Distinguishing Chlorinated Solvent Releases by Stable Isotope Analysis

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DPRA

ZymaX forensics

Chlorinated Solvents

- PCE – dry cleaning solvent
- TCE – vapor degreasing solvent
- TCA – degreasing solvent
- Dissolve in groundwater; migrate easily
- Vapors intrude into overlying buildings

Chlorinated Solvent Issues

- Is PCE or TCE in a single plume from one source or from multiple sources?
- Is PCE or TCE in multiple plumes from the same source or from different sources?
- Is TCE in a PCE plume from degradation of the PCE or from a separate TCE source?

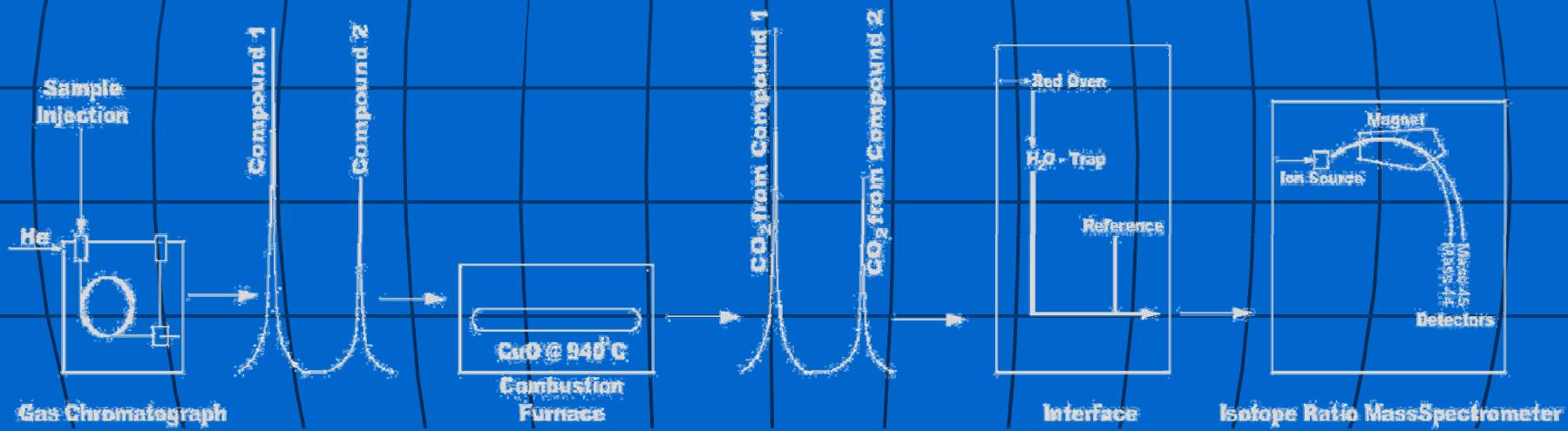
Chlorinated Solvent Characterization

- PCE, TCE etc are single compounds – petroleum products are a mixture of HCs
- Different sources are chemically identical
- May be isotopic differences
- $^{13}C/^{12}C$, $^{37}Cl/^{35}Cl$, D/H ratios differ depending on feedstock and manufacturing process

Compound Specific Isotope Analysis

- Volatiles isolated from groundwater and soil on a Solid Phase Micro Extraction (SPME) fibre
- Volatiles desorbed in inlet of GC/Isotope Ratio Mass Spectrometer
- Isotope ratios measured as $\delta^{13}C$, $\delta^{37}Cl$, and δD in parts per mil ($^{o}/_{oo}$) referenced to standards (0 $^{o}/_{oo}$)

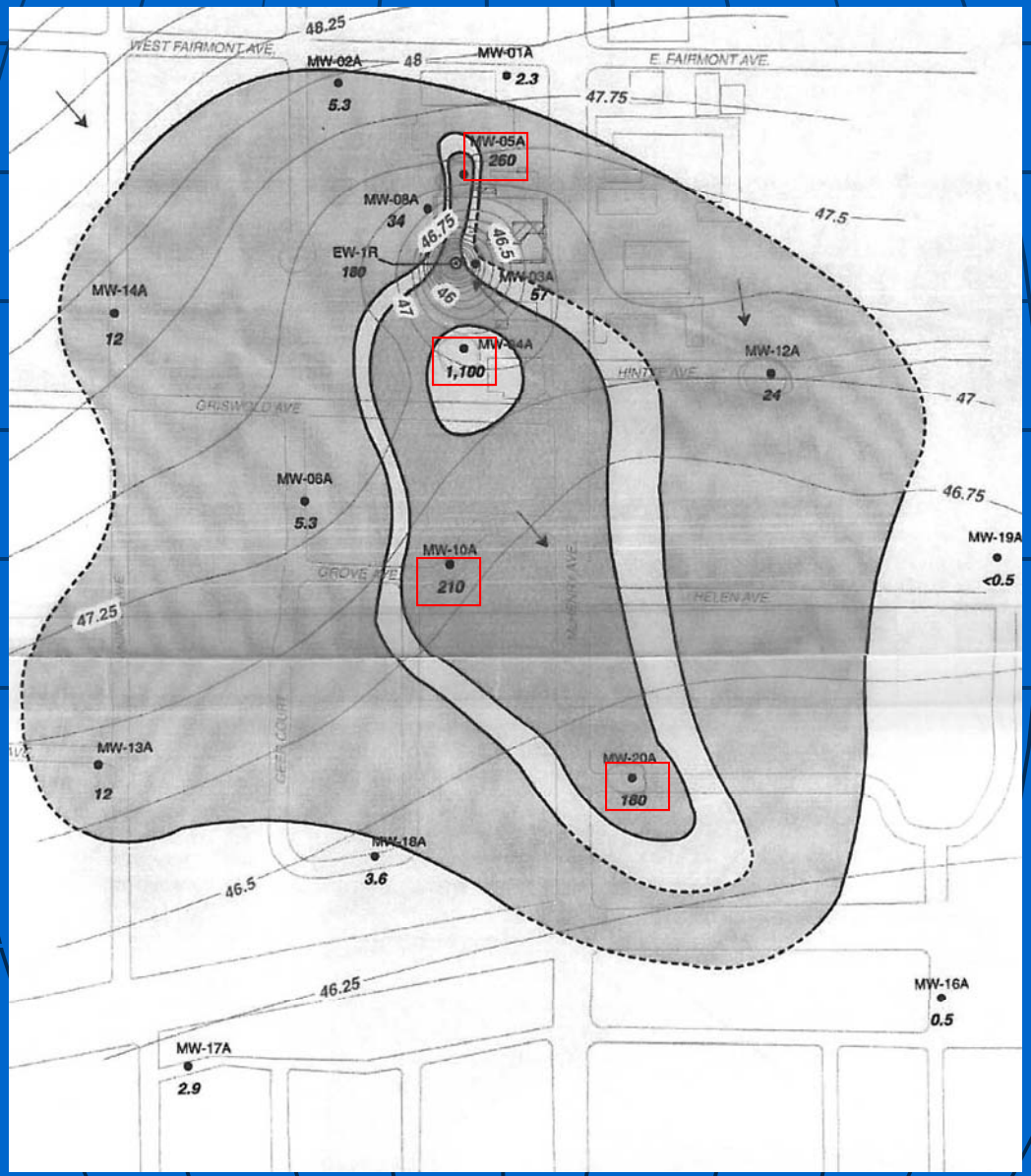
GC/IRMS Instrument Schematic



Case 1: Undegraded PCE in Multiple Aquifers

- Upper and lower aquifers have PCE contamination
- Traces of TCE & *c*DCE - little apparent degradation
- Multiple sources in upper aquifer?
- Different sources in upper and lower aquifer?

PCE Concentrations in Upper Aquifer



ug/L

260

1,100

210

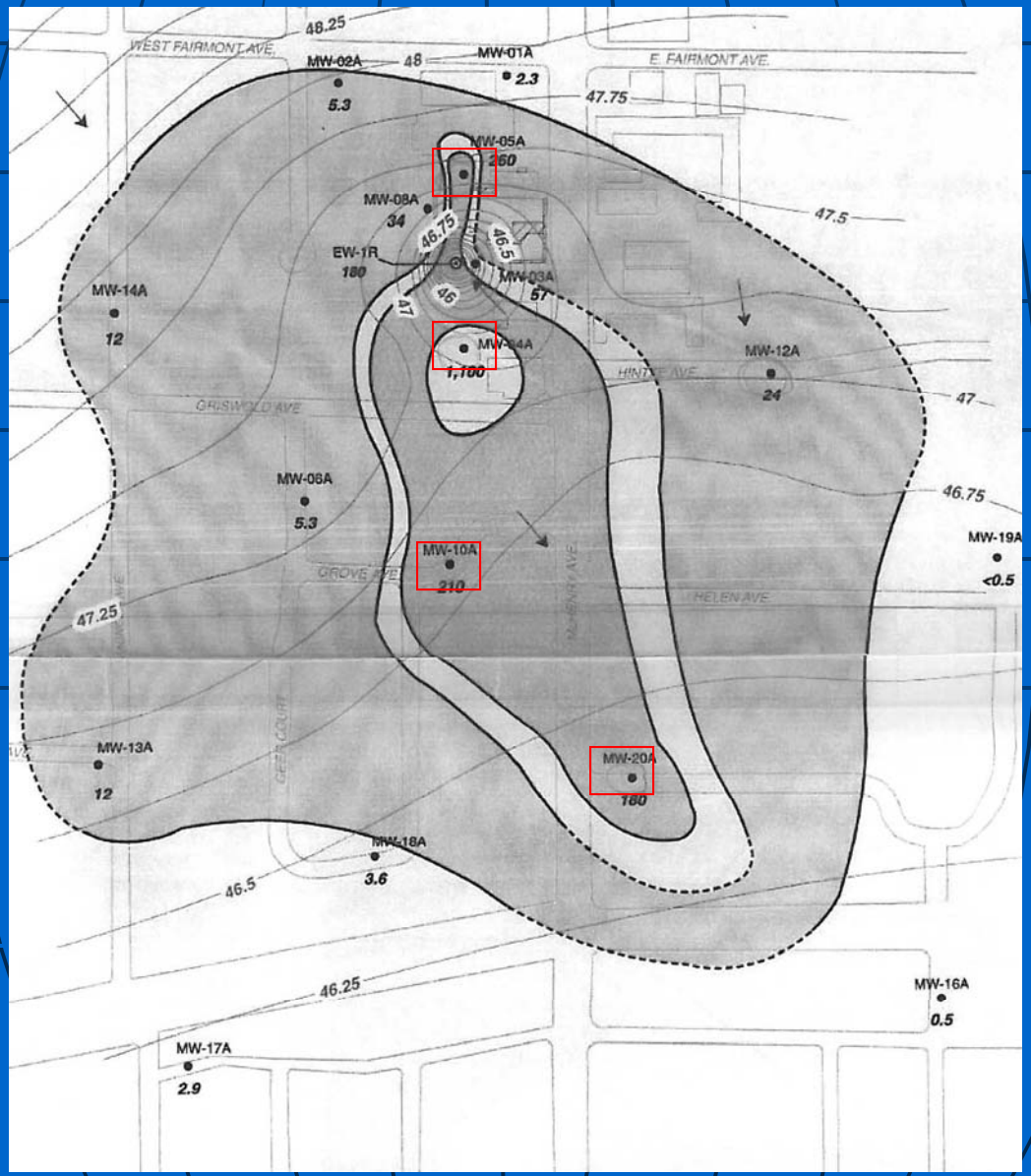
180

PCE Concentrations in Lower Aquifer

ug/L

140

PCE Isotope Ratios in Upper Aquifer



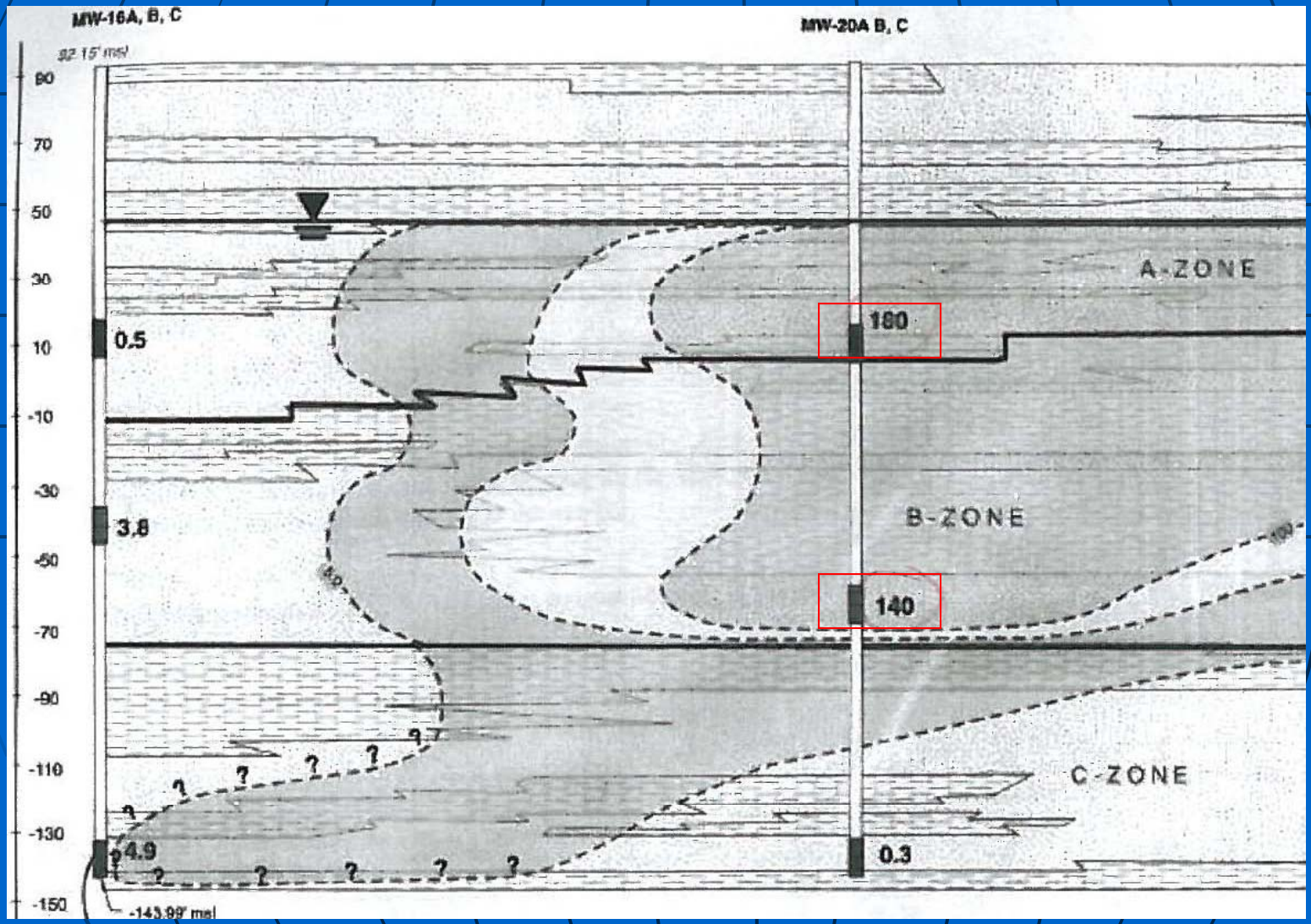
$\delta^{13}C$	$\delta^{37}Cl$
-28.9	-2.0
-29.9	-1.6
-29.3	-0.5
-29.6	-0.8

PCE Isotope Ratios in Lower Aquifer

$\delta^{13}C$ $\delta^{37}Cl$

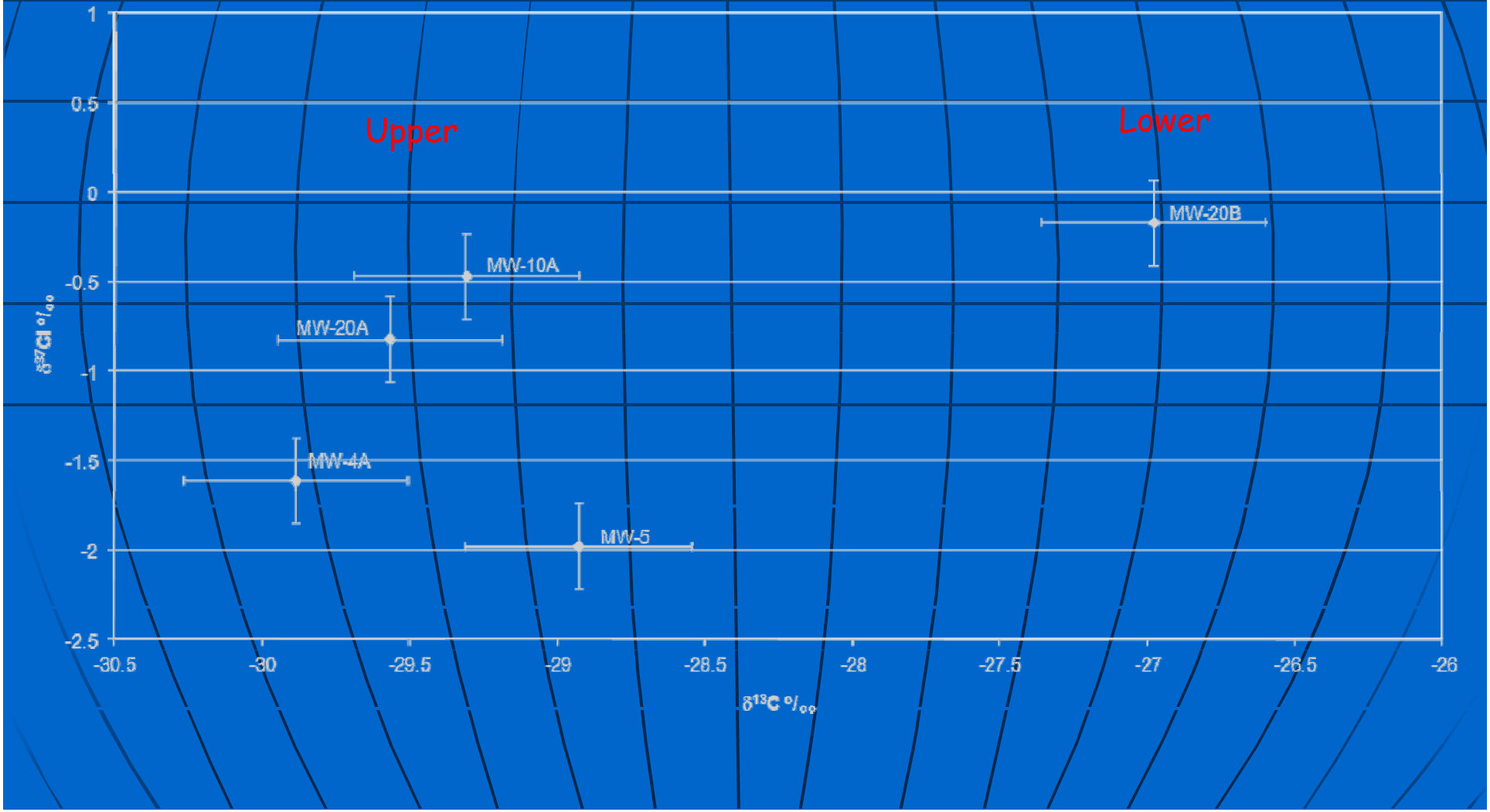
-27.0 -0.2

PCE in Multiple Aquifers



	$\delta^{13}C$	$\delta^{37}Cl$
	-29.6	-0.8
	-27.0	-0.2

PCE in Multiple Aquifers

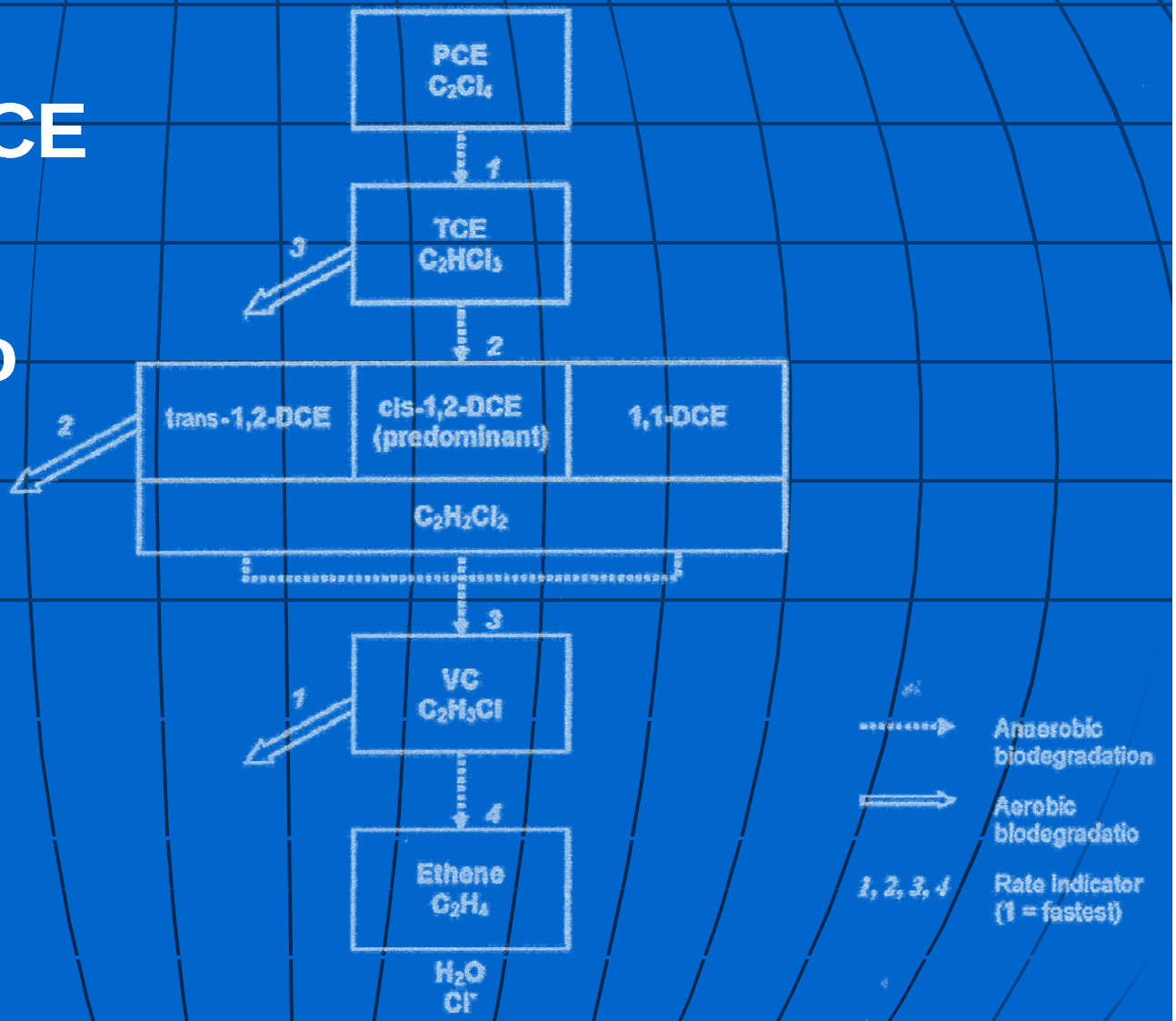


Conclusions

- Some differences in carbon and chlorine isotopes in upper aquifer
- Possibly different sources
- Significant differences between upper and lower aquifers in the same well
- Definitely different sources

PCE and TCE Degradation

As PCE or TCE degrades, isotopic ratio changes



PCE Degradation

^{12}C – X Bonds are weaker than ^{13}C – X Bonds

In a chemical reaction, ^{12}C – X Bonds break faster than ^{13}C – X Bonds

If reaction proceeds to completion – all PCE goes to TCE - isotope ratio in product is the same as in starting material

If reaction is partially completed, ^{12}C is concentrated in product, and ^{13}C is concentrated in starting material

Product (TCE) becomes lighter (more negative);
Starting material (PCE) becomes heavier (less negative)

Isotope Ratio Reconstruction

If isotope ratios and concentrations of daughter products are known, isotope ratio of initial PCE can be calculated

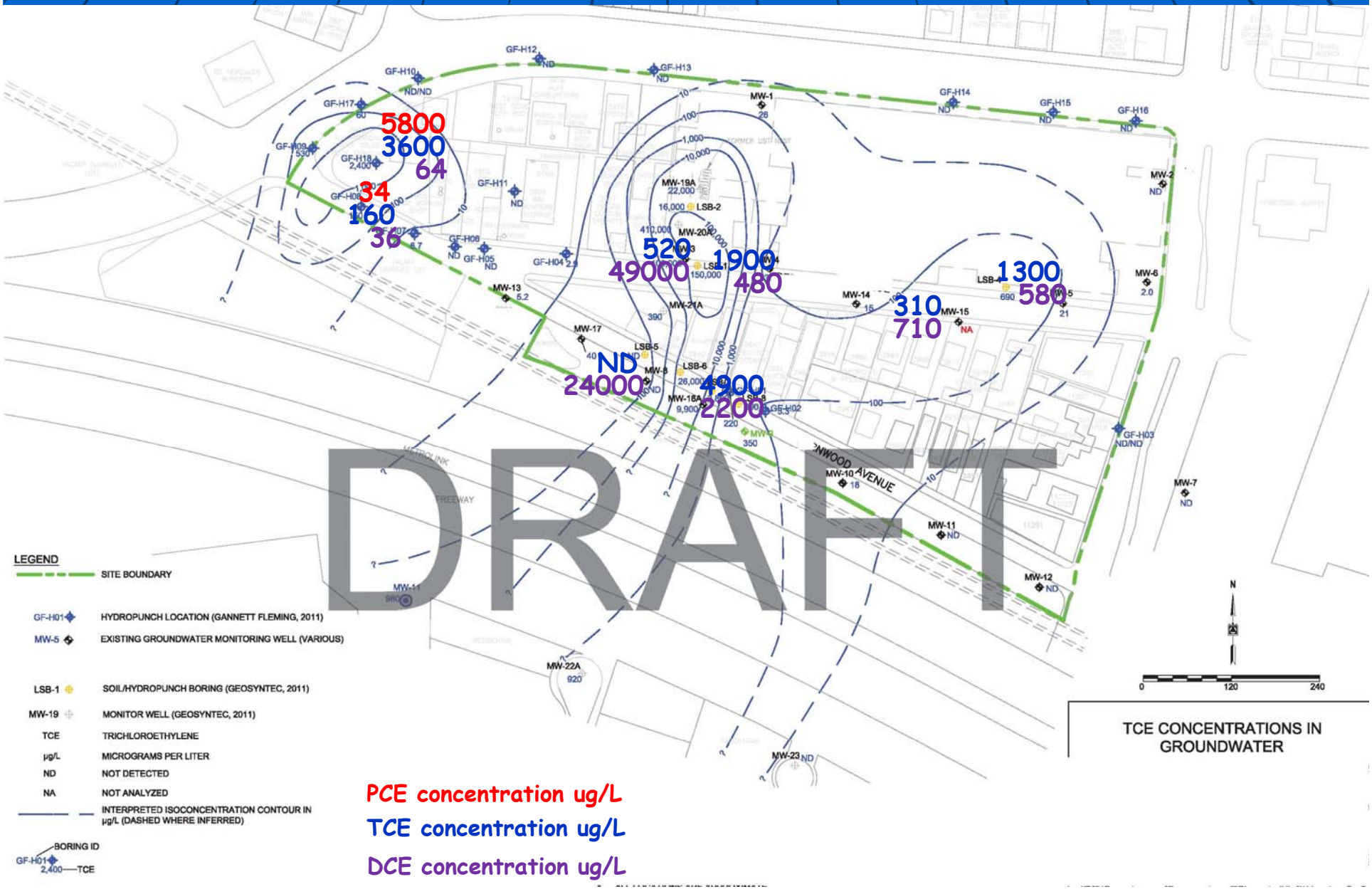
$$\text{Initial PCE } \delta^{13}C = \frac{\text{PCE moles} \times \delta^{13}C + \text{TCE moles} \times \delta^{13}C + \text{DCE moles} \times \delta^{13}C}{\text{PCE + TCE + DCE moles}}$$

Assuming no loss of PCE, TCE, DCE or other daughter products from the system

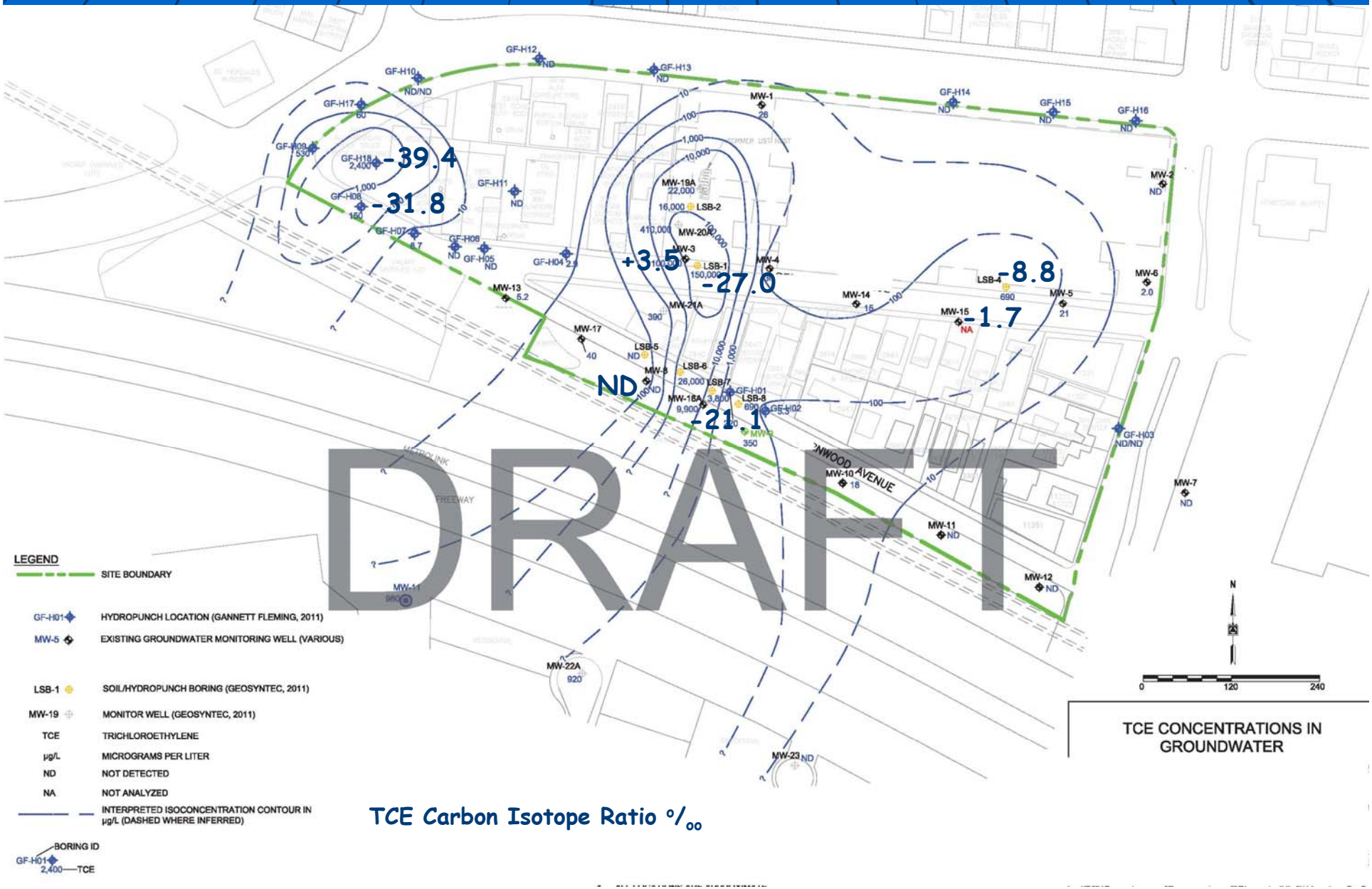
Case 2: Degraded PCE and TCE in Multiple Plumes

- Separate plumes with PCE, TCE, and cDCE – marked differences in degradation within plumes
- No vinyl chloride - little apparent loss of chlorinated solvents in the system
- Multiple TCE sources in the plumes?
- TCE in PCE plume from migration from TCE plumes?

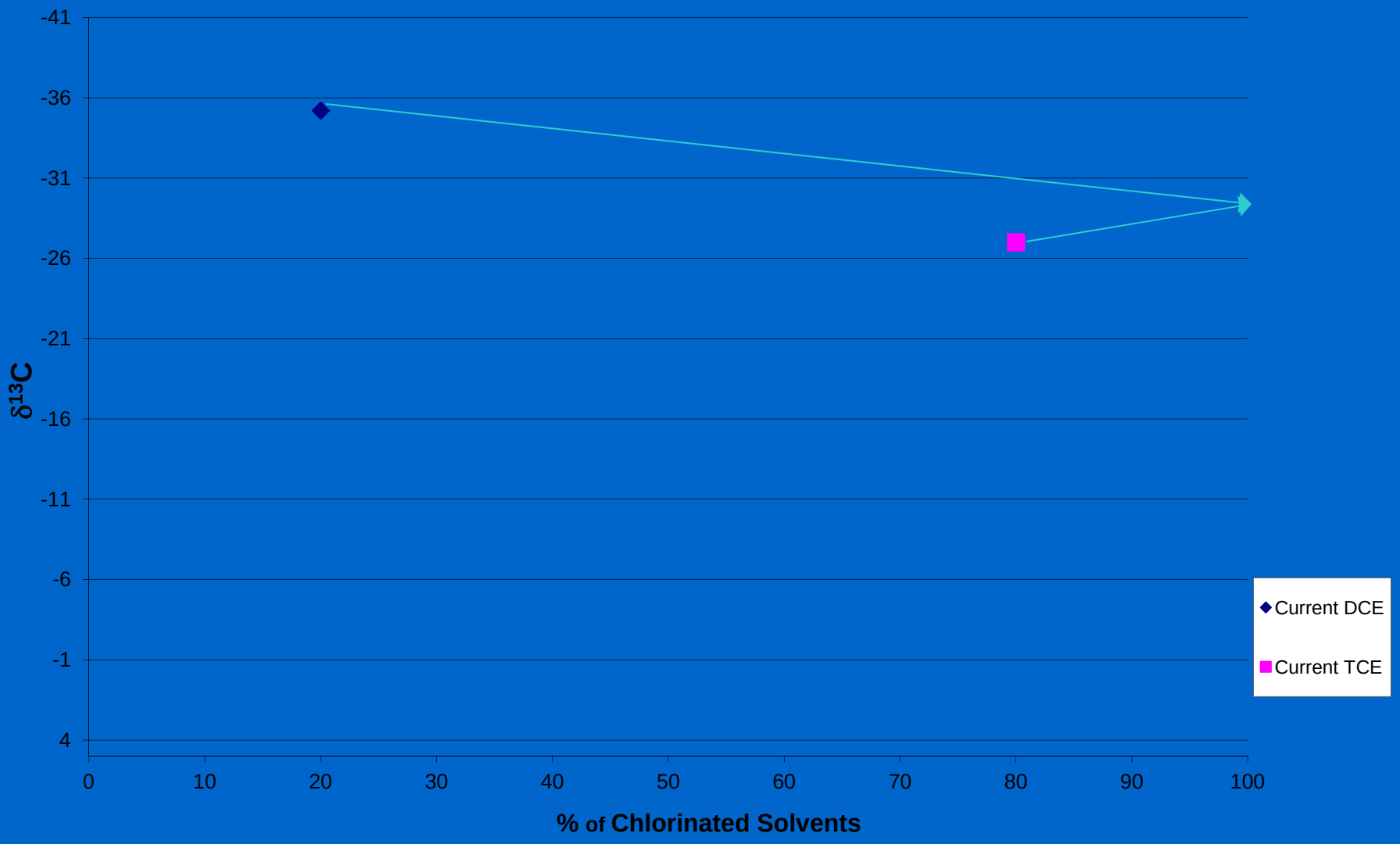
Plume Concentrations



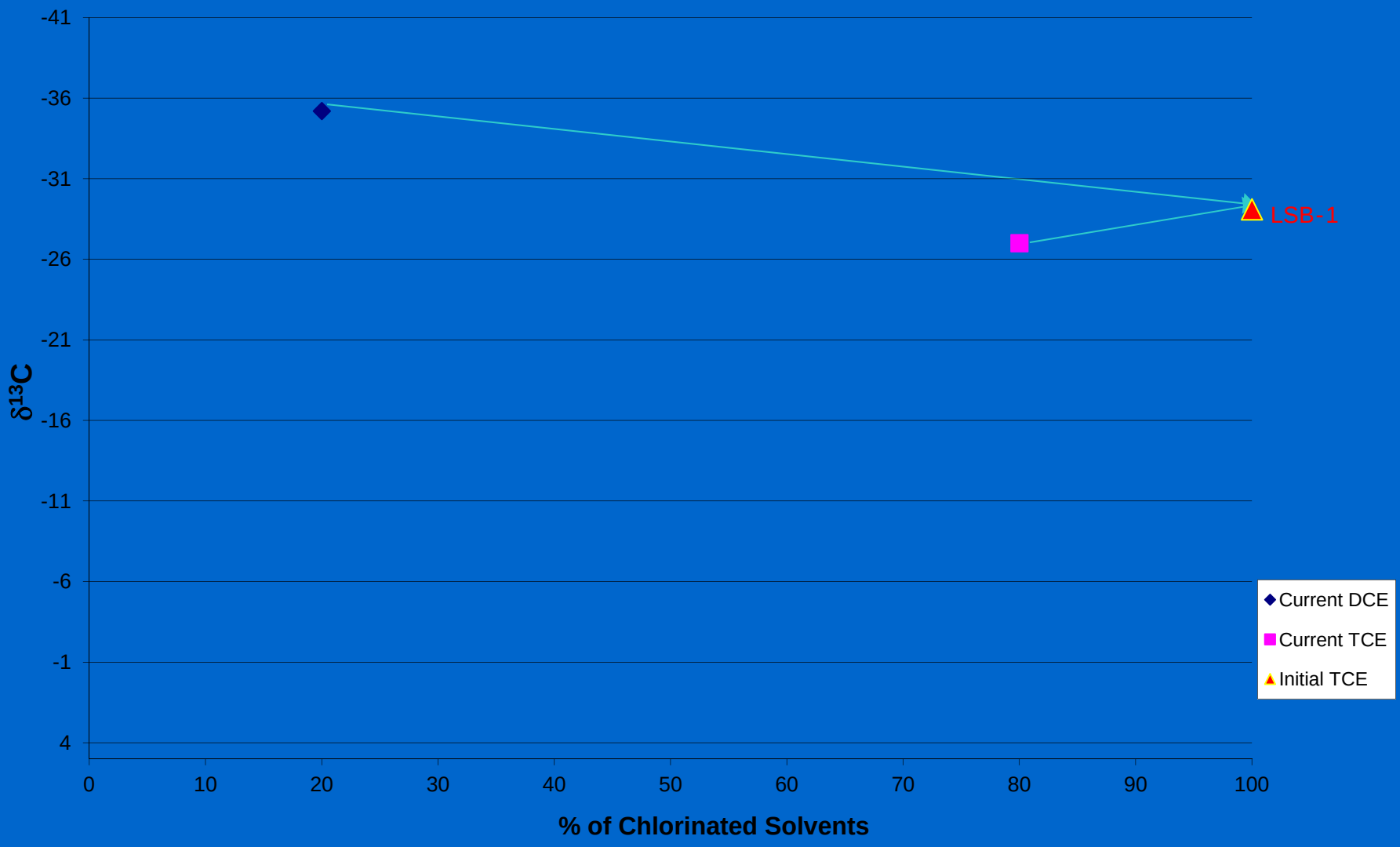
TCE Carbon Isotope Ratios



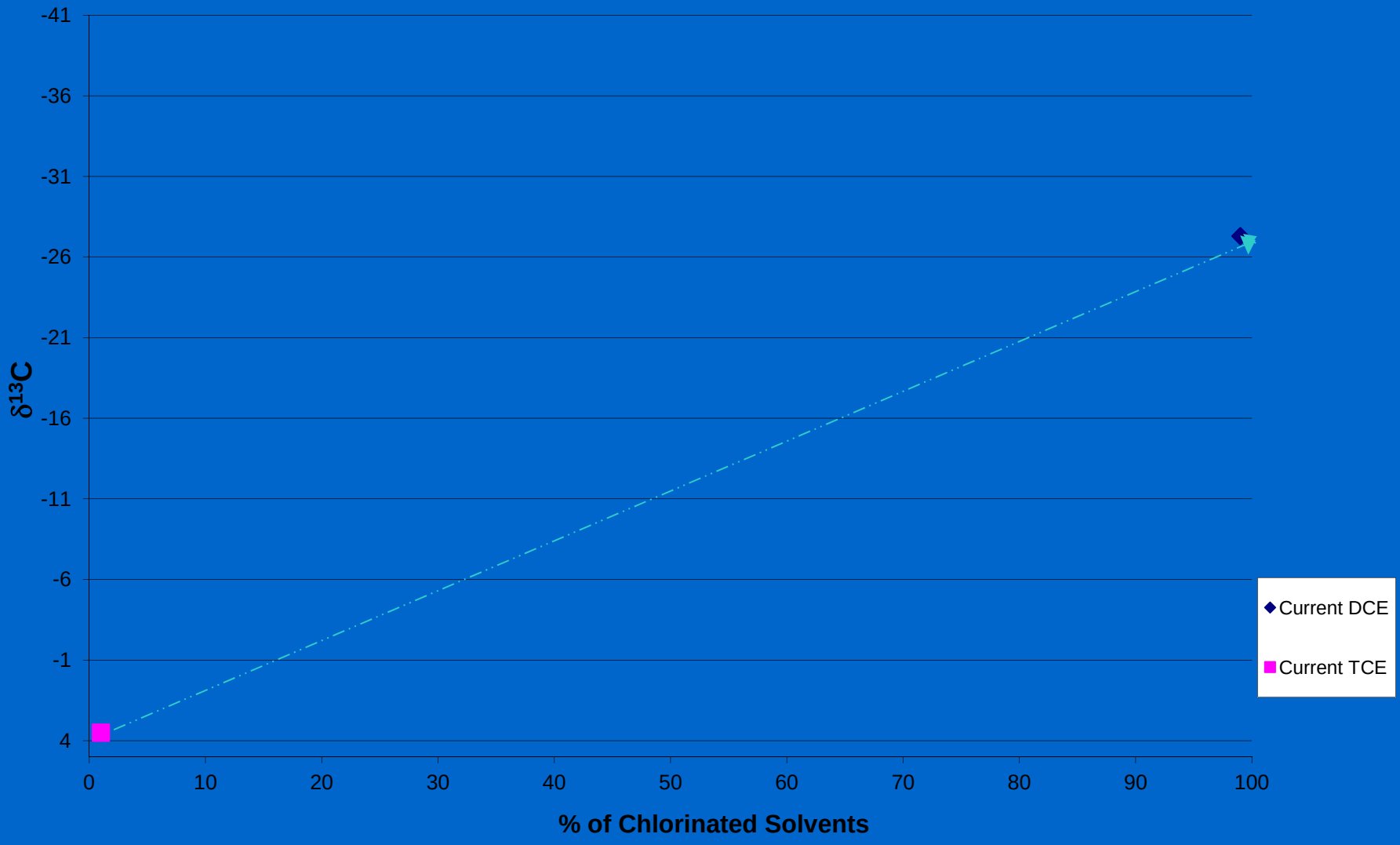
Carbon isotope ratios in Main Plume LSB-1



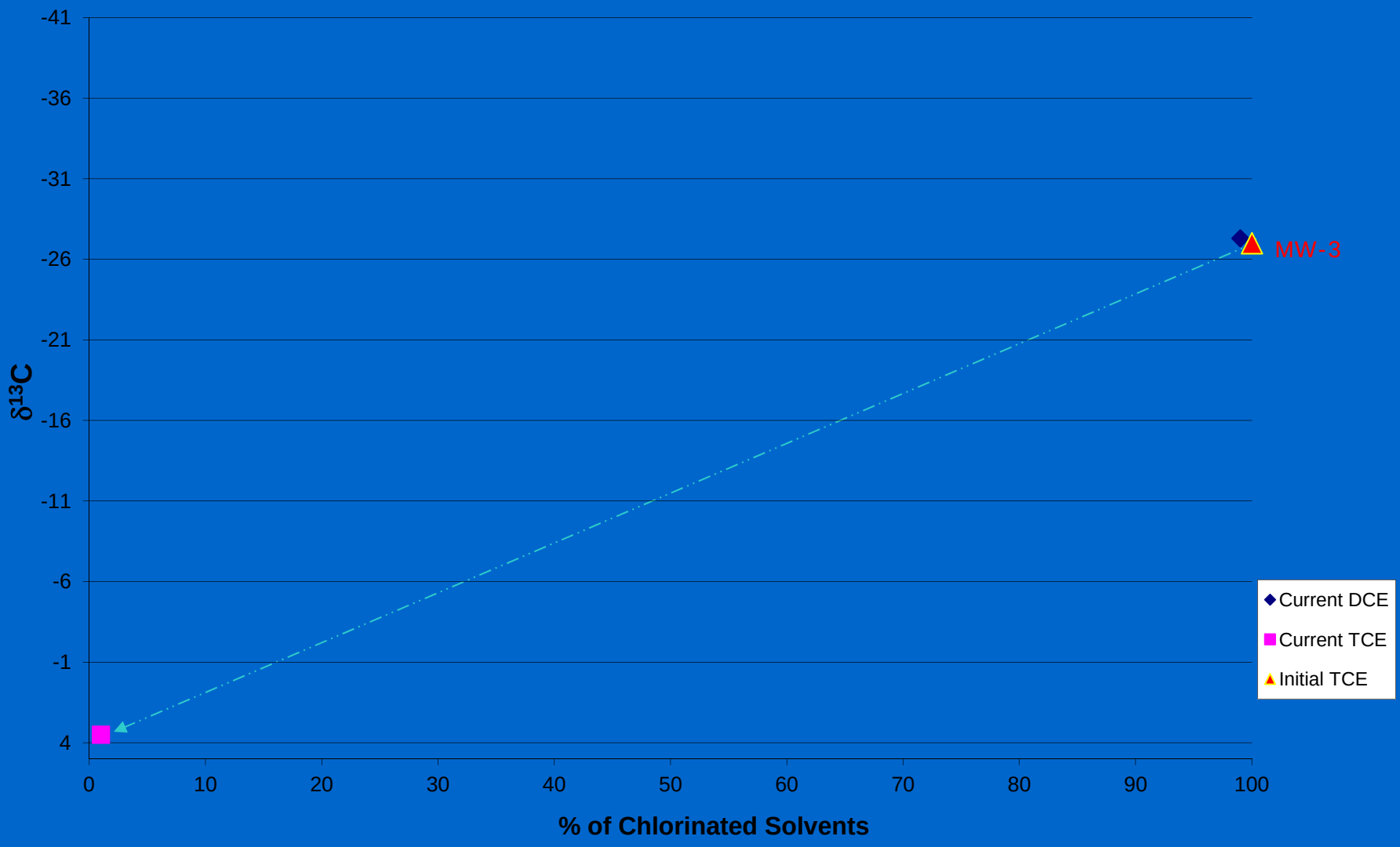
Carbon isotope ratios in Main Plume LSB-1



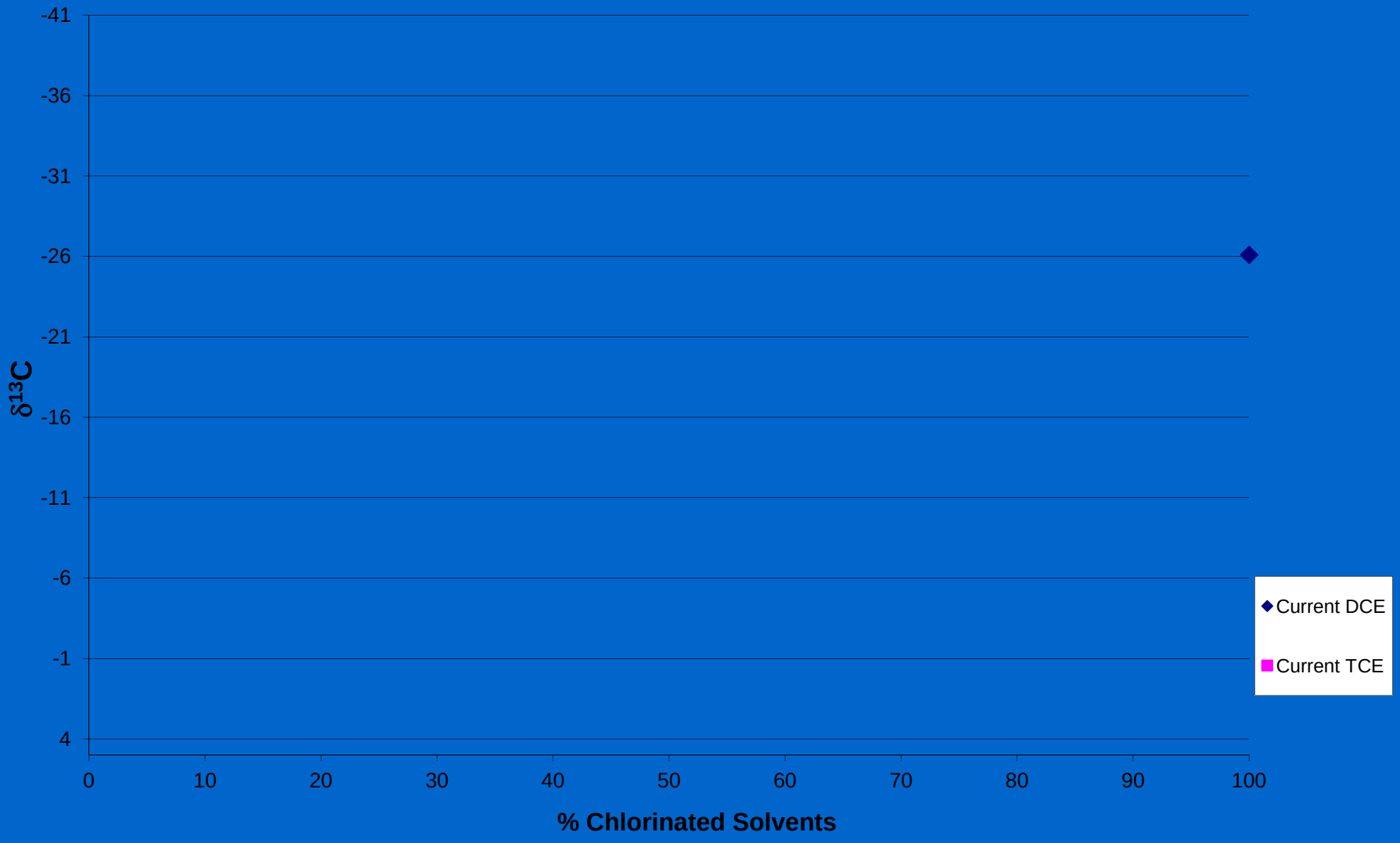
Carbon isotope ratio in Main Plume MW-3



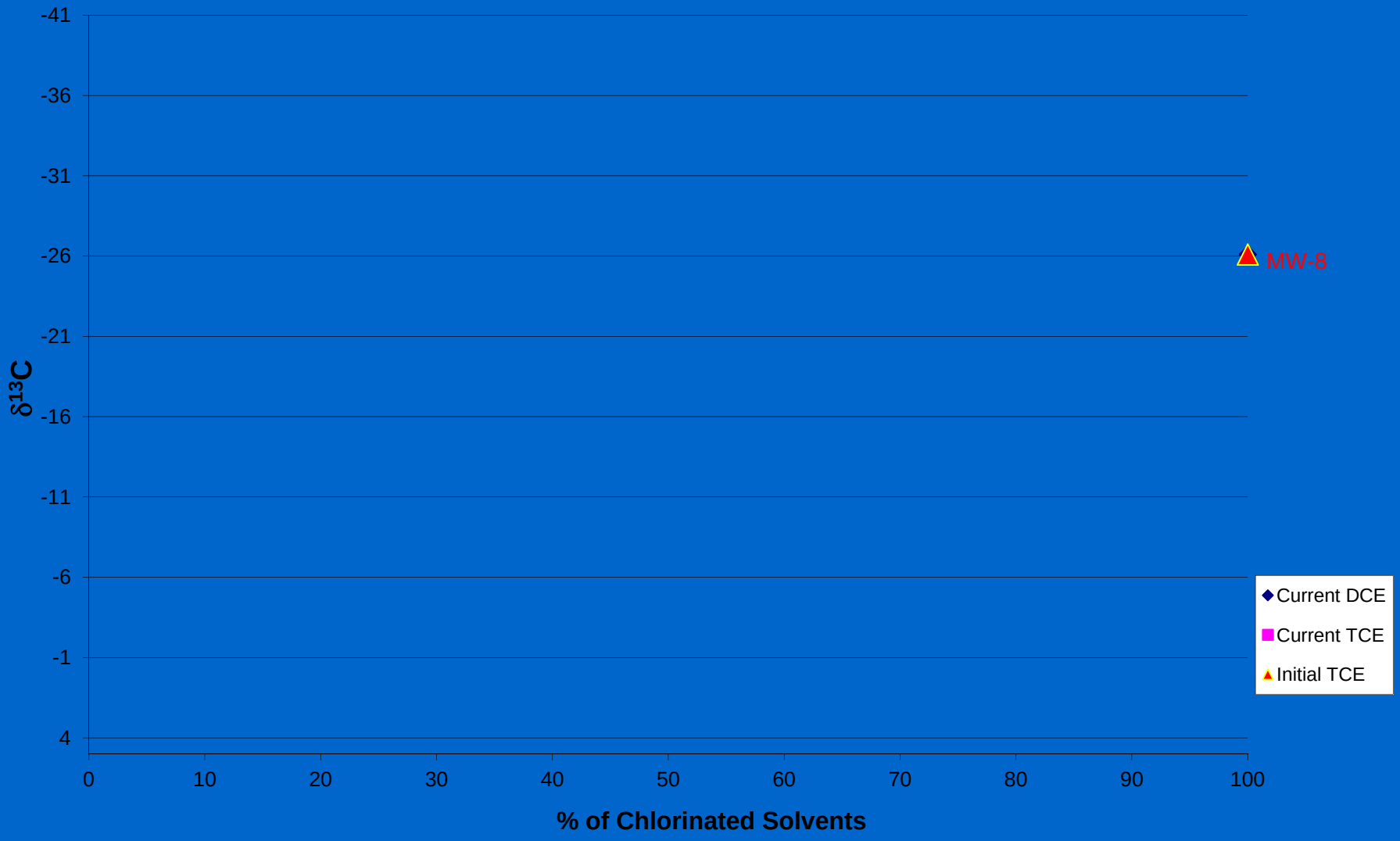
Carbon isotope ratio in Main Plume MW-3



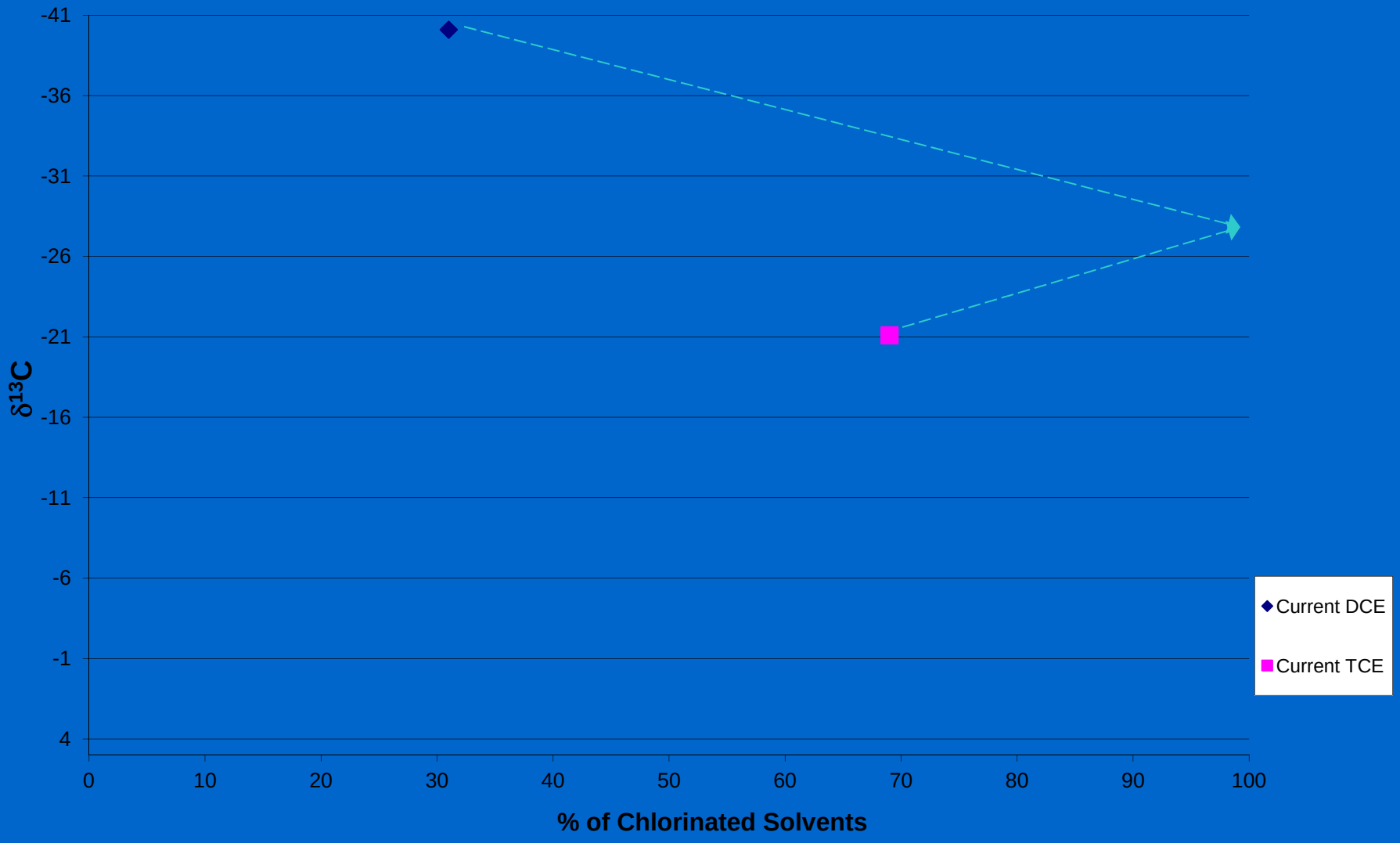
Carbon isotope ratios in Main Plume South MW-8



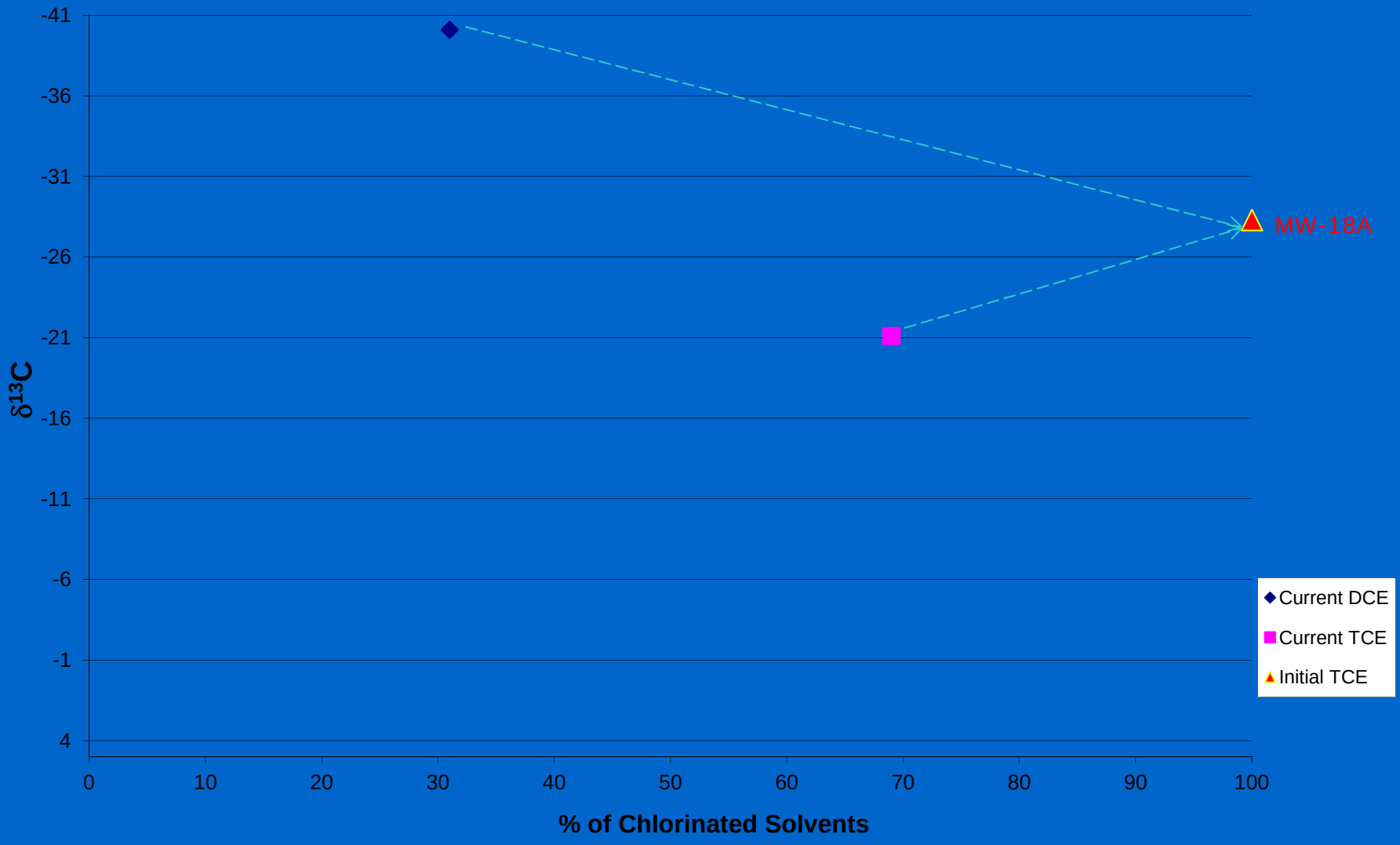
Carbon isotope ratios in Main Plume South MW-8



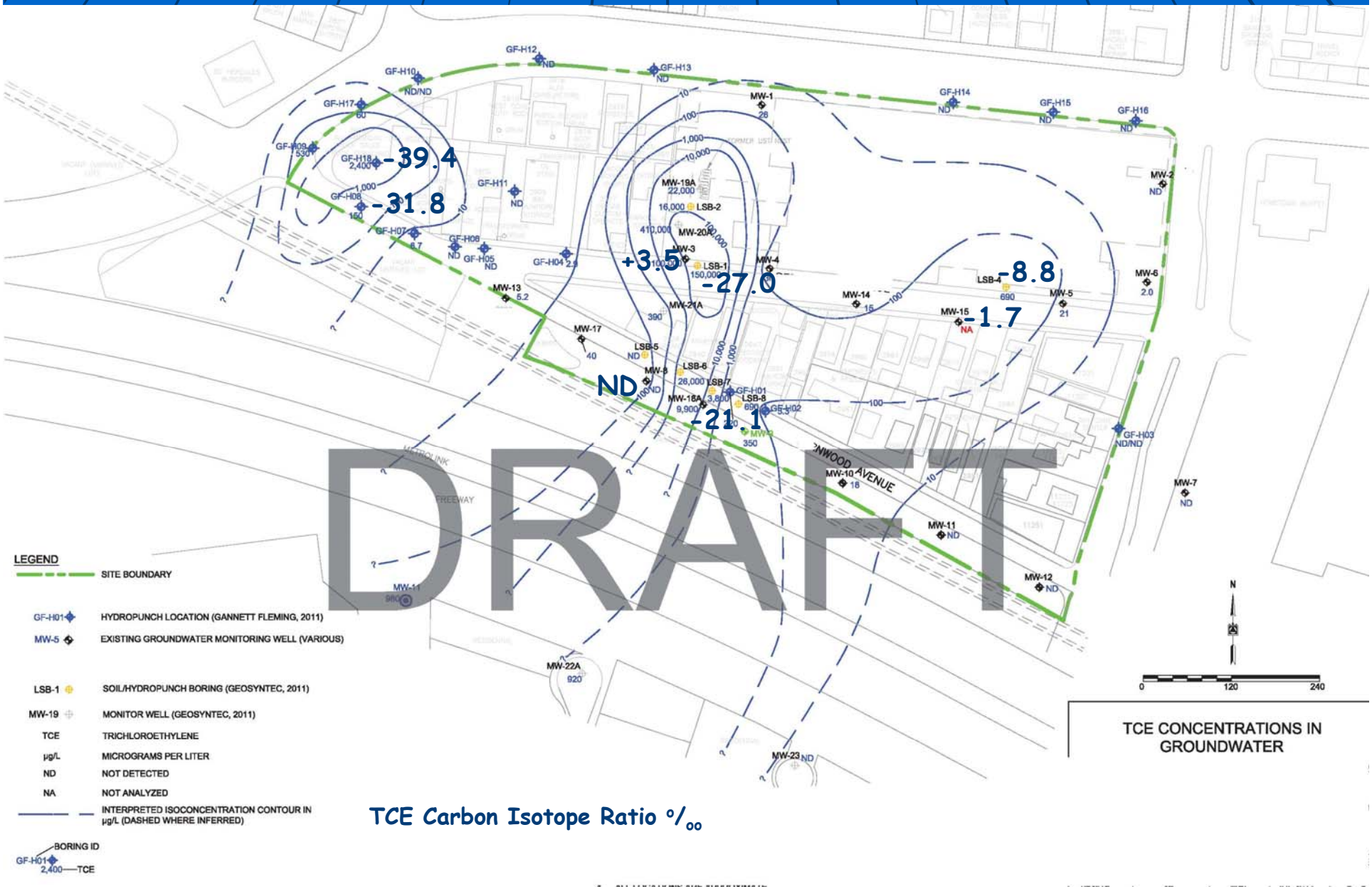
Carbon isotope ratios in Main Plume South MW-18A



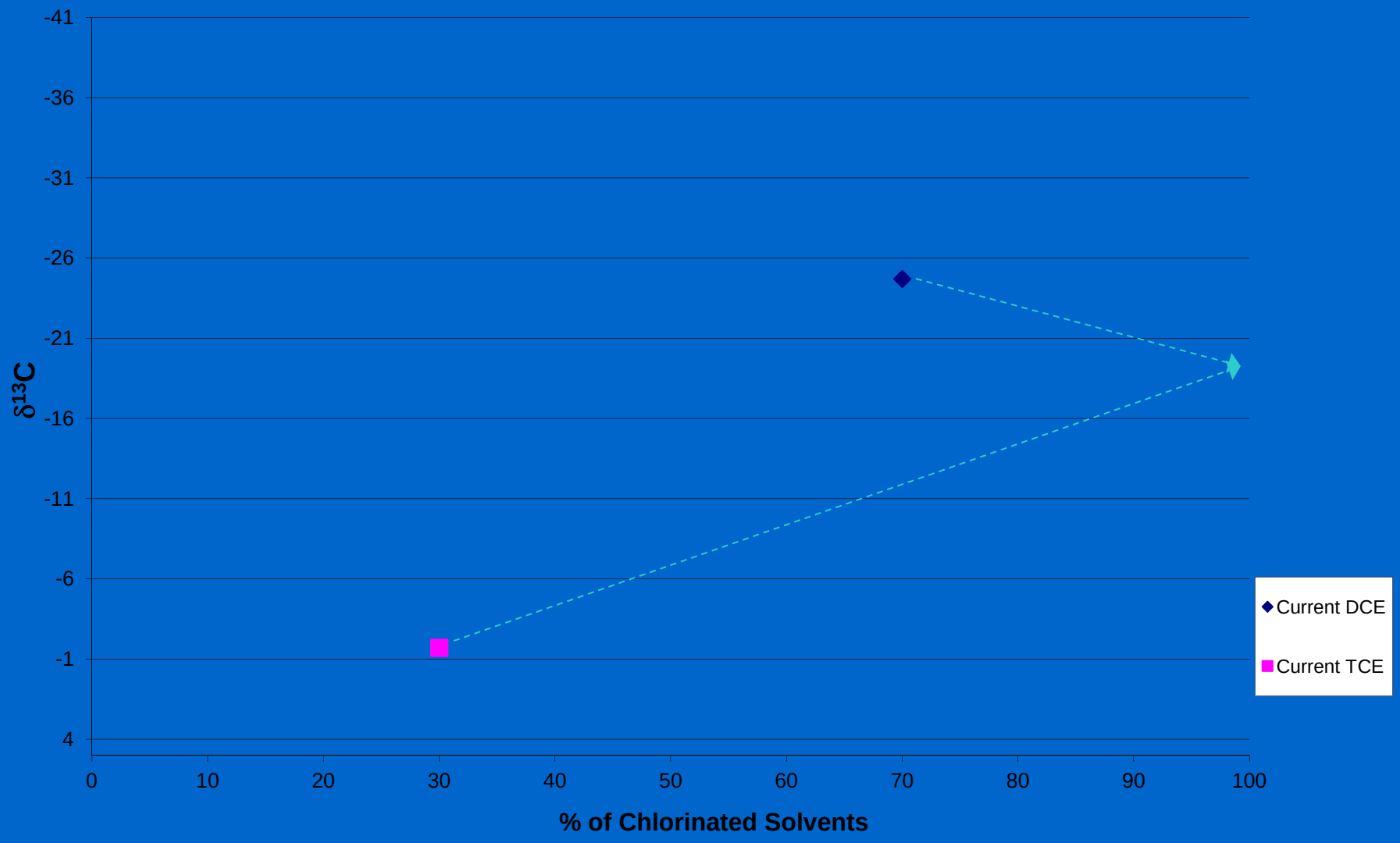
Carbon isotope ratios in Main Plume South MW-18A



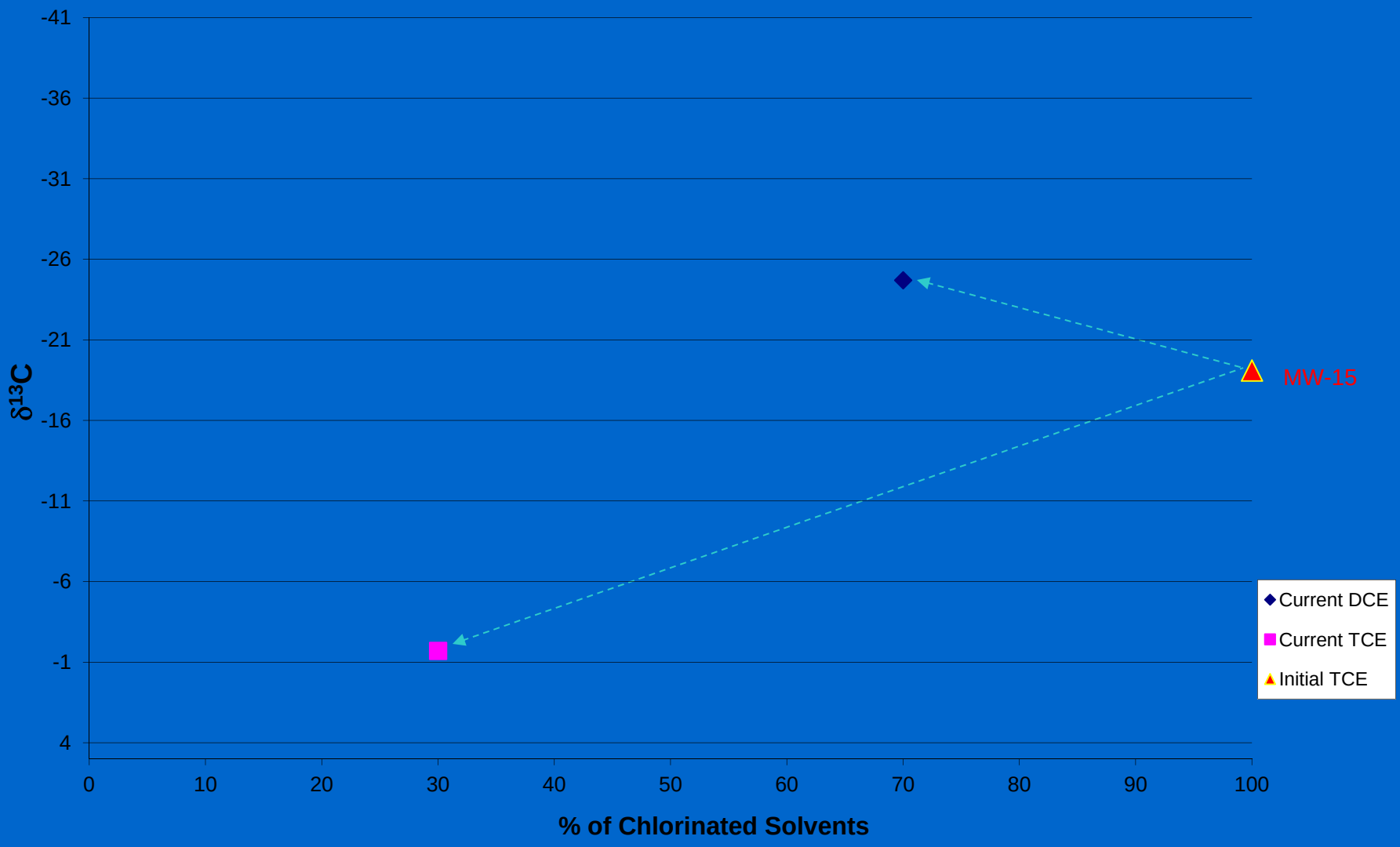
TCE Carbon Isotope Ratios



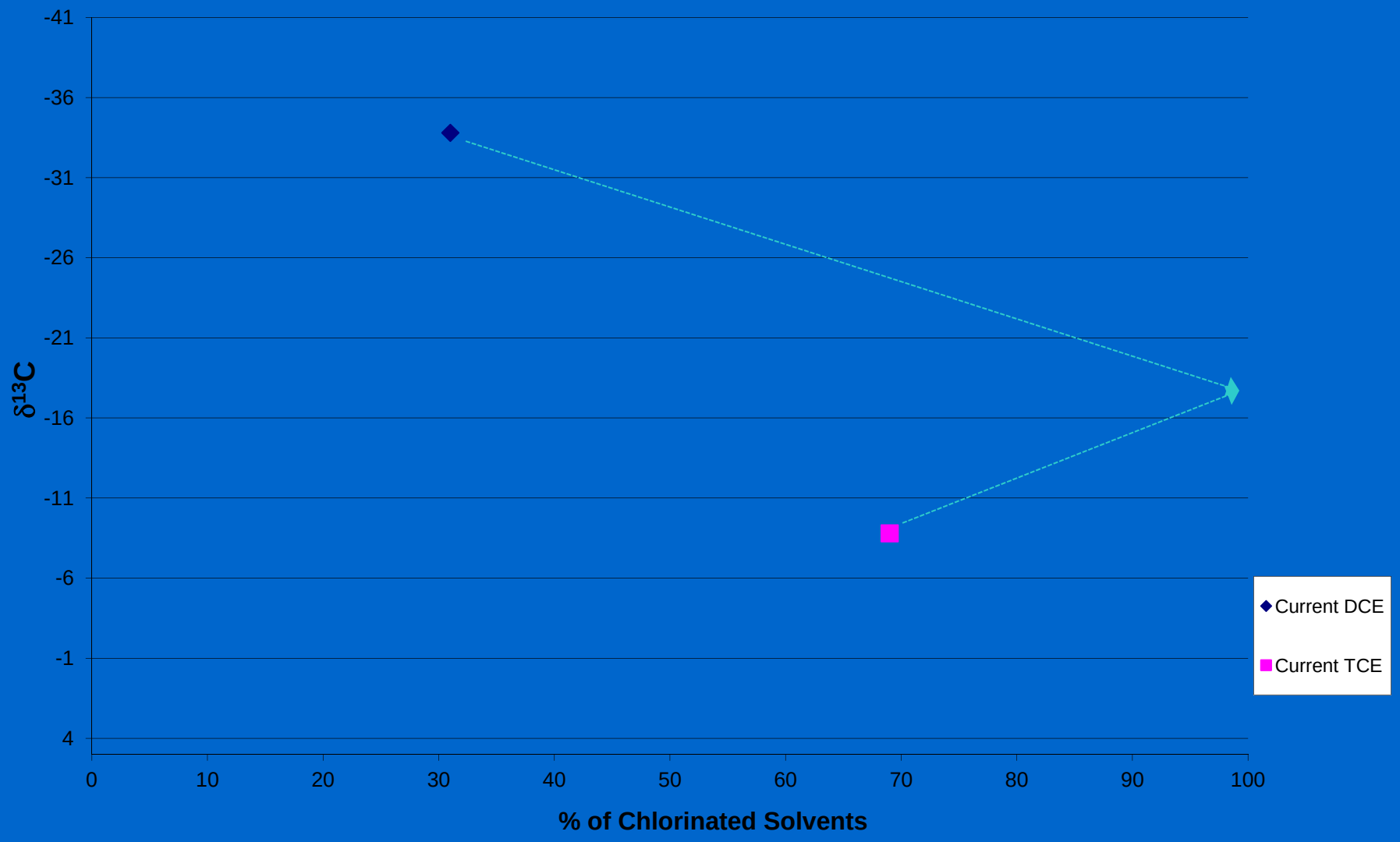
Carbon isotope ratios in East Plume MW-15



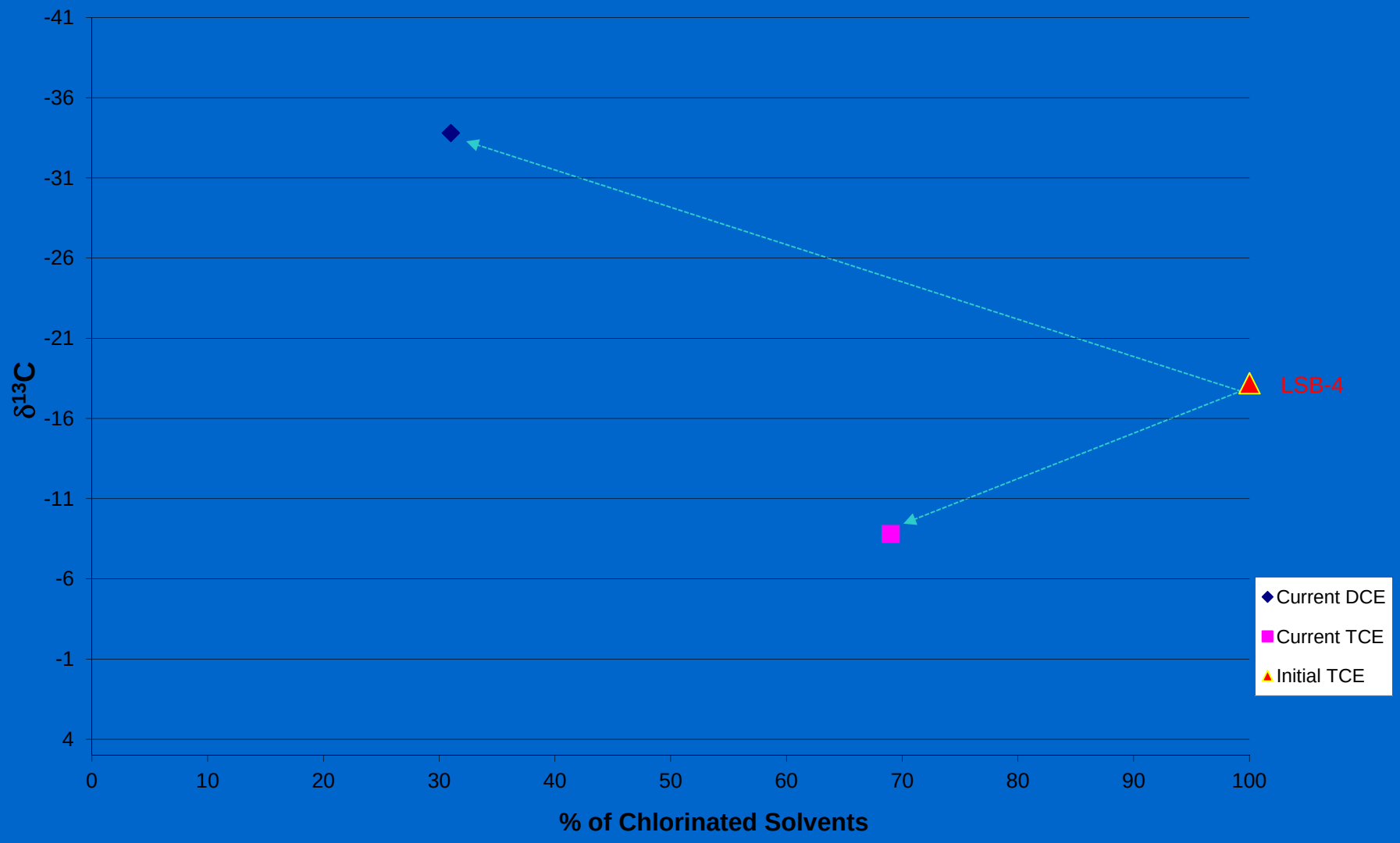
Carbon isotope ratios in East Plume MW-15



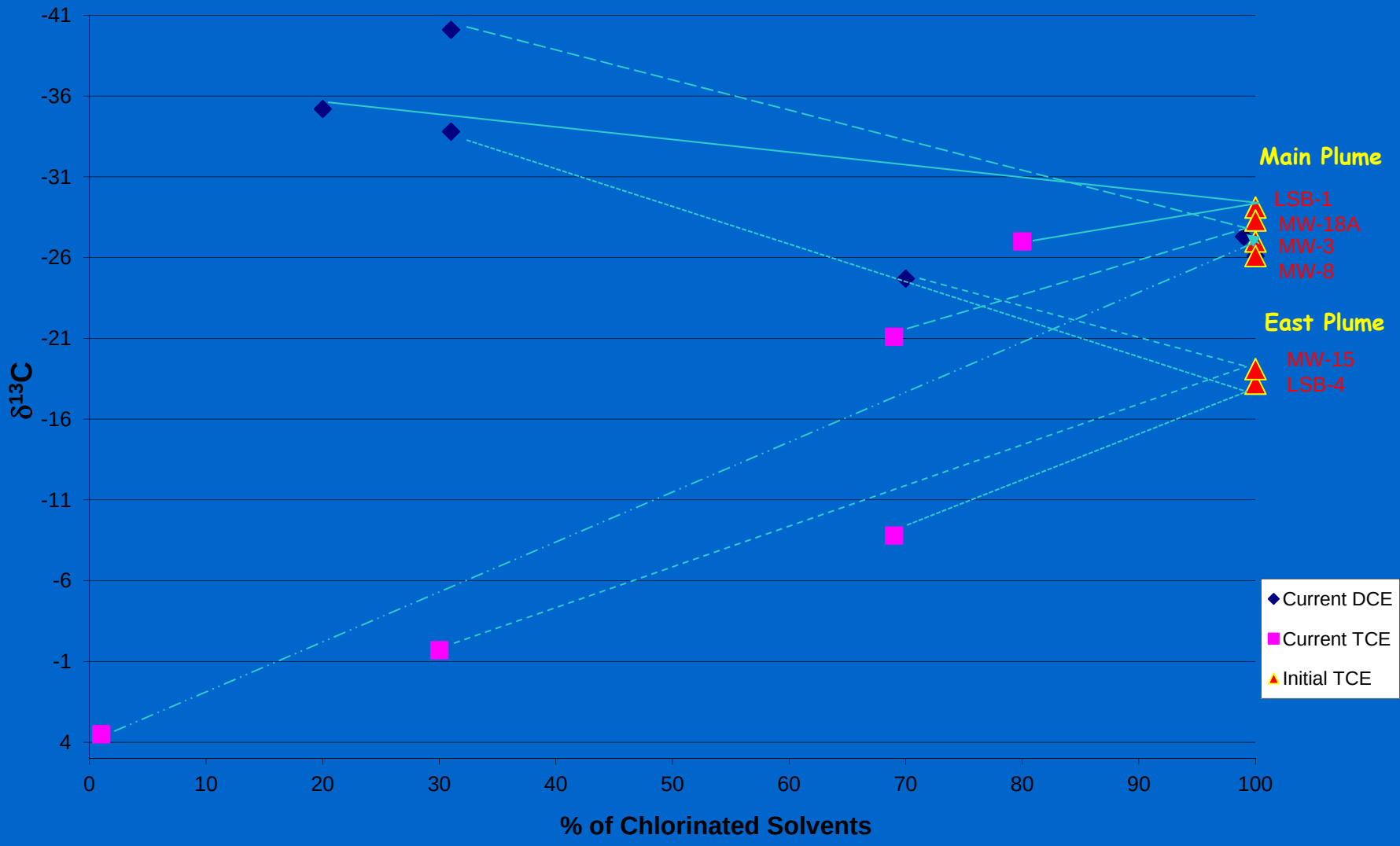
Carbon isotope ratios in East Plume LSB-4



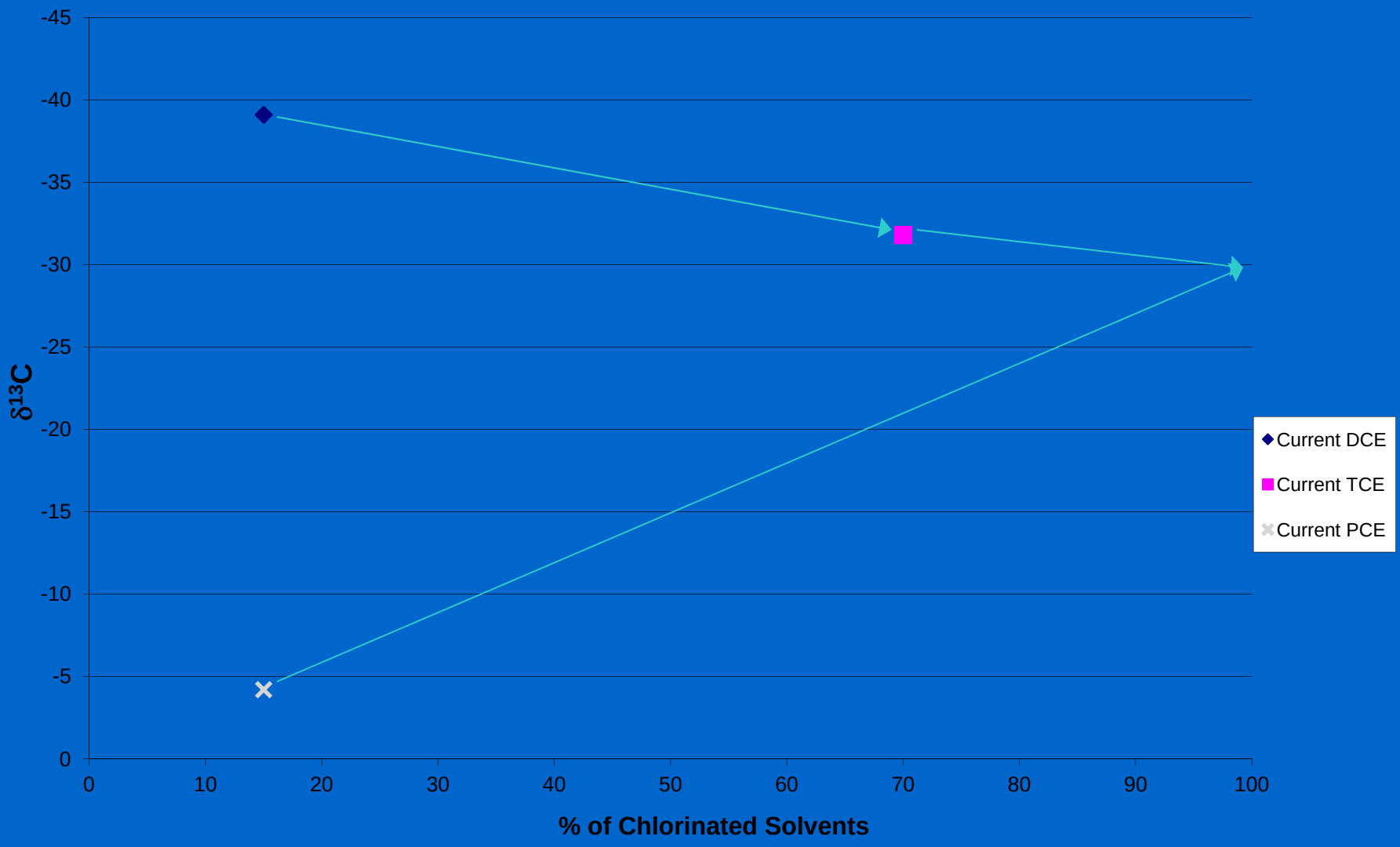
Carbon isotope ratios in East Plume LSB-4



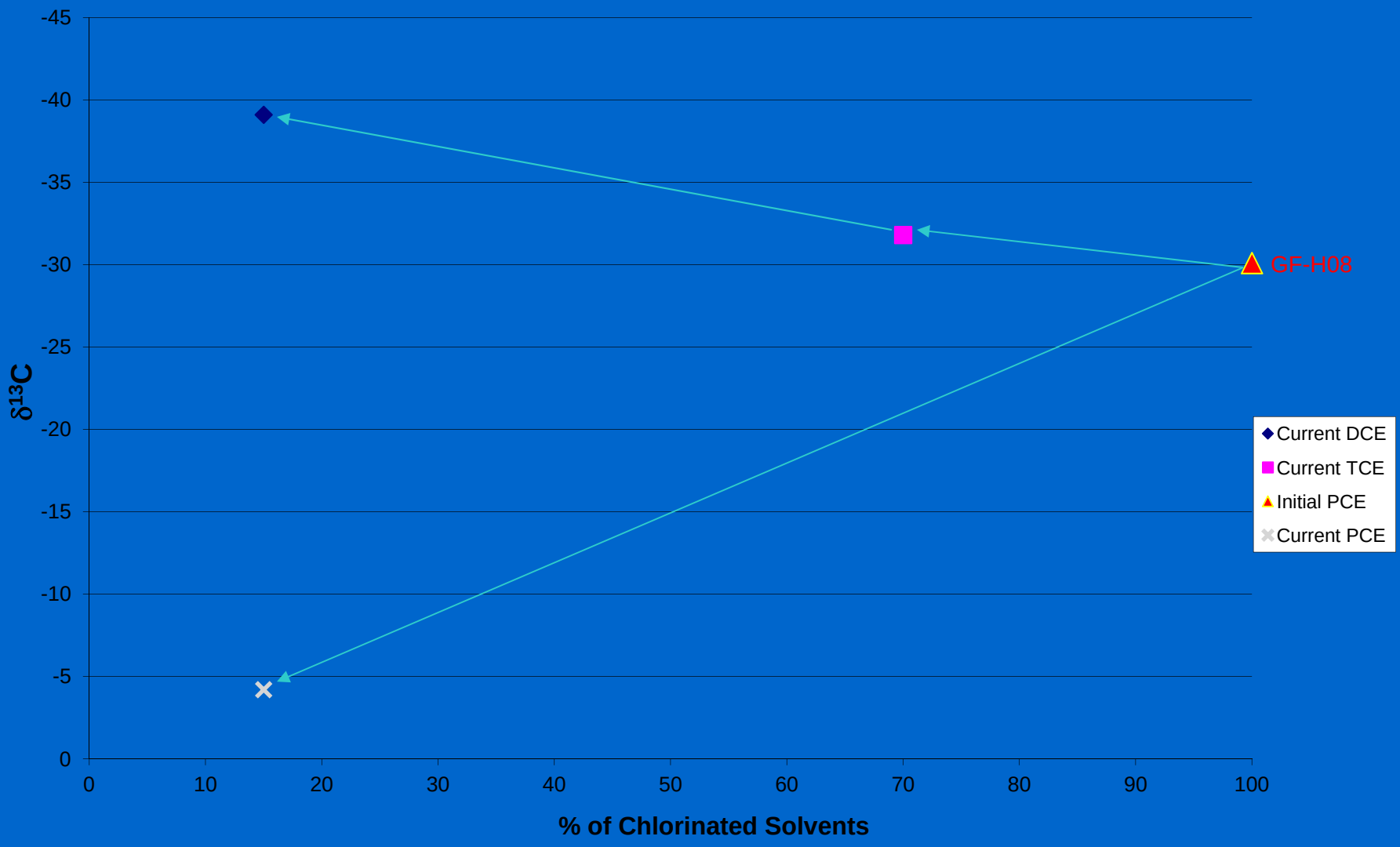
Carbon isotope ratios in Main Plume and East Plume



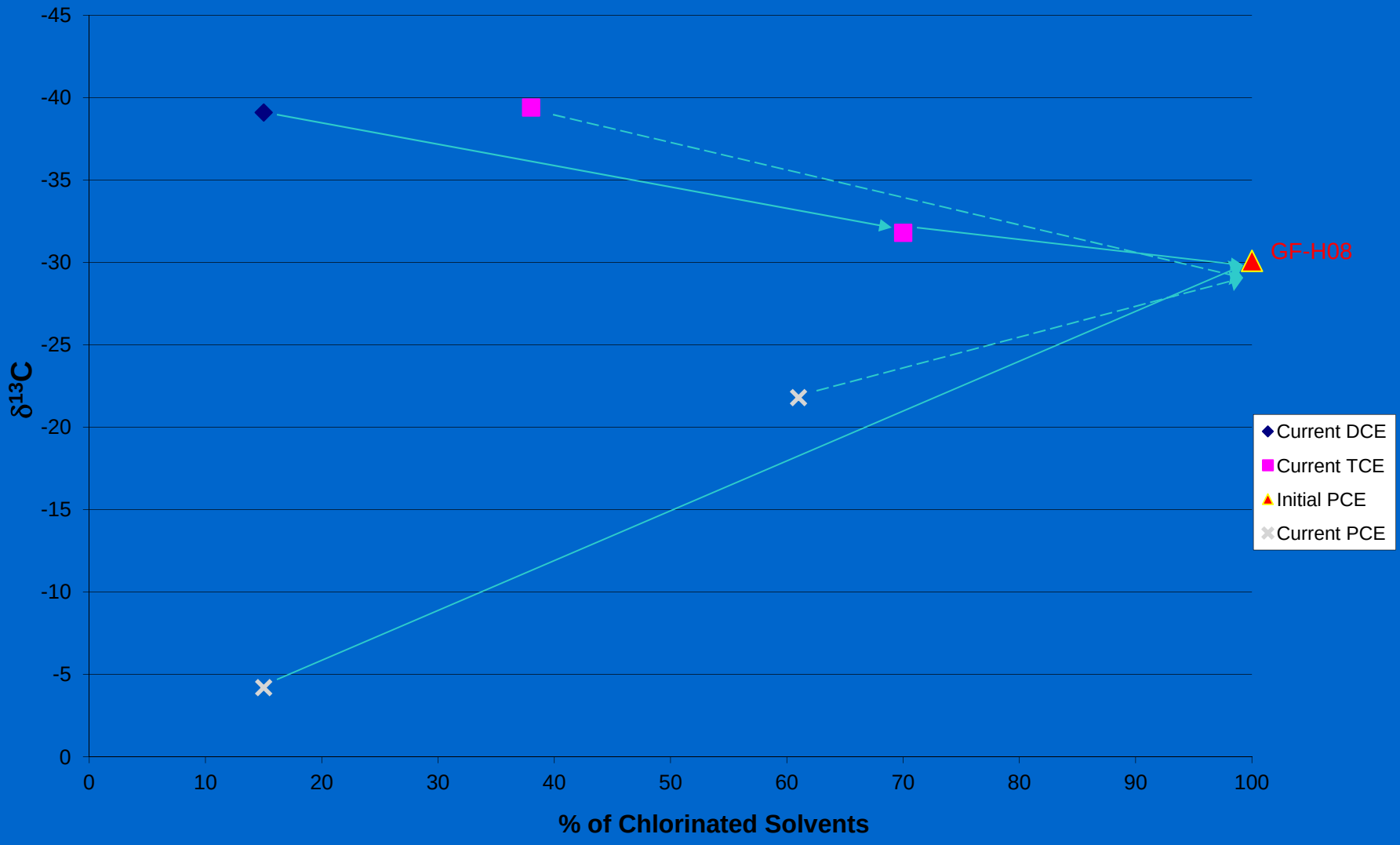
Carbon isotope ratios in West Plume GF-H08



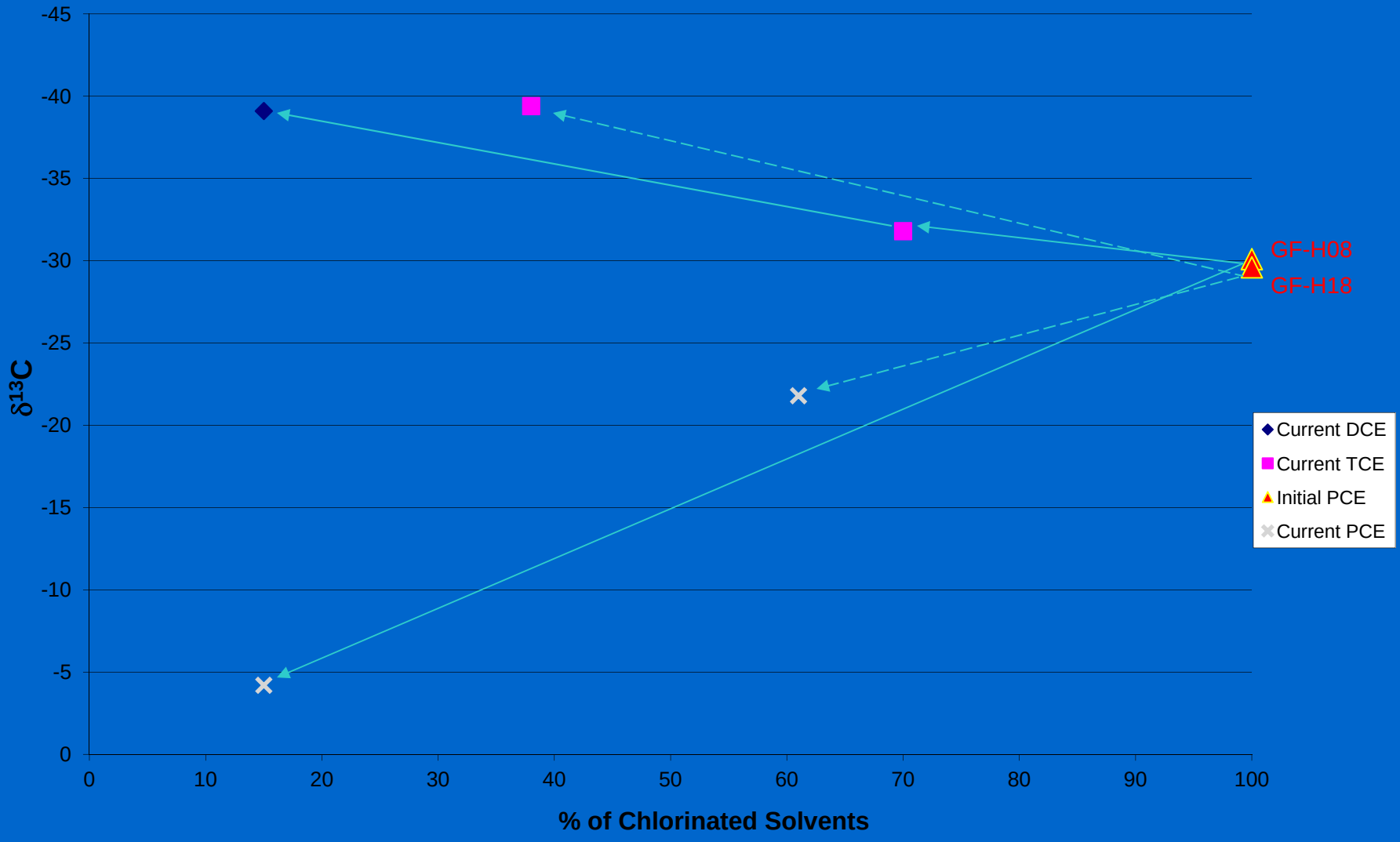
Carbon isotope ratios in West Plume GF-H08



Carbon isotope ratios in West Plume GF-H08 and GF-H18



Carbon isotope ratios in West Plume GF-H08 and GF-H18



Conclusions

- Isotope ratio reconstruction shows at least three chlorinated solvent releases:
- TCE in Main Plume
- Different TCE in East Plume
- PCE in West Plume with no contribution from TCE plumes