Characterizing and distinguishing losses of hydrocarbons from evaporation and dissolution are necessary for calculating mass balances, assessing exposures, and estimating damages following a spill. We investigated these processes following the 2007 M/V Coso Busan heavy fuel oil spill (San Francisco Bay, CA). We examined oil-covered rocks from the coastline of San Francisco Bay by comprehensive twodimensional gas chromatography (GC×GC). GC×GC retention times were used to estimate compound vapor pressures and solubilities. Data within the chromatograms are presented as mass loss tables (MLTs), which allow for visualization of weathering trends as a function of vapor pressure and aqueous solubility.

Modeling the effects of evaporation and dissolution for a heavy fuel oil: the M/V Coso Busan spill
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Abstract
Characterizing and distinguishing losses of hydrocarbons from evaporation and dissolution are necessary for calculating mass balances, assessing exposures, and estimating damages following a spill. We investigated these processes following the 2007 M/V Coso Busan heavy fuel oil spill (San Francisco Bay, CA). We examined oil-covered rocks from the coastline of San Francisco Bay by comprehensive twodimensional gas chromatography (GC×GC). GC×GC retention times were used to estimate compound vapor pressures and solubilities. Data within the chromatograms are presented as mass loss tables (MLTs), which allow for visualization of weathering trends as a function of vapor pressure and aqueous solubility.

To gain a more quantitative understanding, a physiochemical model was developed to describe evaporation and dissolution. This model is distinct from previous efforts because it allows composition of the oil film to vary with depth as diffusion out of the oil occurs. The trends from the model results are consistent with evaporation and dissolution trends observed in the MLTs. The model enables quantitative estimation of evaporation and dissolution for petroleum hydrocarbon compounds following a spill. The model underestimates observed losses for compounds with vapor pressures <~10⁻⁸ Pa. Model sensitivity to input parameters and uncertainty were also examined.

Motivation and Background
Figure 1 (left). Map of San Francisco Bay showing sampling site and track of the M/V Coso Busan.
Figure 2 (right). GC-FID chromatograms of unweathered oil and field samples.

Evaporation and dissolution:
- Act on similar timescales and affect similar compounds
- Are the most important processes in determining oil spill toxicity
- Difficult to distinguish using one-dimensional techniques

Mass Loss Tables (MLTs)
- Created using compound vapor pressures and solubilities estimated from GC×GC retention times
- Show relative mass loss and gain compared to the unweathered oil, for regions in the two-dimensional space
- Enable easy visualization of oil weathering patterns
- Allow more quantitative evaluation of weathering processes than possible by one-dimensional techniques

Wall Boundary Model
Controlling factors:
1. Diffusion within the oil
2. Partitioning between oil and air/water
3. Transport through a boundary layer

Field Sample Mass Loss Tables
Table 2. Modeled losses due to evaporation and dissolution for select compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>8 days</th>
<th>296 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene</td>
<td>22%</td>
<td>21%</td>
</tr>
<tr>
<td>C₁₀ napththalenes</td>
<td>20%</td>
<td>7%</td>
</tr>
<tr>
<td>C₁₁ napththalenes</td>
<td>13%</td>
<td>17%</td>
</tr>
<tr>
<td>C₁₂ napththalenes</td>
<td>2%</td>
<td>8%</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>2%</td>
<td>22%</td>
</tr>
</tbody>
</table>

Question: Is the beached oil an important source of hydrocarbon compounds to the water column following the spill?

Progressive loss of lower molecular weight hydrocarbons (Figure 2) is consistent with evaporation and dissolution.

Of the ~520 kg naphthalene released into the environment following the spill approximately 114 kg were dissolved into the water column

Conclusions
1. Weathering is observed as changes in the total petroleum hydrocarbons. The preferential loss of lower molecular weight compounds is consistent with evaporation and dissolution mechanisms.
2. Higher dimensional techniques are needed to separate the processes of evaporation and dissolution.
3. Mass loss tables provide a useful method of visualizing these weathering trends
4. Evaporation and dissolution trends are seen across the sample set
5. The model developed is able to reproduce weathering trends observed within field samples (underestimates total mass loss by ~16%)
6. Model indicates evaporation is sensitive to temperature and oil film thickness and dissolution is sensitive to water boundary layer depth and oil film thickness.
7. Model uncertainty is estimated to be ±14% (across MLT) for dissolution and ±3 to 7% (depending on MLT location) for evaporation

References
Arey et al., 2007b. Disentangling oil weathering using GC×GC retention indices to estimate environmental part.
Arey et al., 2007a. Disentangling oil weathering using GC×GC retention indices to estimate environmental part.