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Estimation of Dermal Exposure to Oil spill Response and Clean-up Workers after the Deepwater Horizon Disaster

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Appendix A: Exploration into the Trends over Time in the Arithmetic Means Estimates

The findings appear to be counterintuitive, but they are due to the relationship between concentration (which goes down over time), vapor pressure score (which goes up over time, because it is the inverse of vapor pressure, which goes down over time) and viscosity, which goes up over time (because there is less liquid and more “goo” in the oil over time, so it sticks to the skin more).

We focus our response here on the rise between the GDUs in time period (TP) 3 (covering activities with primarily 25% weathering) and TPs 4-6 (comprises activities primarily 30-40% weathering), as these time periods are the most counterintuitive. We present this discussion on weathering and then indicate how it applies to time period. However, we also present 0% weathering data to allow appreciation of the entire trend over the degrees of weathering in our study.

First, we evaluate the various parameters used in the model to determine on which to focus. The model describes the substance of interest by multiplying the product of the concentration, vapor pressure score (more on this below), and wind speed (Gorman et al., 2019):

\[
\text{Substance} = \text{Concentration} \times \text{Vapor Pressure} \times \text{Wind Speed}
\]  

(1)

As wind speed was constant for all chemicals and was deemed to be constant across all time periods, we drop this from the equation for our purposes here. Concentration and vapor pressure vary by substance, and time (which reflects oil weathering), so they will be explored below.

Exposure was deemed to be affected by two pathways: emission (i.e. direct contact with the substance) and surface transfer (contact with a surface contaminated with the substance).

\[
\text{Emission} = \text{Emission Frequency} \times \text{Emission Intensity} \times \text{Viscosity} \times \text{Substance} \times 5 
\]  

(2)

and

\[
\text{Surface transfer} = \text{Surface transfer Frequency} \times \text{Surface transfer Intensity} \times \text{Viscosity} \times \text{Substance} \times 3
\]  

(3)

Emission frequency and intensity, viscosity and the constant (i.e. 5) in equation 2 and surface transfer frequency, intensity, viscosity and the constant (i.e. 3) in equation 3 vary by activity and time period, but are constant for all substances. Viscosity changes consistently with oil weathering. Emission and surface transfer values are assigned to each of 9 body parts, but the same value is applied to all substances, so these variables can be dropped. Other input data to the model (body part affected, personal protective use, seawater) also are constant across the substances but change over time.

Here then we consider the differences among the substances, which means we are only concerned about concentration and vapor pressure. We then describe the effect of viscosity and time. We first discuss THC and PAHs and then discuss BTEX-H because the scales of the variables are different and it is easier to see the changes in the two different sets of graphs.

Concentration and Vapor Pressure

Concentration was used as a continuous proportional variable in the model (i.e. the concentration of the substance/concentration of the oil in grams). The effect of concentration varied by substance:

Table 1. Concentration proportions of substances in weathered oil (note: we consider >25-30% weathered oil to be tar)
<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration Proportion of the Substance in the Oil by Degree of Oil Weathering$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 %</td>
</tr>
<tr>
<td>THC</td>
<td>0.1684</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0023</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>0.00095</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0065</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.00700</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.0140</td>
</tr>
<tr>
<td>PAHs$^3$</td>
<td>0.0390</td>
</tr>
</tbody>
</table>

THC=total hydrocarbons. PAHs=polycyclic aromatic hydrocarbons

$^1$Calculated by concentration_{substance}/ concentration_{tar} in grams. Only the term “oil” is being used as tar is weathered oil.

The proportional concentrations changed little for THC, ethyl benzene, toluene, xylene and PAHs from weathering of 25% to weathering of 40% (Table 1). The largest effects of concentration were for benzene (decreased by almost 75%) and n-hexane (decreased by a factor of 10).

Figure 1. Effect of concentration by percent weathering – THC and PAHs.

![THC & PAHs Concentration versus Percent Weathering](image)

THC=total hydrocarbons. PAHs=polycyclic aromatic hydrocarbons

Figure 1 graphically presents the concentration changes across all weathering (0-40%) in the study. Although THC showed a drop in concentration proportion over time (for 25 and 40% weathering from 0.13 to 0.10, respectively), PAHs showed little change in concentration over any degree of weathering.

Figure 2. Effect of concentration by percent weathering – BTEX-H

The chemical most affected by changes in concentration from 25% to 40% weathering was n-hexane, which dropped almost 90% (concentration proportion went from 0.0039 to 0.0004, Figure 2 and Table 1).

Although we used a continuous variable for concentration, for vapor pressure the model uses a vapor pressure score (Table 2). It should be noted that vapor pressure score in the GuLF DREAM model decreases as vapor pressure increases (Gorman et al., 2019):

### Table 2. Weights assigned to vapor pressure score.

<table>
<thead>
<tr>
<th>Vapor pressure range (Pa)</th>
<th>Vapor pressure score</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;50</td>
<td>1</td>
</tr>
<tr>
<td>50-100</td>
<td>0.75</td>
</tr>
<tr>
<td>101-1000</td>
<td>0.1</td>
</tr>
<tr>
<td>1001-10,000</td>
<td>0.01</td>
</tr>
<tr>
<td>&gt;10,000</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Pa=pascal

### Table 3. Vapor pressure score by substance

<table>
<thead>
<tr>
<th>Substance</th>
<th>Vapor pressure (Pa)</th>
<th>Vapor pressure score</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Weathering</td>
<td>% Weathering</td>
</tr>
<tr>
<td>THC</td>
<td>3986</td>
<td>1798</td>
</tr>
<tr>
<td>Benzene</td>
<td>115</td>
<td>57</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Toluene</td>
<td>83</td>
<td>77</td>
</tr>
<tr>
<td>Xylene</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1025</td>
<td>327</td>
</tr>
</tbody>
</table>
Vapor pressure changed with weathering decreasing from 25 to 40% (about 50% for THC, 50% for benzene and 90% for n-hexane; only slightly for the other chemicals) (Table 3). The effect of the change on the vapor pressure score, however, was for THC, benzene and n-hexane 10, 1.2 and 10x, respectively, with no change for the other substances, due to the application of categories (Table 2).

Figure 3. Effect of concentration * vapor pressure score by weathering – THC & PAHs

For definitions, see Figure 1.

Figure 3 shows that, compared with Figure1, the vapor pressure score for THC remained about the same across all degrees of weathering except for the final change of 35% to 40%, when the product of concentration*vapor pressure score rose 10x from weathering of 35% to weathering of 40% (0.01 to 0.1). (Note the scale change of 0 to 0.18 in Figure 1 vs 0 to 0.45 in Figure 2.) This rise indicates that the greater decrease in vapor pressure (from 1798 Pa, resulting in a (lower) vapor pressure score of 0.01, to 821 Pa (Table 3), resulting in a (higher) vapor pressure score of 0.1 (table 3) (again, the vapor pressure score is the inverse of the vapor pressure) outweighed the small change in concentration 0.1263 to 0.1011, respectively (Table 1). So vapor pressure (score) appears to be one reason for the increase in THC between 35% and 40% weathering. PAHs were not affected by vapor pressure score (vapor pressure score=1 from 25% to 40% weathering).
For definitions, see Figure 2. Note that this scale covers a range of 0.000 to 0.008, half of the scale of Figure 2.

After incorporating the effect of vapor pressure score, Figure 4 shows that, compared with Figure 2, there is little effect due to vapor pressure score on any of the BTEX-H chemicals with weathering increasing from 25 to 40%, except to n-hexane. (The change in vapor pressure score for benzene from 25% to 30% weathering of 0.75 to 1 is offset by the decrease in concentration proportion from 0.00100 to 0.00073.) For n-hexane, weathering resulted in an increase in vapor pressure score of 10x. This degree of change, along with the decrease in concentration, resulted in a moderate increase in the product of concentration*vapor pressure score.

The change from 25% to 40% for all of the remaining substances remained about the same as was seen for concentration proportion.

Viscosity

Viscosity is the stickiness of the substance and indicates how easily the substance is removed from the skin. For viscosity the GuLF DREAM model uses two sets of scores, depending on whether the pathway was emission (direct contact with the substance) or surface transfer (contact with a surface contaminated with the substance) (Table 4) (Gorman et al., 2019).

Table 4. Weights assigned to viscosity score

<table>
<thead>
<tr>
<th>Viscosity (in centipoise) (examples)</th>
<th>Ordinal category</th>
<th>Viscosity score</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Emission</td>
</tr>
<tr>
<td>1 (water)</td>
<td>Low</td>
<td>1</td>
</tr>
<tr>
<td>2 (milk), 2-5 (diesel fuel), 18 (ethylene)</td>
<td>Medium low</td>
<td>2</td>
</tr>
</tbody>
</table>
See Gorman et al., for the basis of the viscosity weights.

Viscosity does not vary by substances; rather it is a function of the degree of weathering. Thus, for the same degree of weathering, all substances will be affected similarly.

Concentration, vapor pressure and viscosity

As can be seen in Figure 5, as compared to Figure 3, PAHs were substantially affected by viscosity between 25% (medium high viscosity) and 40% (high) weathering. The viscosity score increased the product of concentration*vapor pressure score by 50%. In contrast, viscosity had little effect on THC: the curves are similar in Figures 3 and 5.

Figure 5. Effect of concentration * vapor pressure (VP) score * viscosity (Visc) score by % weathering – THC & PAHs

For definitions, see Figure 1.

In contrast to concentration and vapor pressure score, viscosity appeared to have had a much greater effect on TEX-H (Figure 6). The product of concentration*vapor pressure score*viscosity of each chemical rose about 2x. The exception was for benzene, where the decrease seen previously was modulated.
Figure 6. Effect of concentration * vapor pressure (VP) score*viscosity (Visc) score on BTEX-H by weathering

For definitions, see Figure 2. Note that this scale covers a range of 0.000 to 0.07, almost 2X the scale of Figure 4.

Table 5 summarizes the effect each component (concentration proportion, vapor pressure score, and viscosity score) had on each substance, as well as the total effect. And up arrow (↑) means that the corresponding GDU value was higher at 40% weathering than that observed at 25% weathering. A down arrow (↓) indicates the reverse. With THC, the GDU total effect increased with greater weathering primarily due to decrease in vapor pressure, which resulted in an increase in the VPS. With benzene, the overall GDU effect decreased with increased weathering, the only chemical where this was observed. It appears that the decrease in concentration was not impacted by a decrease in vapor pressure (increase in VPS) as much as the other substances. For ethylbenzene, toluene, and xylene, it appears that the overall GDU effect is driven by the viscosity score. With toluene, the overall GDU effect is similar to ethylbenzene and xylene but the greater concentration drop is due to it being somewhat more volatile. With n-hexane the overall GDU effect was comparable to ethylbenzene and xylene, but this was due to the decrease in concentration offsetting the decrease vapor pressure (increase in VPS). With PAHs, there was minimal increase in concentration and no change in VPS, therefore the change was driven by viscosity score. These observations imply that for THC, TEX-H and PAHs, an appreciable portion of the change in total GDU effects was due to the model and the weights applied. Thus, for THC and n-hexane, the increase seen in going from 25% to 40% weathering was primarily due to the decrease in vapor pressures (and increase in vapor pressure score). For ethylbenzene, toluene, xylene and PAHs, viscosity had the greatest impact of the 3 parameters. For benzene, the concentration proportion was most important.
Table 5. Impact of Concentration, Vapor pressure and Viscosity on THC, BTEX-H and PAHs at 25 and 40% weathering

<table>
<thead>
<tr>
<th>Substance</th>
<th>% Change by Component</th>
<th>Overall Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration</td>
<td>Vapor pressure score (VPS)</td>
</tr>
<tr>
<td>THC</td>
<td>20.0↓</td>
<td>900↑</td>
</tr>
<tr>
<td>Benzene</td>
<td>74.0↓</td>
<td>33.3↑</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>6.7↓</td>
<td>0</td>
</tr>
<tr>
<td>Toluene</td>
<td>24.5↓</td>
<td>0</td>
</tr>
<tr>
<td>Xylene</td>
<td>6.3↓</td>
<td>0</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>89.7↓</td>
<td>900↑</td>
</tr>
<tr>
<td>PAHs</td>
<td>2.7↑</td>
<td>0</td>
</tr>
</tbody>
</table>

THC=total hydrocarbons. PAHs=polycyclic aromatic hydrocarbons

where:

\[
\text{% Change by Component} = \frac{(\text{Value}_{25} - \text{Value}_{40})}{\text{Value}_{25}} \times 100 \tag{3}
\]

\[
\text{Overall Change (\%)} = \frac{(\text{Conc}_{25} \times \text{VPS}_{25} \times \text{Viscosity Score}_{25} \{\text{Medium High} = 6\})}{(\text{Conc}_{40} \times \text{VPS}_{40} \times \text{Viscosity Score}_{40} \{\text{High} = 9\}))} \times 100 \tag{4}
\]

Some of the changes in exposures over time, however, may have had to do with the particular activities/tasks being performed in a particular time period, which may be impacting the observations for benzene in particular. For illustration, taking an average of the percentage of weathering across all activities/tasks of “all other water operations” and “all land” combined finds values of 23.1 (N EGs=390), 26.6 (N=388), 35.67 (n=263), and 39.1 (N=179) for TP3, 4, 5 and 6, respectively.