



Chlorinated solvent impacts in volatile F1 petroleum hydrocarbon groundwater data: Is it significant and what can be done about it?



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The Problem:

- My site has a history of chlorinated solvent (cVOC) impacts,
 - PCE, TCE, TCA, DCE, DCA, VC etc.
- No known source of petroleum hydrocarbon volatiles:
 - e.g. gasoline, varsol, kerosene, diesel



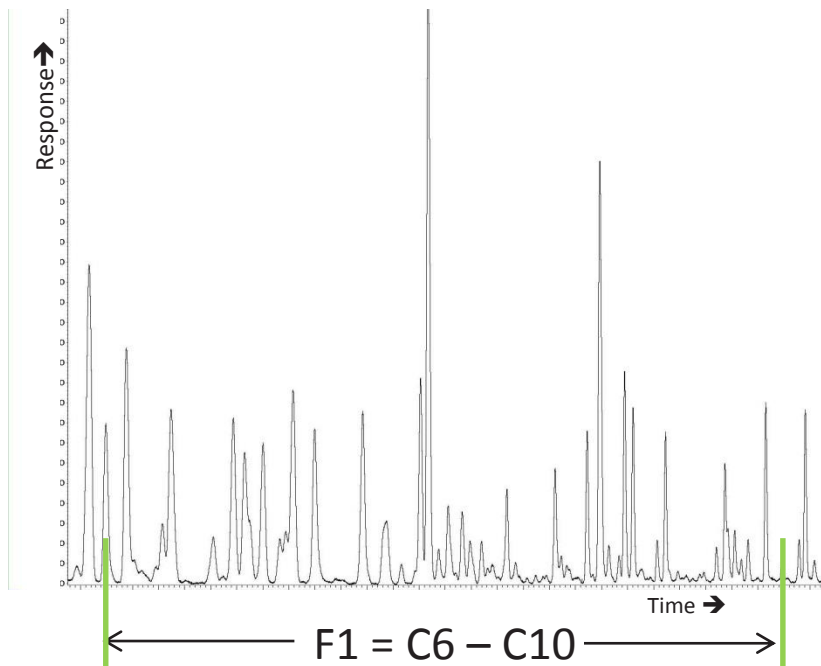
Why does my report show both chlorinated solvent and F1 exceedances?

Short (Unsatisfactory) Answer

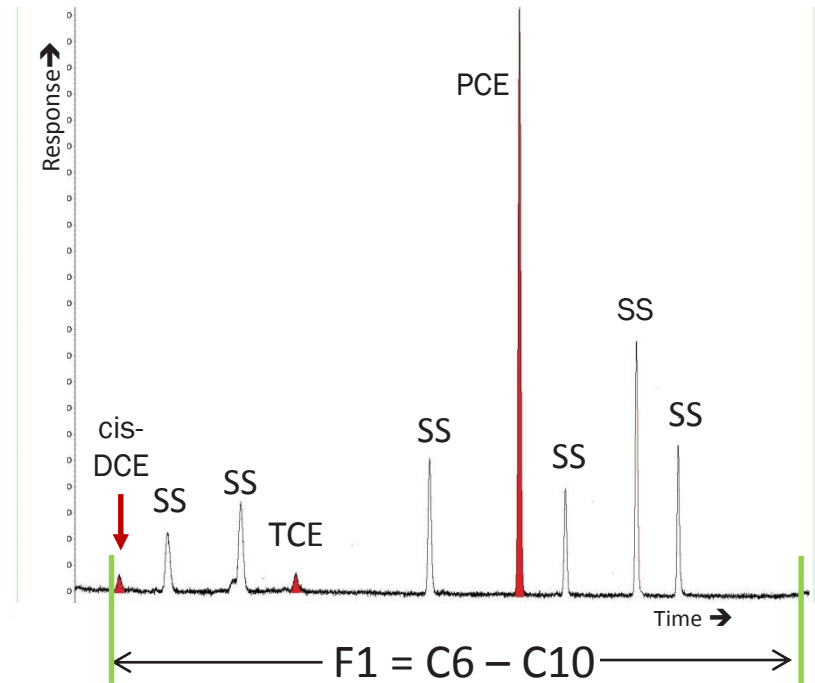
- Standard F1 method not designed to isolate just the volatile PHCs.
 - Gas Chromatography / FID detector.
 - FID detectors respond to anything with a carbon.
- Anything that comes off the GC column in the C6 to C10 range, and responds to an FID, is reported as F1.
- Some cVOC are in this range.

F1 (Gasoline) and cVOC Chromatograms

Gasoline GC-FID Signal



cVOC GC-FID Signal

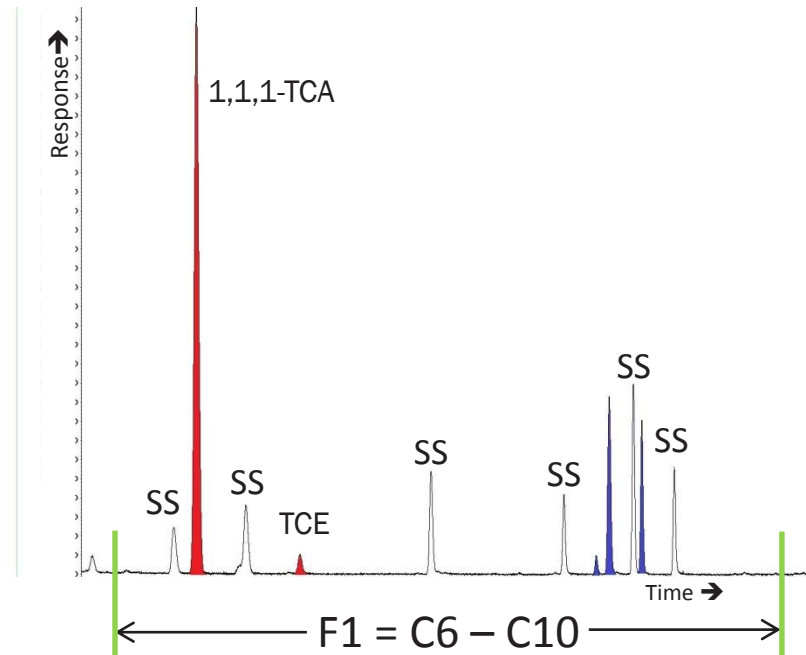


SS: system standards

What cVOC elute in the same window?

- cis 1,2-dichloroethylene: DCE
(not trans or 1,1-DCE)
- all trichloroethylene: TCE
- tetrachloroethylene: PCE
- all dichloroethane: DCA
- all trichloroethane: TCA
- tetrachloroethane: PCA

cVOC GC-FID Signal



Why is this a problem?

- F1 and chlorinated solvents are regulated separately.
- Not reasonable to have chlorinated solvent impacts alone result in F1 exceedances.
- What solutions are available?

Can we just subtract the total cVOC concentration from the F1 concentration?

Sample A

Compound	Conc. (µg/L)	Compound	Conc. (µg/L)
Benzene	<0.2	1,1-DCA	19
Toluene	3	cis 1,2-DCE	157
Ethyl benzene	<0.2	PCE	<0.2
Total Xylenes	<0.2	111-TCA	2
F1	768	112-TCA	16
F1-BTEX	765	TCE	2,900
		Total cVOC	3,100

Sample B

Compound	Conc. (µg/L)	Compound	Conc. (µg/L)
Benzene	32	1,1-DCA	3,000
Toluene	17,000	cis 1,2-DCE	17,000
Ethyl benzene	4,300	PCE	2,200
Total Xylenes	83,000	111-TCA	29,000
F1	124,000	112-TCA	500
F1-BTEX	20,000	TCE	19,000
		Total cVOC	71,000

No – This does not work!

Why doesn't this work??

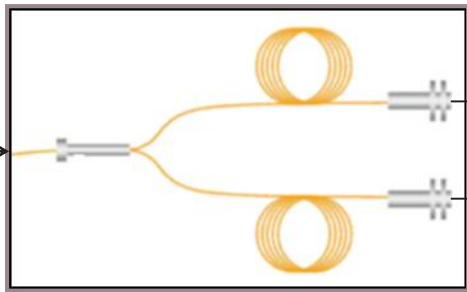
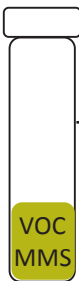
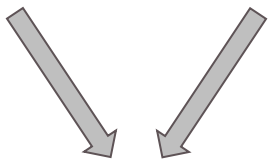
- cVOC - reported by GC/MS.
- F1 - reported by GC/FID

GC/MS/FID System

- cVOCs have much lower responses to FID than BTEX and F1
 - response factors are lower by ~3-5x



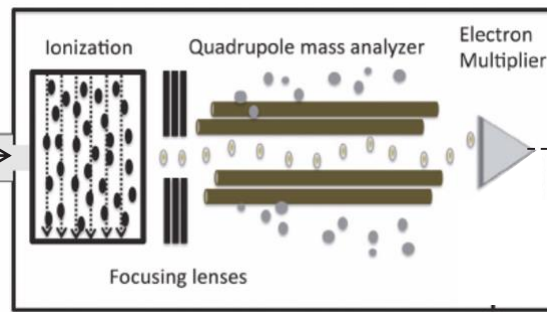
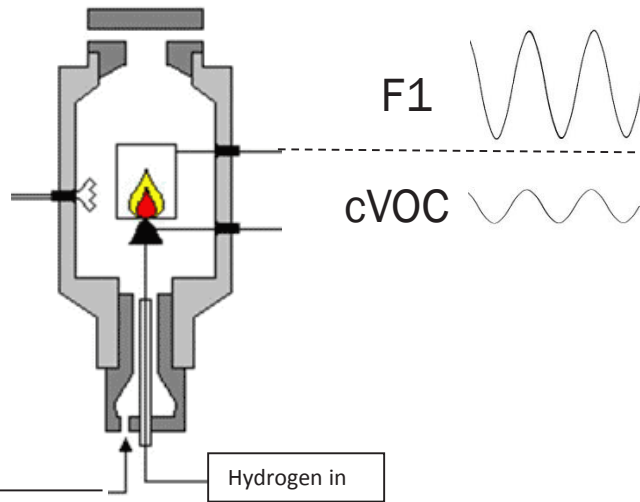
System Standards



Gas Chromatograph

Flame Ionization Detector

Measures anything that has a carbon



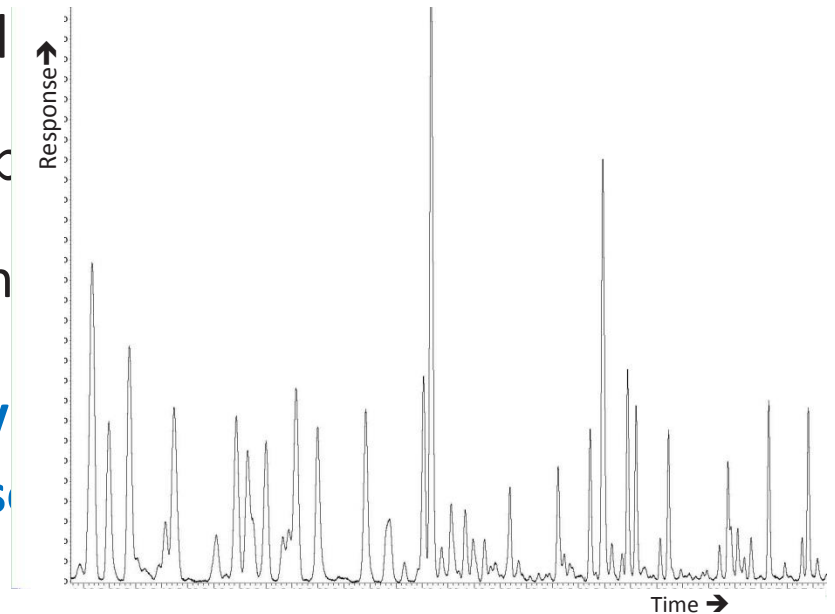
Mass Spectrometer
Measures only selected masses

GC/MS/FID System

How is F1 Measured?

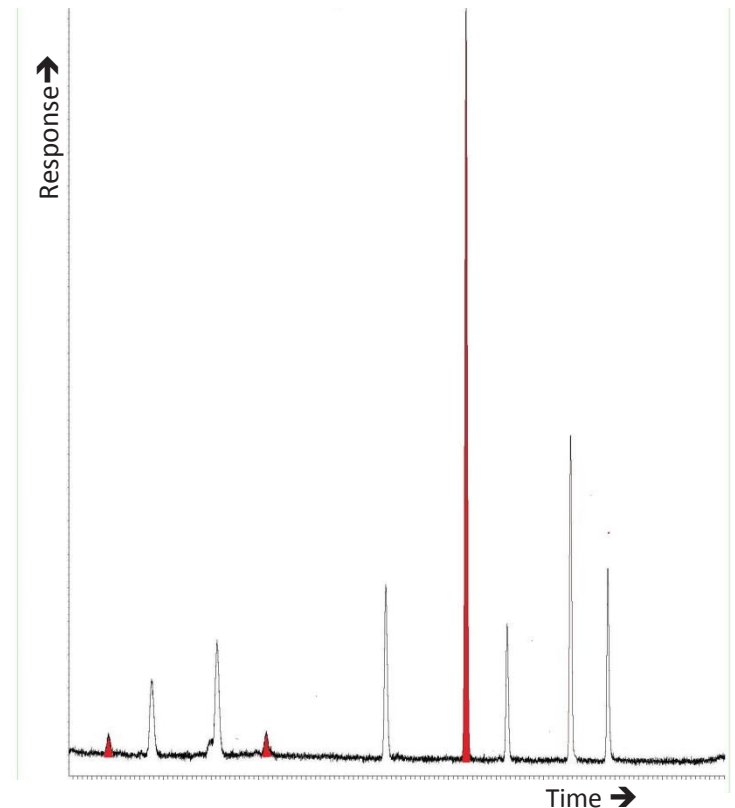
1. Total area under all peaks from C6 – C10 is measured.
2. A PHC F1 response factor is calculated: calibration curve.
 - $RF = F1 \text{ concentration} / \text{peak area}$.
 - All hydrocarbons have similar response factors.
 - cVOC have ~3-5x lower response factors.
3. Peak area multiplied by F1 response factor.

Because cVOC RF is too low, F1 cVOC concentrations would be low-bias



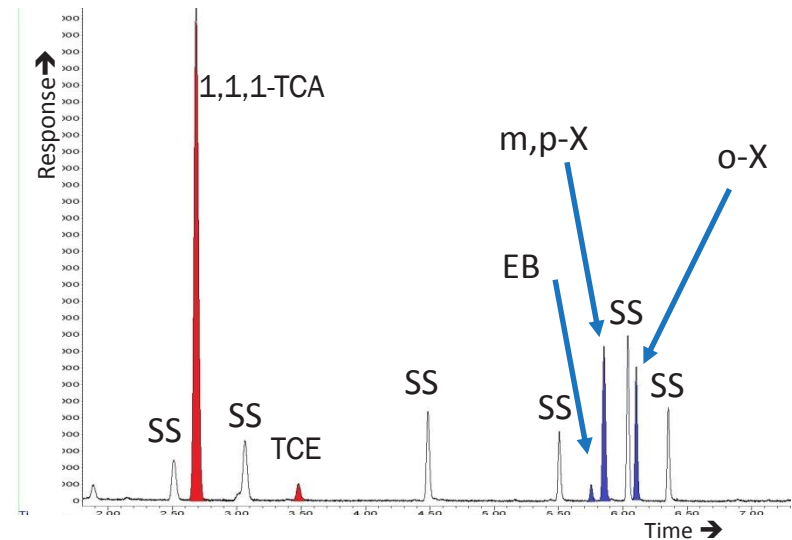
As a Result:

- Highlighted peaks are cis-DCE, TCE and PCE.
 - No BTEX
 - No gasoline signature
- cVOC in F1 measured at 30 $\mu\text{g/L}$
- cVOC actually = 170 $\mu\text{g/L}$



Solution:

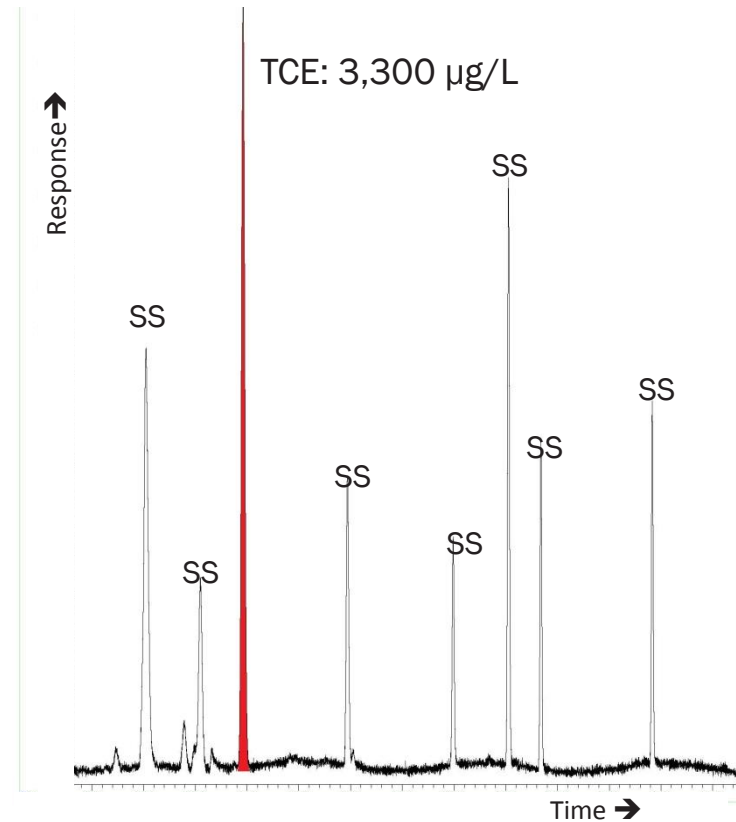
- Measure total F1 area of cVOC peaks.
- Calculate F1 equivalent cVOC concentration.
- Subtract cVOC contribution from the total F1 concentration.
- Visual confirmation: chromatogram interpretation.



Example 1: F1 + cVOC

	Concentration ($\mu\text{g}/\text{L}$)
Total F1	1,800
BTEX	70
F1- BTEX	1,730
F1 cVOC contribution	1,000
F1-BTEX-CVOC	730
Actual CVOC*	3,500

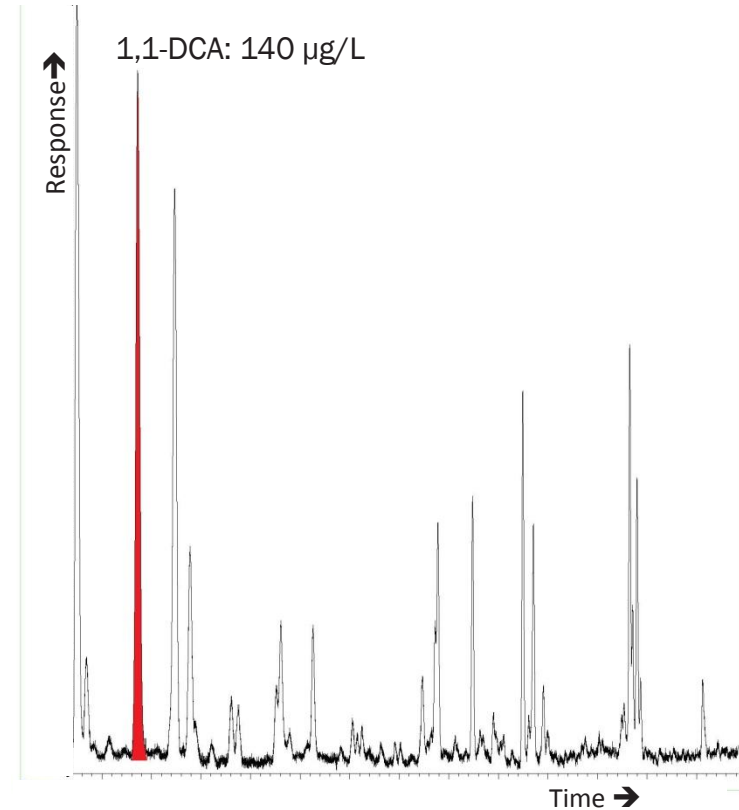
*mostly TCE



Example 2: F1 + cVOC

	Concentration ($\mu\text{g}/\text{L}$)
Total F1	90
BTEX	30
F1- BTEX	60
F1 cVOC contribution	5
F1-BTEX-CVOC	55
Actual CVOC*	160

*mostly 1,1-DCA



Is This a Satisfactory Solution?

- **Pros:**
 - Quantitative elimination of cVOC interference.
 - Specific – visual confirmation from chromatogram.
- **Cons:**
 - Time consuming = expensive.
 - Not routine, not accredited.
 - Real F1 peaks can interfere with measuring cVOC peak areas.

What Can Report Data Tell Us?

Sample A

Compound	Conc. (µg/L)
Benzene	<0.2
Toluene	3
Ethyl benzene	<0.2
Total Xylenes	<0.2
F1	768
F1-BTEX	765

F1 ≈ F1-BTEX

Compound	Conc. (µg/L)
1,1-DCA	19
cis 1,2-DCE	157
PCE	<0.2
111-TCA	2
112-TCA	16
TCE	2,900
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F1 > F1-BTEX

Compound	Conc. (µg/L)
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cis 1,2-DCE	17,000
PCE	2,200
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TCE	19,000
Total cVOC	71,000

Total cVOC 3-5x F1-BTEX

Checks for Possible cVOC Interference with F1

1. Check F1 and F1-BTEX
 - Most PHC products will have some BTEX in them
 - If F1 and F1-BTEX are the same, F1 is not likely from a PHC product – although it could be from individual alkanes e.g. cyclohexane.
 - Caution: may not be reliable for very low F1 concentration samples.
2. Check if total of cVOC target list is >3-4x F1-BTEX
 - Total cVOC would be > 1,000 µg/L to cause a F1 exceedance.
3. Check for gasoline additives in VOC report:
 - MEK, MIBK, MTBE; if present F1 is likely real.

If cVOC interference seems likely.....

Possible Next Steps:

- Ask for a resemblance comment to be added to your report.
- Ask the lab if there is a PHC signature in the F1 chromatogram.
- Ask if there are significant isolated peaks in the F1 chromatogram.

If interference suspected and you need data, request a manual cVOC subtraction for confirmation.

We can provide a signed letter report.

Keep in mind:

- This takes a couple of hours of analyst time per sample, is non-routine, and cannot be done quickly.
- Can only be done at the Mississauga lab.
- Not an accredited method.

Summary

- Chlorinated solvents can interfere with F1 petroleum hydrocarbon analysis, resulting a high bias or artificial F1 concentration.
- Quite high levels of cVOC ($\sim 1,000 \mu\text{g/L}$) are required to cause an artificial F1 exceedance.
- Although not a common issue – cVOC not usually seen at high concentration in water samples with PHC – it is good to know how to recognize it.
- A set of simple checks were presented to identify potential cVOC interference.
- Contact us if you need assistance with further confirmation.

Thank You!

Questions?

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