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Crude oil quantification using EPA Method 8015 may underreport the amount of oil present and the application of a "correction factor" to remediation data sets should be evaluated

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Outline

- Shortcomings of EPA 8015 method
- Crude oil project case study – movie!
- The need for a “correction factor”

EPA Method 8015 is Frequently Used for Soil Cleanups

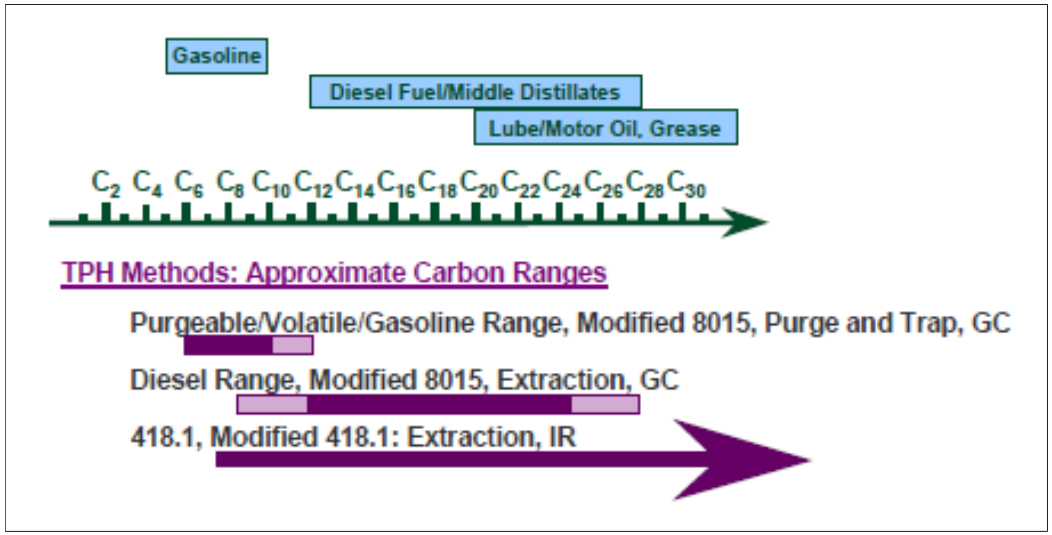
The State of California requires the use of EPA Method 8015 to quantify the volume of oil during a cleanup:

*"For quantification of TPH, applicable EPA or ASTM methods, such as **EPA Method 8015A** by gas chromatography flame ionization detector or EPA Method 8270B **shall be used**."*

$$\text{Volume of } oil = \frac{Weight\ of\ soil \times TPH\ concentration\ in\ soil}{Oil\ Density}$$

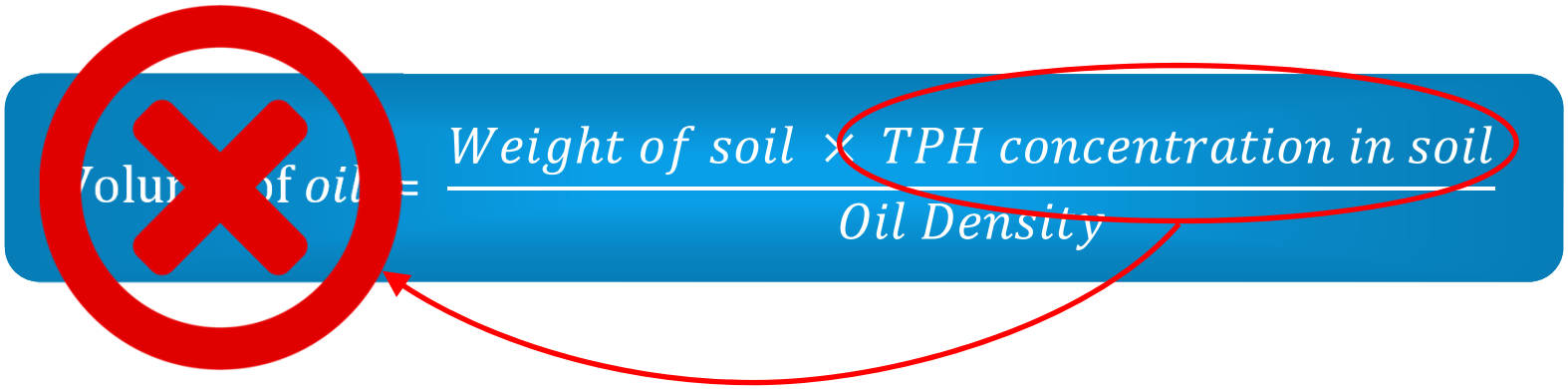
California Code of Regulations Title 14, Section 877

EPA Method 8015 Uses Gas Chromatography Which Can Only Analyze a Limited Range of Petroleum Hydrocarbons



Source: API 4709

Under-reporting the Oil Concentration by 8015 Leads to Under-reporting the Oil Volume

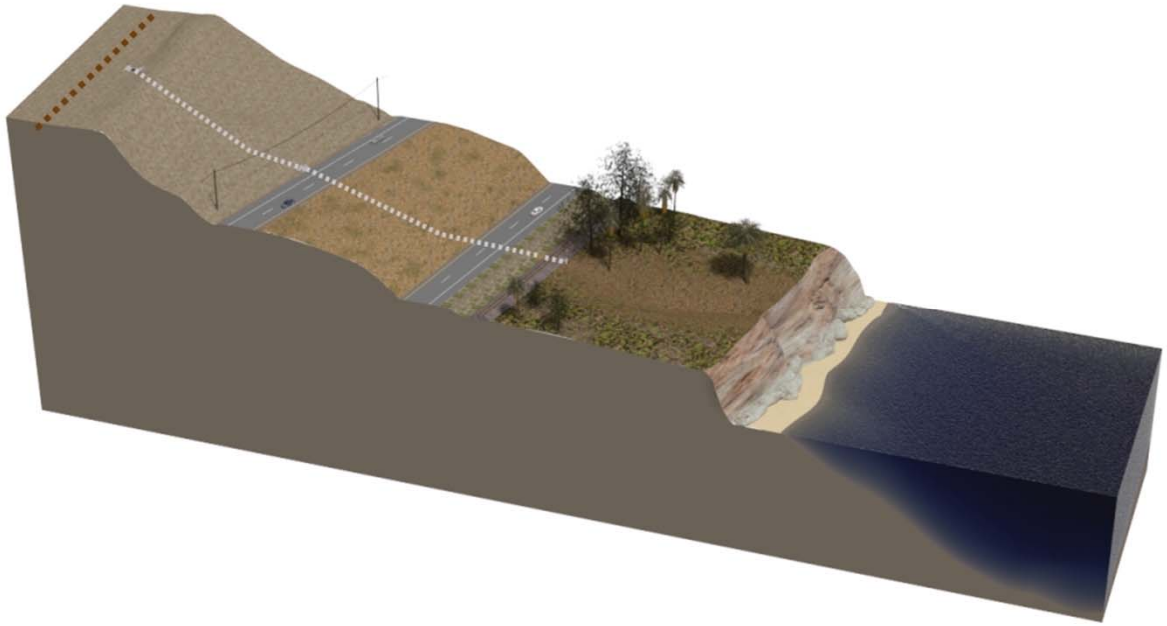


You may not get credit for the oil cleaned up
or you may think you have missing oil

Case Study with Crude Oil Released from a Pipeline

- ~3,000 bbl of crude oil (API 19) were released from an underground pipeline in California
- Some of the oil reached the ocean
- Our objective was to figure out how much oil reached the ocean
- We started by understanding where the oil remained on land and quantifying those volumes recovered

Crude Oil Release Movie



How Much Oil Remained on Land?

- During cleanup, approximately 6,300 tons of soils were excavated
- Soils from 1 of every 5 roll-off bins were sampled (CA-approved method)
- Oil volume in soils quantified using EPA Method 8015 and a diesel standard
- Using 8015 oil concentrations, 450 bbl of oil quantified in soils

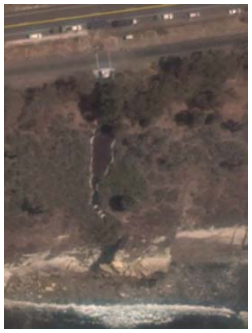
Data Analysis Revealed that Quantified Oil Volume Didn't Match Expected Volume

- Photographic evidence suggested much more oil in the soils

1st oil accumulation area

Impacted soil volume = 20,578 ft^3
Expected oil volume = 1,200 bbl
Measured oil volume = 375 bbl

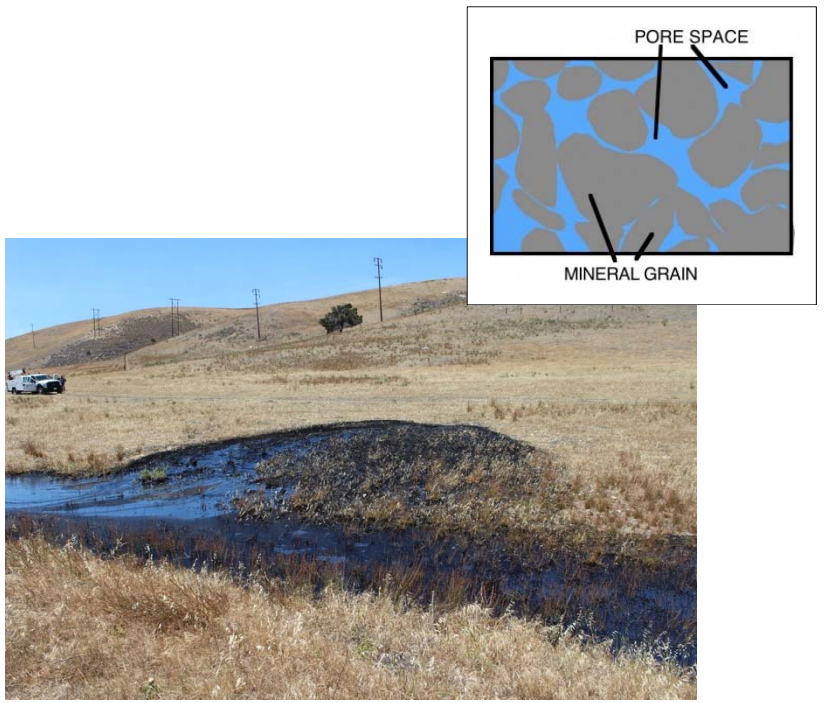
2nd oil accumulation area



Impacted soil volume = 3,982 ft^3
Expected oil volume = 280 bbl
Measured oil volume = 75 bbl

Oil Concentrations Didn't Match Those Expected for Saturated Soils

- Saturated soils expected directly beneath pooled oil
- Expected oil concentration in saturated soils = soil porosity
  - For sand ~ 30% by volume
- Actual highest soil concentration = 51,300 mg/kg = 9% by volume

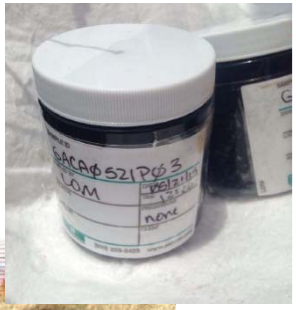


Was Method 8015 under-reporting the oil concentration?

Was this the reason why measured oil volumes didn't match expected oil volumes?

100% Crude Oil Samples Sent to 2 Labs

- 3 crude oil samples sent to 2 separate labs
  - 1 oil sample from pipeline
  - 2 oil samples from pooled oil on land
- Samples analyzed by EPA Method 8015 using diesel standard following exact same procedure as soil samples



Both Labs Could Only Measure Less Than Half the Oil

Sample	Lab A (Soil Analysis Lab)	Lab B	Lab A (Soil Analysis Lab)	Lab B
Pipeline oil sample	300,000 mg/kg	411,867 mg/kg	**30%**	**41%**
24-hr pooled oil sample	360,000 mg/kg	389,005 mg/kg	**36%**	**39%**
48-hr pooled oil sample	320,000 mg/kg	385,518 mg/kg	**32%**	**38%**

On average, only **~33%**
of the oil was being quantified

This Makes Sense Analytically

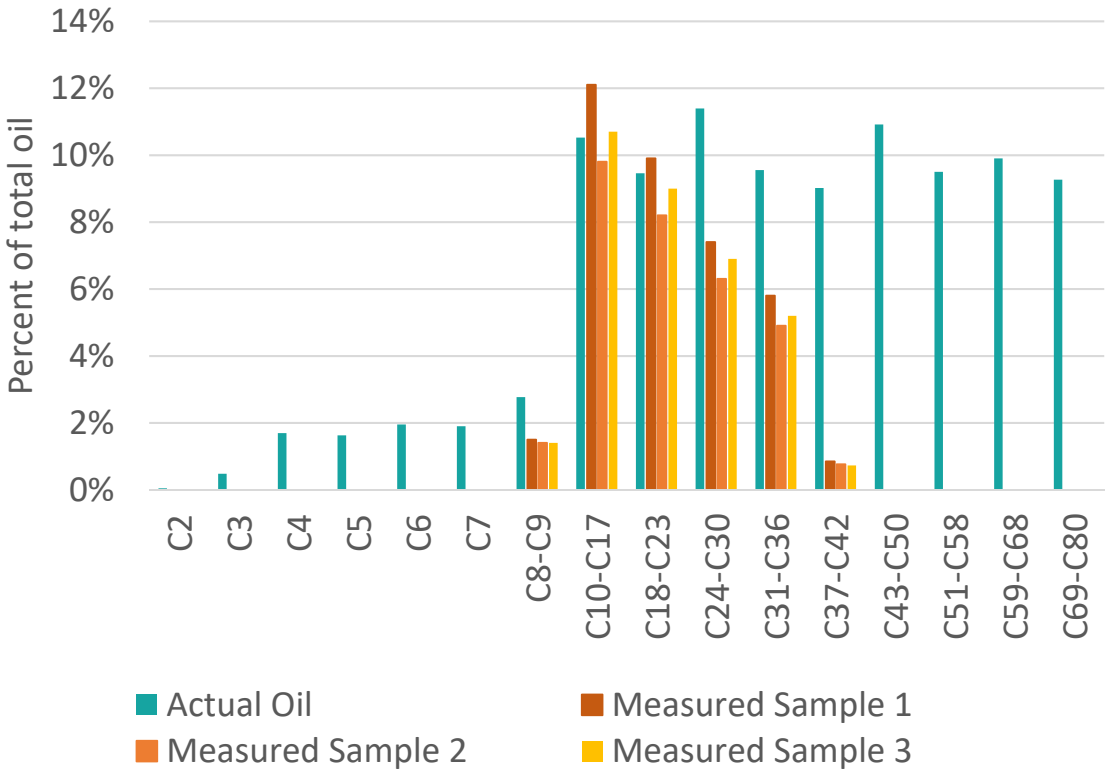
- EPA Method 8015 only measures C8-C44
- 47% by weight of carbon fractions are outside the analytical range
- We would not expect to measure all the oil present in the sample

Crude Oil Carbon Fractions

Carbon Fraction	Mole Fraction	Mass Fraction
C2	0.43	0.044
C3	3.205	0.479
iC4	2.229	0.439
nC4	6.382	1.257
iC5	3.029	0.740
nC5	3.181	0.778
cC5	0.453	0.108
C6	6.764	1.950
C7	5.719	1.901
C8	4.483	1.702
C9	2.466	1.068
C10-C17	17.153	10.525
C18-C23	9.886	9.458
C24-C30	9.054	11.395
C31-C36	6.083	9.553
C37-C42	4.862	9.019
C43-C50	5	10.915
C51-C58	3.708	9.501
C59-C68	3.319	9.904
C69-C80	2.648	9.266

Diesel Standard Used by Lab for 8015 Quantification is Not Ideal

- 53% theoretical analysis ≠ 33% actual analysis
- This is likely due to use of a diesel standard rather than a crude oil standard



Development of a Correction Factor

- A correction factor was needed to correct for the under-reporting of the measured data

$$Correction\ factor = \frac{1}{average\ measured\ oil\ content}$$

- Given an average measured oil content = 327,000 mg/kg = 0.327

$$Correction\ factor = \frac{1}{0.327} = 3.06$$

Application of the Correction Factor

- The correction factor of 3.06 was applied to all oil in soil measured using EPA Method 8015
  - Not applied to liquid oils or dissolved-phase oil

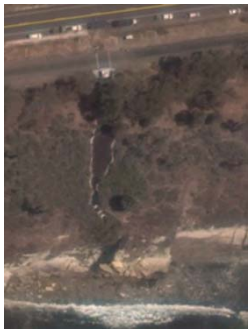
$$Actual\ oil\ volume = Measured\ oil\ volume \times correction\ factor$$

The Corrected Oil Volumes Made Sense

1st oil accumulation area

Impacted soil volume = 20,578 ft^3
Expected oil volume = 1,200 bbl
Corrected oil volume = 1,144 bbl

2nd oil accumulation area



Impacted soil volume = 3,982 ft^3
Expected oil volume = 280 bbl
Corrected oil volume = 232 bbl

The Corrected Oil Concentration Made Sense

- Saturated soils expected beneath pooled oil
- Expected oil concentration in saturated soils = soil porosity
  - For sand ~ 30% by volume
- Corrected oil concentration = 156,880 mg/kg = 27% by volume

The Correction Factor is Lab-Dependent

- The correction factor depends on the specific lab and the specific analytical method
  - e.g. analytical run time
- Data from single lab (Lab A) used

Sample	Lab A (Soil Analysis Lab)	Lab B
Pipeline oil sample	**30%**	**41%**
24-hr pooled oil sample	**36%**	**39%**
48-hr pooled oil sample	**32%**	**38%**

Conclusions

- EPA Method 8015 may significantly under-report the oil concentrations of crude oil in soil and sediment samples
- A correction factor may be critical for more accurate determination of cleanup volumes
- The correction factor cannot be determined theoretically, but must be measured:
  - You must have a pure oil sample to determine the correction factor
  - More samples is better
  - The correction factor must be measured by the same lab doing the rest of the analysis

Thank you!

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