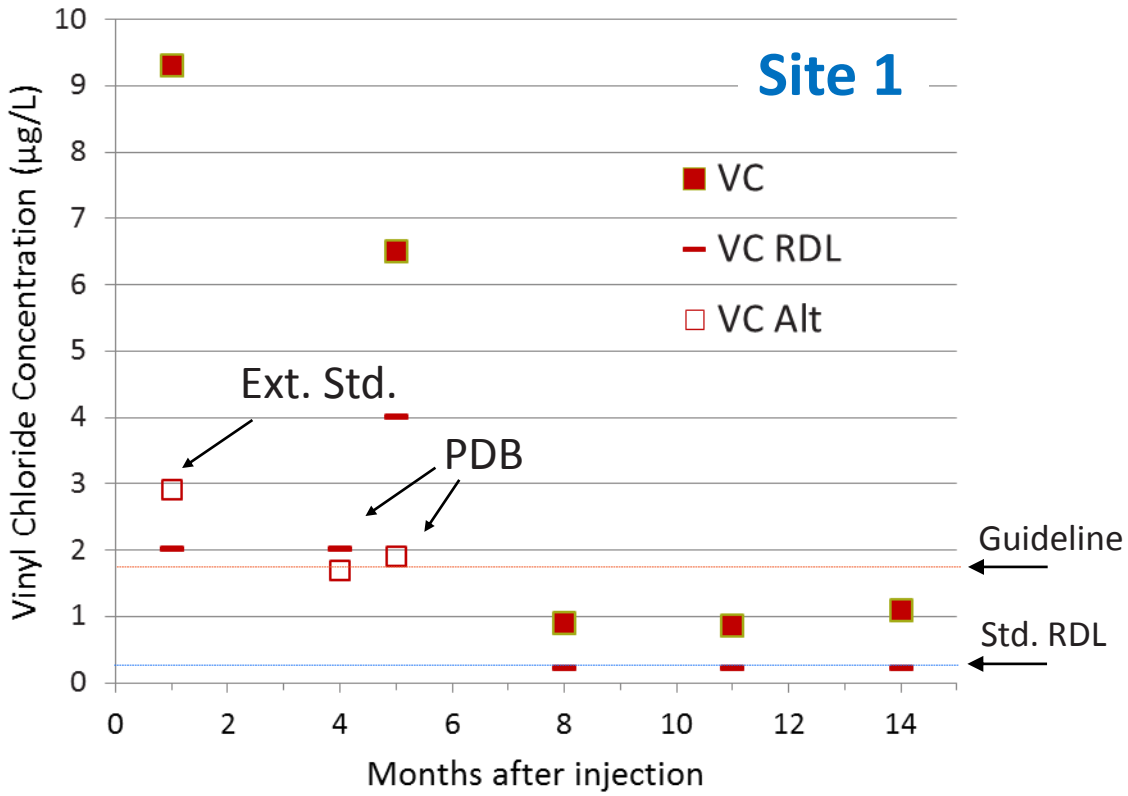
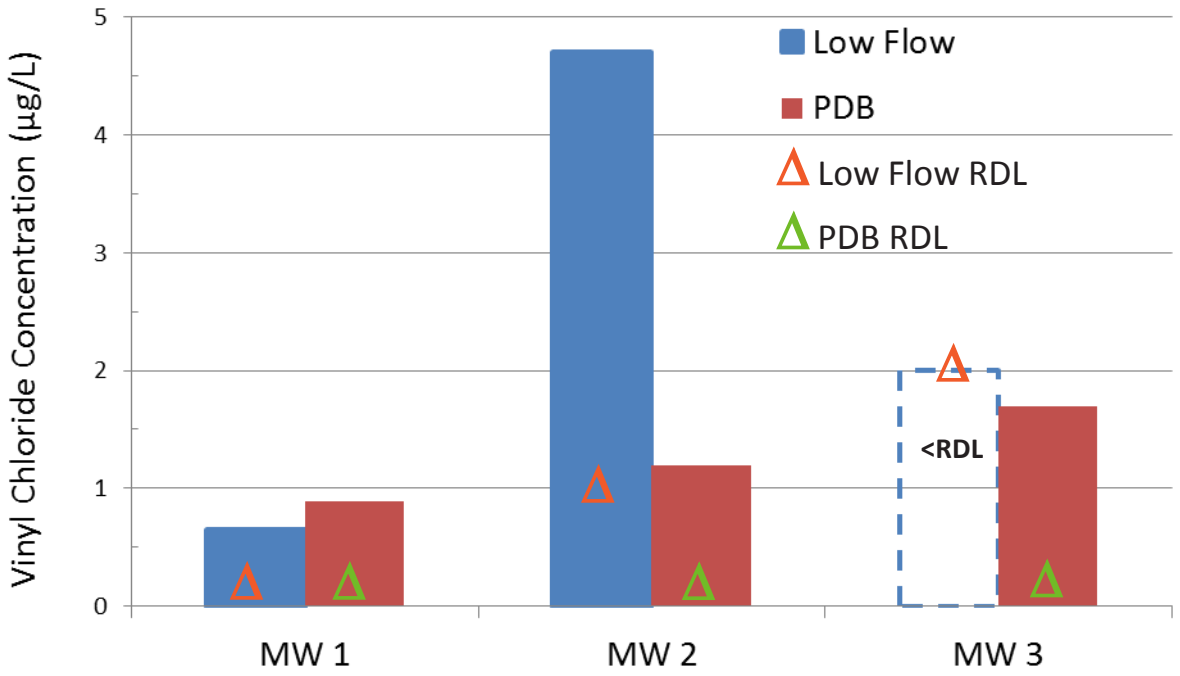


- Regular VC analysis reports total concentration
- Ext. Std. and PDB, free concentration, RDL 0.2 µg/L
- Free concentration assessment: early evidence of remedial progress.
- Three repeated standard analyses at 8-14 months verify remedial success.

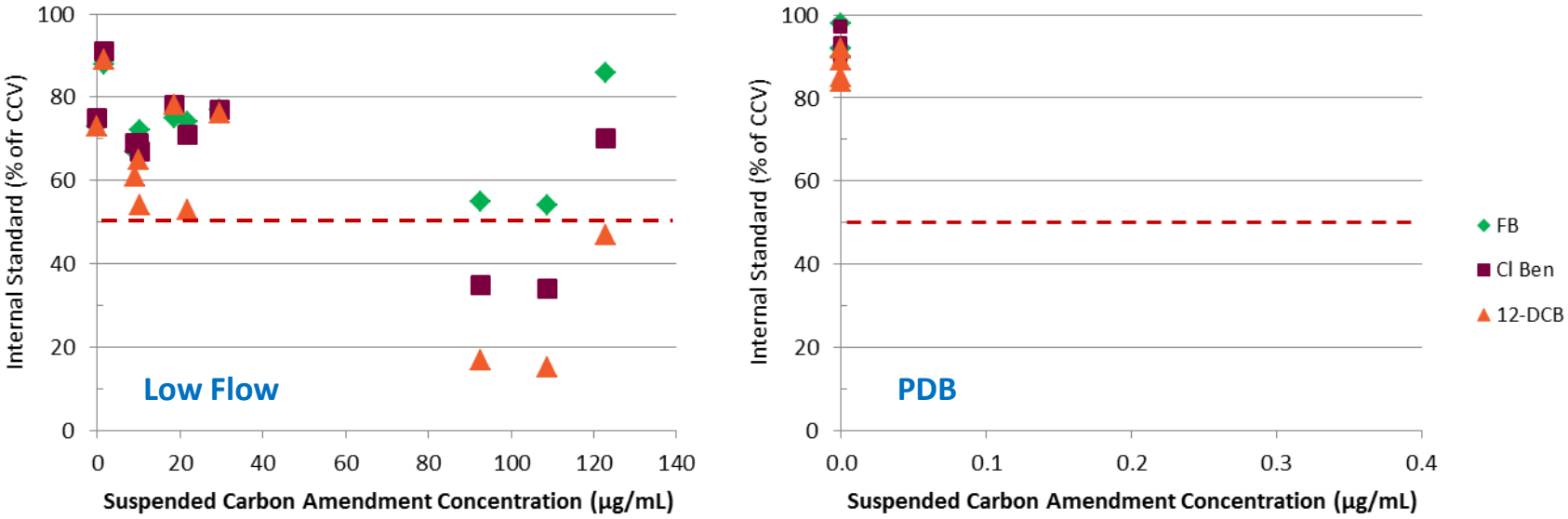
Site 1: Low Flow vs PDB - 4 mo. Post Injection



- Low Flow and PDB data in good agreement (within 10x)
  - PDB RDLs well below guideline
- Low Flow data likely higher due to inclusion of suspended colloid-associated VC

Site 1: Internal Standards – no dilution

Two sampling approaches: same wells, same time

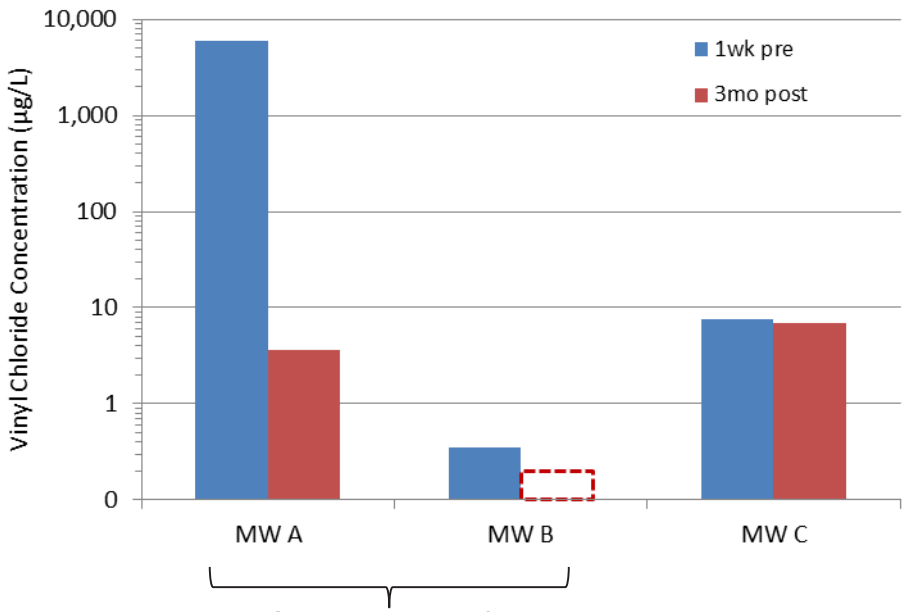


- No carbon concentration in PDBs
- Good clustering of IS recoveries in PDB samples

Site 2: Low Flow vs. Passive Diffusion Bags

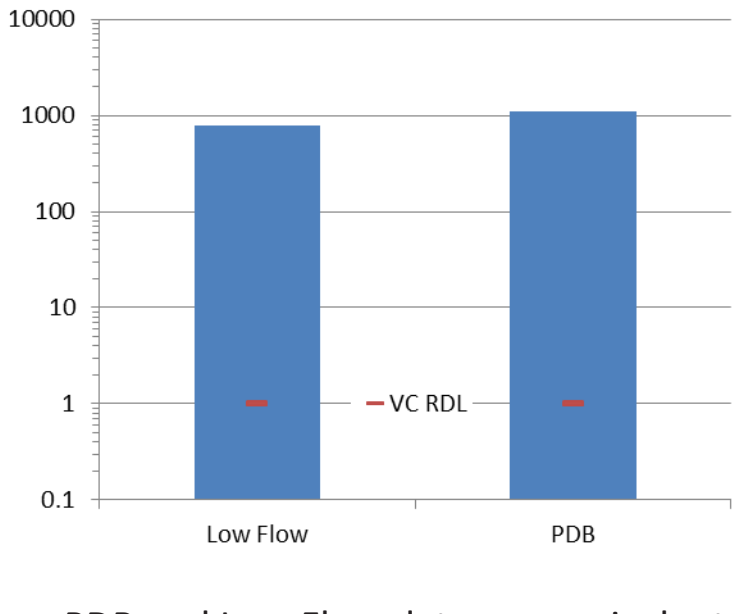
High Vinyl Chloride, High Carbon Load

PDB – Pre and 3 months post injection, three wells



VC concentration reduction

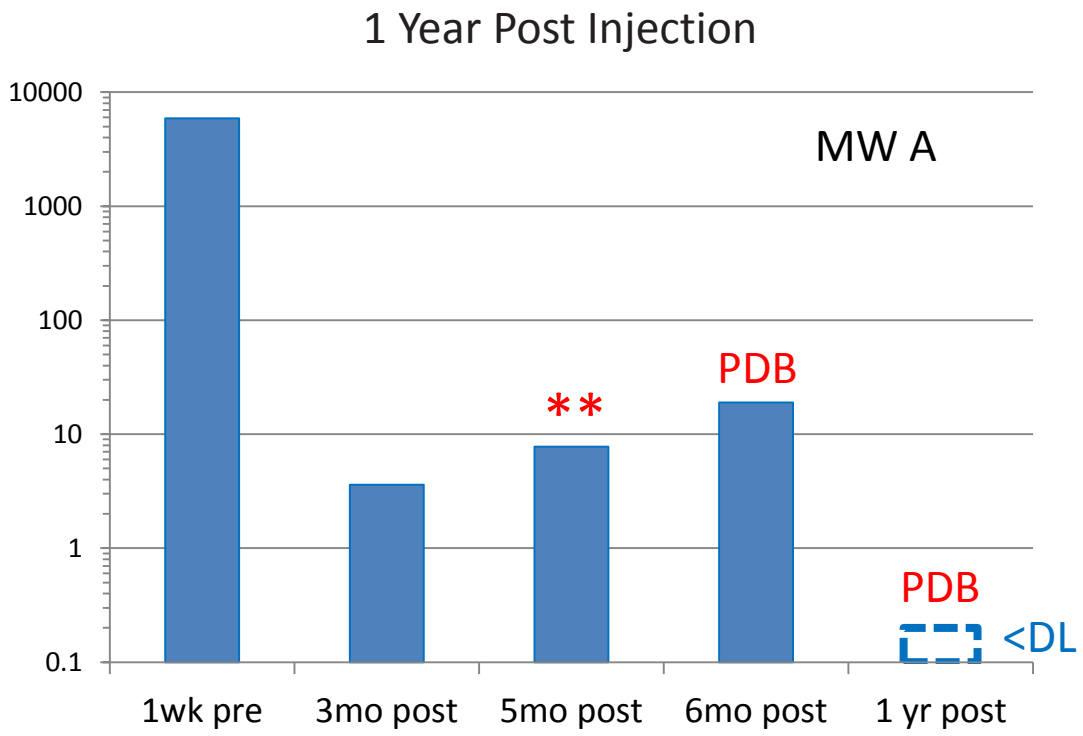
Low Flow vs. PDB in same well 3 months post injection



PDB and Low Flow data are equivalent at high VC concentration

Site 2: 12 Month Remedial Progress

Some vinyl chloride at months 5-6, likely due to degradation of precursors: TCE, DCA



** LAC still observed

Conclusions

- Colloidal activated carbon was an effective remedial approach at both low and high concentration cVOC sites.
- High suspended carbon in monitoring wells interferes with lab analysis,
- Where it is not possible to obtain results with sufficiently low RDL due to residual carbon, use of passive diffusion bags – reporting freely dissolved concentrations – can verify remedial progress.
- Once carbon settles, PDB and standard analyses are the same.

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