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.

Kristin Robrock, Ph.D., P.E.  
October 8, 2019  
Paul Boehm, Ph.D.
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.**”

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

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

![Equation Diagram]

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 ft³
- Expected oil volume = 1,200 bbl
- Measured oil volume = 375 bbl

2nd oil accumulation area

- Impacted soil volume = 3,982 ft³
- 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

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

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

<table>
<thead>
<tr>
<th>Carbon Fraction</th>
<th>Mole Fraction</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>0.43</td>
<td>0.044</td>
</tr>
<tr>
<td>C3</td>
<td>3.205</td>
<td>0.479</td>
</tr>
<tr>
<td>iC4</td>
<td>2.229</td>
<td>0.439</td>
</tr>
<tr>
<td>nC4</td>
<td>6.382</td>
<td>1.257</td>
</tr>
<tr>
<td>IC5</td>
<td>3.029</td>
<td>0.740</td>
</tr>
<tr>
<td>nC5</td>
<td>3.181</td>
<td>0.778</td>
</tr>
<tr>
<td>cC5</td>
<td>0.453</td>
<td>0.108</td>
</tr>
<tr>
<td>C6</td>
<td>6.764</td>
<td>1.950</td>
</tr>
<tr>
<td>C7</td>
<td>5.719</td>
<td>1.901</td>
</tr>
<tr>
<td>C8</td>
<td>4.483</td>
<td>1.702</td>
</tr>
<tr>
<td>C9</td>
<td>2.466</td>
<td>1.068</td>
</tr>
<tr>
<td>C10-C17</td>
<td>17.153</td>
<td>10.525</td>
</tr>
<tr>
<td>C18-C23</td>
<td>9.886</td>
<td>9.458</td>
</tr>
<tr>
<td>C24-C30</td>
<td>9.054</td>
<td>11.395</td>
</tr>
<tr>
<td>C31-C36</td>
<td>6.083</td>
<td>9.553</td>
</tr>
<tr>
<td>C37-C42</td>
<td>4.862</td>
<td>9.019</td>
</tr>
<tr>
<td>C43-C50</td>
<td>5</td>
<td>10.915</td>
</tr>
<tr>
<td>C51-C58</td>
<td>3.708</td>
<td>9.501</td>
</tr>
<tr>
<td>C59-C68</td>
<td>3.319</td>
<td>9.904</td>
</tr>
<tr>
<td>C69-C80</td>
<td>2.648</td>
<td>9.266</td>
</tr>
</tbody>
</table>
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

\[ \text{Correction factor} = \frac{1}{\text{average measured oil content}} \]

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

\[ \text{Correction factor} = \frac{1}{0.327} = 3.06 \]
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 × correction factor
The Corrected Oil Volumes Made Sense

1st oil accumulation area

Impacted soil volume = 20,578 ft³
Expected oil volume = 1,200 bbl
Corrected oil volume = 1,144 bbl

2nd oil accumulation area

Impacted soil volume = 3,982 ft³
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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lab A (Soil Analysis Lab)</th>
<th>Lab B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipeline oil sample</td>
<td>30%</td>
<td>41%</td>
</tr>
<tr>
<td>24-hr pooled oil sample</td>
<td>36%</td>
<td>39%</td>
</tr>
<tr>
<td>48-hr pooled oil sample</td>
<td>32%</td>
<td>38%</td>
</tr>
</tbody>
</table>
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!

Kristin Robrock, Ph.D., P.E
Exponent, Oakland, CA
krobrock@exponent.com
510-268-5003