Modeling the effects of evaporation and dissolution for a heavy fuel oil: the M/V Cosco 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 *Cosco Busan* heavy fuel oil spill (San Francisco Bay, CA). We examined oil-covered rocks from the coastline of San Francisco Bay by comprehensive two-dimensional 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^{-3} Pa. Model sensitivity to input parameters and uncertainty were also examined.

Motivation and Background

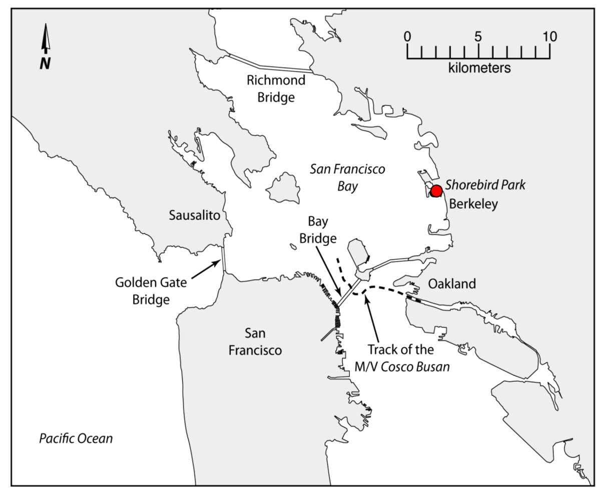


Figure 1 (left). Map of San Francisco Bay showing sampling site and track of the M/V *Cosco Busan.*

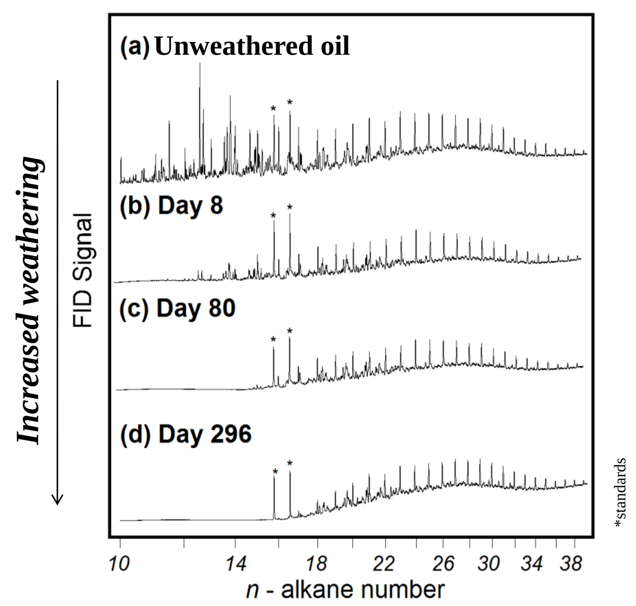


Figure 2 (right). GC-FID chromatograms of unweathered oil and field samples.

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

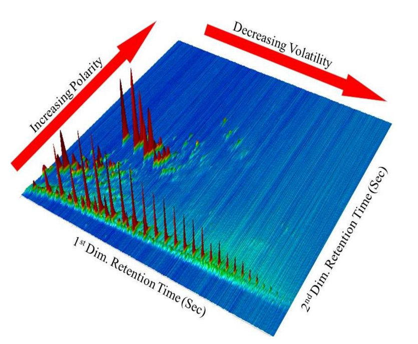
Progressive loss of lower molecular weight hydrocarbons (Figure 2) is consistent with evaporation and dissolution.

Evaporation and dissolution:

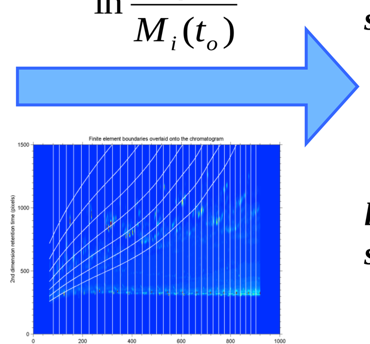
- Act on similar timescales and affect similar compounds
- Are the most important processes in determining oil spill toxicity
- Difficult to distinguish using one-dimensional techniques (Arey *et al.*, 2007b)

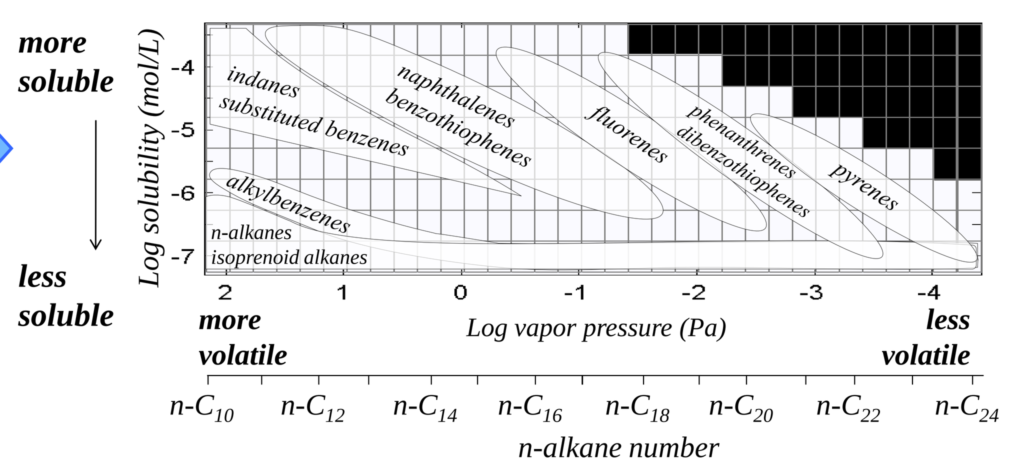
Mass Loss Tables (MLTs)

- Created using compound vapor pressures and solubilities estimated from GC×GC retention times (Arey *et al.*, 2005; 2007a)
- 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



$$\ln \frac{M_i(t)}{M_i(t_o)}$$





Field Sample Mass Loss Tables

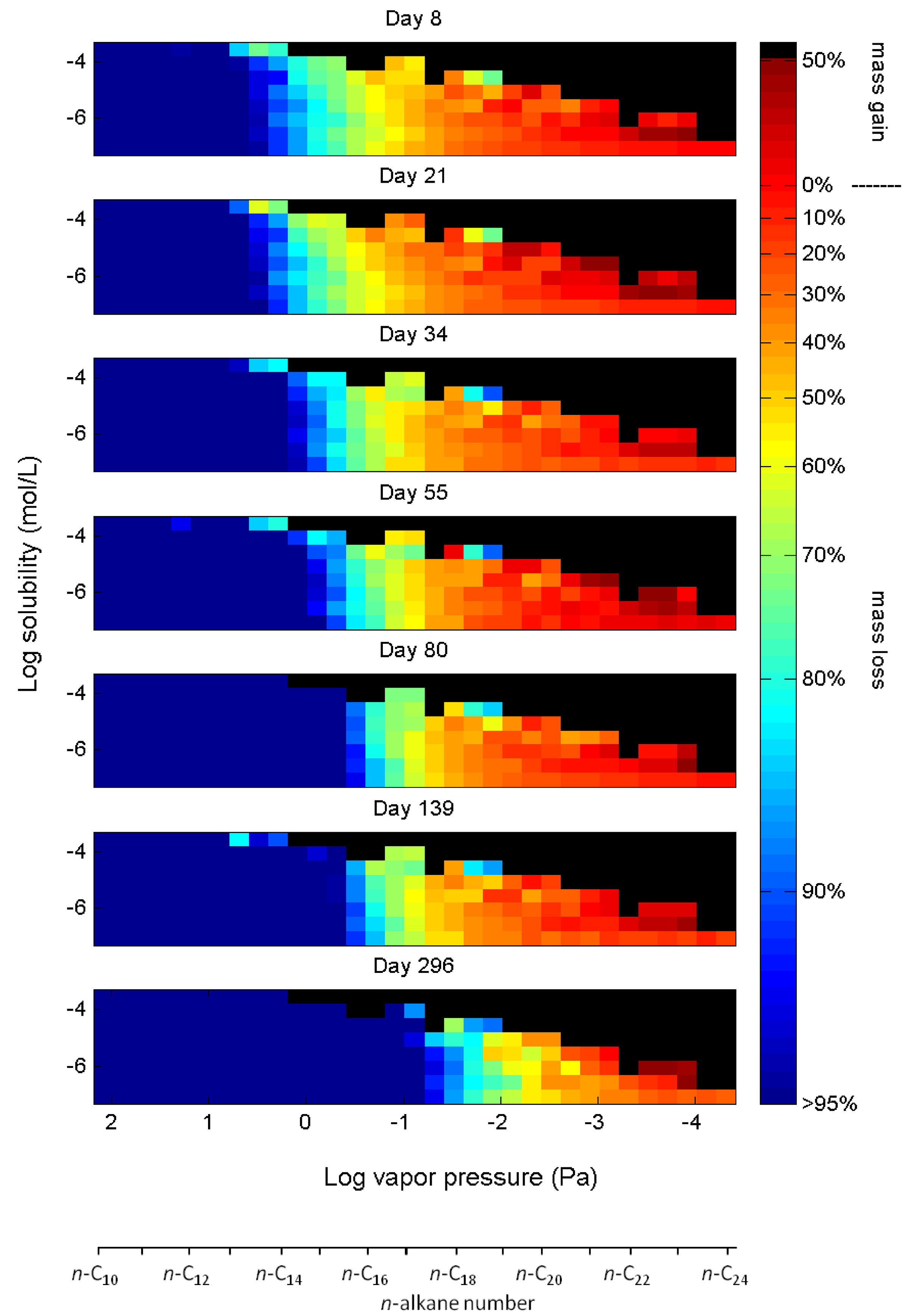
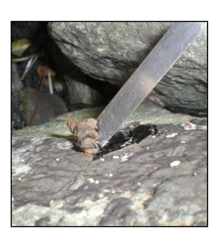


Figure 3. MLTs of field samples collected from 8 to 296 days post-spill. Blue indicates a relative loss of compounds and red indicates no change or slight increase in mass relative to the unweathered oil. Red arrows indicate the location of the evaporation front for each sample, defined as the loss of greater than 80% of compounds present at a given vapor pressure.

Wall Boundary Model



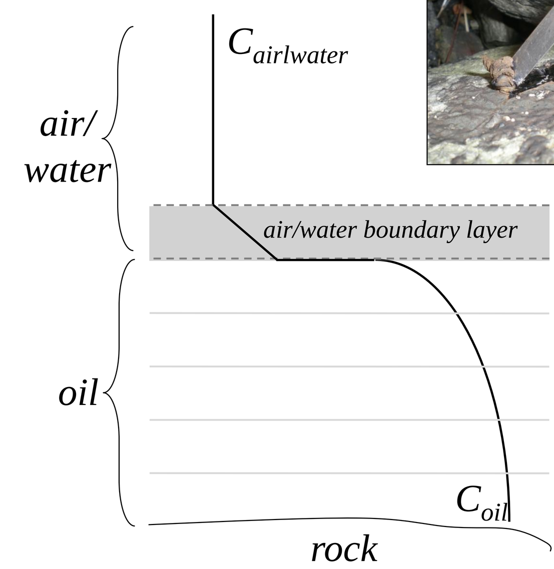


Table 1. Mass transfer model input parameters.[a]

Parameter	Abbreviation	Value
water-side boundary layer thickness	δ_{water}	2 mm
air-side boundary layer thickness	δ_{air}	10 mm
oil thickness	δ_{oil}	0.85 mm
water temperature	T_{water}	9.2 to 24.7 °C
air temperature	T_{air}	4.7 to 35.0 °C
oil density	ρ_{oil}	950 kg m^{-3}
oil viscosity	μ_{oil}	0.361 kg m^{-1} s^{-1}

[a] Parameters varying with compound identity are not listed.
[b] Arey et al., 2007b

$$\frac{dM}{dt} = -\left(\frac{dM_i}{dt}\right)_{evap} - \left(\frac{dM_i}{dt}\right)_{diss}$$

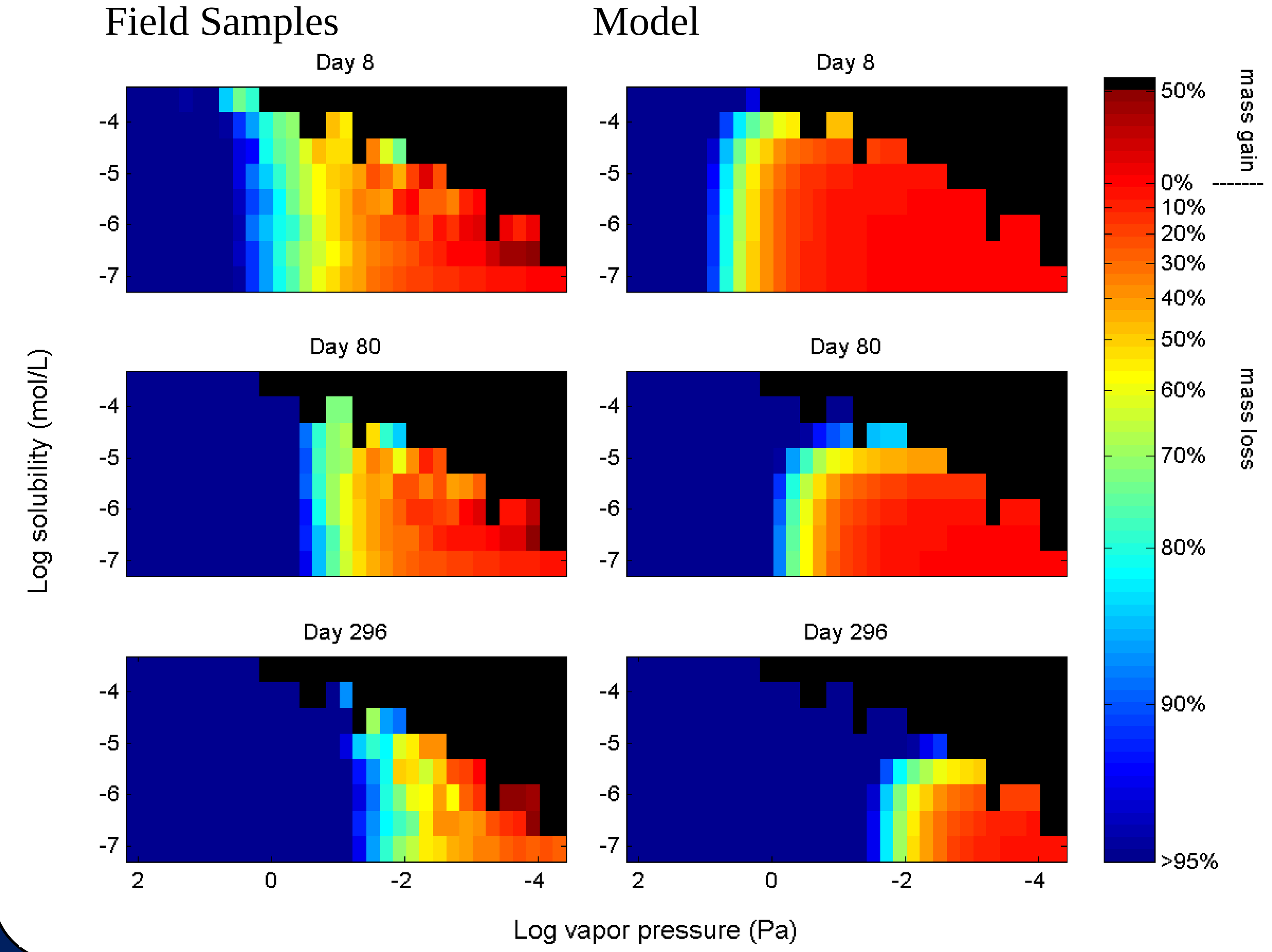
$$\left(\frac{dM_i}{dt}\right)_{evap} = \frac{D_{bl}}{\delta_{oil}\delta_{air}}\left(\frac{M_{i,air}^{eq} - M_{i,air}^{0}}{1+\Psi(t)}\right)$$

$$\Psi(t) = \left(\frac{\pi \cdot dt}{D_{i,oil}}\right)^{1/2}\left(\frac{D_{i,bl}}{\delta_{air}} \cdot \frac{1}{K_{i,oil/air}}\right)$$

Controlling factors:

1. Diffusion within the oil
2. Partitioning between oil and air/water
3. Transport through a boundary layer

Model Comparison



Fate of Specific Compounds

Table 2. Modeled losses due to evaporation and dissolution for select compounds.

	8 days		296 days	
Compound	% loss due to dissolution	% loss due to evaporation	% loss due to dissolution	% loss due to evaporation
n -C_{11}	0%	96%	0%	100%
naphthalene	22%	75%	22%	78%
C_1-naphthalenes	25%	60%	29%	71%
C_2-naphthalenes	13%	32%	30%	70%
C_3-naphthalenes	2%	13%	17%	83%
phenanthrene	22%	7%	78%	22%

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 thickness and oil film thickness.
7. Model uncertainty is estimated to be ±14% (across MLT) for dissolution and ±3 to 7% (dependant on MLT location) for evaporation

References

Arey, J.S., Nelson, R.K., Xu, L., Reddy, C.M., 2005. Using comprehensive two-dimensional gas chromatography retention indices to estimate environmental partitioning properties for a complete set of diesel fuel hydrocarbons. Analytical Chemistry 77, 7172-7182.
Arey, J.S., Nelson, R.K., Plata, D.L., Reddy, C.M., 2007a. Disentangling oil weathering using GC×GC. 2. Mass transfer calculations. Environmental Science & Technology 41, 5747-5755.
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