CHARACTERIZATION OF GASOLINES,
DIESEL FUELS
&
THEIR WATER SOLUBLE FRACTIONS

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Contract# 2-028-120-0
September 1983

93 '9 '24 076 0382030
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INTRODUCTION

Characterization of six gasolines and two diesel fuels and their water-soluble fractions (WSF's) by gas chromatography was undertaken to ascertain the types of compounds which may appear in ground water as a result of gasoline contamination. In addition, the diffusion constants for gasoline components into water were estimated thus enabling prediction of the kinetics of dissolution. A bibliography of the open literature on gasoline characterization and toxicity has been included.

MATERIALS AND METHODS

Samples of six gasolines (two regular, two unleaded, and two premium gasolines) and two diesel fuels were purchased at retail outlets [Chevron (Brand A) and Snell (Brand B)] in Oakland, CA, April 7, 1983 and placed in chloroform-rinsed metal solvent cans.

Preparation of water-soluble fractions, WSF's. Tap water, 1890 mL, was placed in a 2 L drain flask and allowed to cool to room temperature, 18°C. Gasoline, 210 mL, was added carefully on top of the water avoiding droplet formation. The mixture was stirred slowly so that the miniscus remained intact. Samples were removed from the drain at the bottom of the flask for ultraviolet spectroscopy, pentane extraction, or headspace analysis. UV spectra were recorded from 350-240 nm. In a preliminary experiment the time dependence to the UV spectra was studied. A plot of the absorbance at 270 nm of Shell regular as a function of time indicated the dissolution was 95% complete in 17.5 hr. Mixtures were stirred for 48 hr to ensure that equilibrium had been reached.

Determination of Dispersion constants. Mixtures of gasolines or diesel fuels with tap water were prepared as above except that the mixtures were not stirred. Formation of the water soluble fraction was followed by UV spectroscopy. Dispersion constants were calculated from the slope of the regression of Ln[(A - A0)/A0] on time, where A0 is the extrapolated equilibrium absorbance and A is the absorbance at time, t.

Pentane extraction of WSF's. The aqueous WSF solution, 800 mL, was extracted with 10.0 mL pentane, Burdick & Jackson glass distilled, after the addition of 10 uL dodecane standard and 20 g NaCl. The pentane solution was analyzed by gas chromatography. Each solution was analyzed also without addition of the dodecane standard.

Headspace analysis of WSF's. The aqueous WSF solution, 10 mL, was placed in a 30 mL serum bottle containing 4 g NaCl under a nitrogen atmosphere. Immediately, heptane, 0.1 or 0.5 uL was added as a standard and the bottle sealed. The mixture was shaken vigorously and 50 uL of the
headspace was analyzed by gas chromatography. Each WSF solution was analyzed without addition of the heptane standard also.

Gas chromatography of Gasolines and their WSF's. Separation of the major components of the fuels and their WSF's was achieved on a 1.8 m by 2 mm column of 1.5% OV-101 on 100/120 Chromasorb G/HP programmed from 50 to 150°C at 10°C/min on a Varian 2740 gas chromatograph equipped with a flame ionization detector. Components were tentatively identified based on their retention times except as noted below. In one case the saturated components were partially separated by dry column chromatography on a silica gel column 93 x 5.5 mm.

Gas chromatography of Diesel Fuels and their WSF's. Separation of the major components of the fuels and their WSF's was achieved on a 1.8 m by 2 mm column of 1.5% OV-101 on 100/120 Chromasorb G/HP programmed from 100 to 275°C at 8°C/min on a Varian 2740 gas chromatograph equipped with a flame ionization detector. Components were tentatively identified based on their retention times.

Gas Chromatography/Mass spectrometry of WSF components. Samples of the WSF of Chevron premium and Shell regular were analyzed by GC/MS. Aliquots of each sample were subjected to a 12 min He purge at 40 mL/min. The volatile components were collected on a sorbent trap and desorbed onto a 1.8 m x 2mm 1% SP-1000 column programmed from 70°C to 225°C at 10°C/min.

RESULTS

Analysis of Gasolines.

Gas chromatographic analysis of the six gasoline samples indicated the presence of at least 56 individual components. The majority of these components are C1 to C14 hydrocarbons, including benzene, toluene, ethylbenzene, xylenes, and several C2-benzenes. A typical chromatogram of gasoline is shown in Figure 1. The saturated hydrocarbons (denoted s in Fig. 1) were identified by gas chromatography after partial separation by dry column chromatography on silica gel. Chromatograms of all other gasolines are shown in the appendix figures A1-A5. The estimated amounts of the major monooaromatic hydrocarbons in the gasolines range from 1.8-2.6% benzene, 4.6-18.1% toluene, 8.5-22.5% C2-benzenes, and 6.5 to 13.0% C3-benzenes (Table 1). All gasolines contained similar amounts of benzene. Generally premiums contained the largest amounts of toluene and the regular gasolines contained the least toluene, C2-benzenes, and C3-benzenes. The increased amount of alkylbenzenes in the premium samples probably results from the inclusion of additional product from catalytic reforming (National Research Council, 1981). The agreement between the composition of the gasolines reported herein and that reported previously (Mayrsuhn, et al., 1978) is excellent.
**Figure 1.**

Regular Gasoline (Shell)

- $S = $ saturated hydrocarbon
- $a = $ aromatic hydrocarbon
- $? = $ unidentified unsaturated or polar compound

**C$_4$ - C$_6$ hydrocarbons:**

- Ethylbenzene
- o-Xylene
- m-, p-Xylene
- n-C$_9$
- n-C$_8$
- n-C$_7$
- C$_3$-benzenes
Table I. Estimation of Aromatic hydrocarbon content of gasolines by gas chromatography.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzene %</th>
<th>Toluene %</th>
<th>C\textsubscript{2}-Benzenes %</th>
<th>C\textsubscript{3}-Benzenes %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand A premium</td>
<td>1.8</td>
<td>18.1</td>
<td>22.5</td>
<td>13.0</td>
</tr>
<tr>
<td>Brand B premium</td>
<td>2.3</td>
<td>17.2</td>
<td>13.9</td>
<td>9.3</td>
</tr>
<tr>
<td>Brand A unleaded</td>
<td>2.5</td>
<td>10.5</td>
<td>13.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Brand B unleaded</td>
<td>2.0</td>
<td>6.2</td>
<td>10.6</td>
<td>9.5</td>
</tr>
<tr>
<td>Brand A regular</td>
<td>2.1</td>
<td>5.5</td>
<td>8.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Brand B regular</td>
<td>2.6</td>
<td>4.6</td>
<td>9.3</td>
<td>8.6</td>
</tr>
<tr>
<td>L.A. Composite\textsuperscript{b}</td>
<td>1.34</td>
<td>6.73</td>
<td>11.30</td>
<td>9.05</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Amounts of aromatic hydrocarbons as % of volatile components were calculated assuming equal flame responses for all components, and the estimates include small amounts of unseparated saturated hydrocarbons. Identifications are based on retention time comparisons. C\textsubscript{2}-Benzenes include ethylbenzene and o-,m-,p-xylenes. C\textsubscript{3}-benzenes include various methylethylbenzenes, trimethylbenzenes, and propylbenzenes.

\textsuperscript{b}Weight % from Mayrsohn et al., 1978.

The diesel fuels contained a complex mixture of hydrocarbons from C\textsubscript{10} to C\textsubscript{18} (Figures A20-A21). The normal alkanes from C\textsubscript{11} to C\textsubscript{24} and pristane and phytane are easily visible in the chromatograms of the diesel fuels. The amounts of individual monoaromatics which were less than 0.1% of the total volatile hydrocarbons (Table I) were not detected.

Analysis of WSF's

The chemical composition of the WSF's were determined by both headspace analysis (Table II, Figures A6-A13) and pentane extraction (Table III, Figures A14-A19). The identity of the major components of two of the samples was further substantiated by GC/MS analysis (Table IV). The WSF's contained a mixture of C\textsubscript{4} to C\textsubscript{6} non-aromatic hydrocarbons which are mostly saturated butanes, pentanes and hexanes and several monoaromatics including benzene, toluene and the xylenes. Estimates of the low boiling nonaromatic hydrocarbons range from 25 to 64 mg/L as determined by headspace analysis (Table II.) These estimates are probably low on the basis of comparison to the dynamic headspace analysis data (Table IV.) The best estimates of the levels of aromatic hydrocarbons appear to be the data in Table III because of incomplete extraction in headspace analysis. Benzene values range from 19.1 to 42.5 mg/L, toluene from 17.3 to 61.4 mg/L, and the xylenes from 9.5 to 27.7 mg/L. The WSF's from regular gasolines exhibited the lowest levels of benzene, toluene, and xylenes. The agreement between the pentane extraction technique and the dynamic
headspace analysis is good for benzene and toluene. For comparison with gasoline the composition of the water-soluble fraction determined by headspace analysis is presented as percentages in Table V. The compositions of the WSF's were enriched in benzene, 10 times, and toluene, 2.3 times, compared to the original gasoline.

The WSF's of the diesel fuels are quite different from those of gasoline. The procedures used for the gasolines did not adequately characterize these WSF's. Considerably lower levels of hydrocarbons were observed in water equilibrated with diesel fuel. Further analysis is required for their characterization.

Table II. Chemical Composition of the Water-Soluble Fraction of Gasolines and Diesel Fuels by Static Headspace Analysis.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>C_{4-6} Non-arom. Hydrocarbons mg/L</th>
<th>Benzene mg/L</th>
<th>Toluene mg/L</th>
<th>C_{2}-Benzenes mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand A premium</td>
<td>64</td>
<td>44</td>
<td>76</td>
<td>25</td>
</tr>
<tr>
<td>Brand A premium(^a)</td>
<td>70</td>
<td>35</td>
<td>70</td>
<td>13</td>
</tr>
<tr>
<td>Brand B premium</td>
<td>25</td>
<td>17</td>
<td>26</td>
<td>7.8</td>
</tr>
<tr>
<td>Brand A unleaded</td>
<td>38</td>
<td>26</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>Brand B unleaded</td>
<td>25</td>
<td>12</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Brand A regular</td>
<td>30</td>
<td>14</td>
<td>9</td>
<td>2.5</td>
</tr>
<tr>
<td>Brand B regular</td>
<td>42</td>
<td>12</td>
<td>11</td>
<td>4.3</td>
</tr>
<tr>
<td>Brand B regular(^a)</td>
<td>75</td>
<td>18</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>Brand A diesel</td>
<td>0.4</td>
<td>0.03</td>
<td>0.03</td>
<td>-0.005</td>
</tr>
<tr>
<td>Brand B diesel</td>
<td>1.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

\(^a\) determined by dynamic headspace analysis (see Table 3).  
\(^b\) includes ethylbenzene and xylenes.
Table III. Chemical Composition of the Water-Soluble Fraction of Gasolines by pentane extraction.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Benzene mg/L</th>
<th>Toluene mg/L</th>
<th>C_2-Benzenes mg/L</th>
<th>Other mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand A premium</td>
<td>42</td>
<td>61</td>
<td>28</td>
<td>11</td>
</tr>
<tr>
<td>Brand B premium</td>
<td>26</td>
<td>41</td>
<td>17</td>
<td>9.0</td>
</tr>
<tr>
<td>Brand A unleaded</td>
<td>42</td>
<td>41</td>
<td>19</td>
<td>10</td>
</tr>
<tr>
<td>Brand B unleaded</td>
<td>28</td>
<td>25</td>
<td>14</td>
<td>9.4</td>
</tr>
<tr>
<td>Brand A regular</td>
<td>25</td>
<td>20</td>
<td>9.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Brand B regular</td>
<td>19</td>
<td>17</td>
<td>11</td>
<td>12</td>
</tr>
</tbody>
</table>

Table IV. Gas chromatography/mass spectrometry identification of Volatile components of the WSF's of representative gasolines.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Brand A premium</td>
</tr>
<tr>
<td>Brand B regular</td>
</tr>
</tbody>
</table>

\( C_4 \)-HC and \( C_5 \)-HC are hydrocarbons containing 4 and 5 carbon atoms, resp.
Table V. Estimation of Aromatic hydrocarbon content of the WSF's of
gasolines by head space gas chromatography

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzene</th>
<th>Toluene</th>
<th>C₂-Benzenes</th>
<th>C₃-Benzenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand A premium</td>
<td>21.5</td>
<td>38.5</td>
<td>11.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Brand B premium</td>
<td>22.5</td>
<td>32.7</td>
<td>11.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Brand A unleaded</td>
<td>25.3</td>
<td>28.1</td>
<td>10.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Brand B unleaded</td>
<td>24.0</td>
<td>21.0</td>
<td>11.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Brand A regular</td>
<td>25.8</td>
<td>17.4</td>
<td>7.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Brand B regular</td>
<td>17.1</td>
<td>15.4</td>
<td>5.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Amounts of aromatic hydrocarbons as % of volatile components were
calculated assuming equal flame responses for all components.
Identifications are based on retention time comparisons. C₂-Benzenes
include ethylbenzene and o-,m-,p-xylenes. C₃-benzenes include various
methylethylbenzenes, trimethylbenzenes, and propylbenzenes.

Determination of Diffusion constants.

Molecules of gasoline components diffuse from the gasoline-water
interface in solution according to Fick's First Law of Diffusion:

\[
dm/dt = -DA(C/X)_{yz}
\]

Where

\[
D = \text{diffusion coefficient} \\
m = \text{mass of substance} \\
A = \text{area of interface} \\
t = \text{time} \\
X = \text{distance} \\
C = \text{concentration}
\]

Then the approximation, \(((C-C_s)/X) = (C/X)_{yz}\), can be
substituted for the concentration gradient with

\[
C = \text{concentration in solution} \\
C_s = \text{concentration at interface} \\
X_s = \text{distance at which C is measured.}
\]
Then 
\[ \frac{dm}{dt} = -DA(C - C_s)/X \]

For a container of volume \( V \), the above equation becomes:

\[ \frac{dc}{dt} = -DA(C - C_s)/XV \]

Integration yields:

\[ C = (C_s - C_s) \exp(-DA/t/XV) \]

assuming \( C_s = C \) at equilibrium or \( C_e \), then

\[ (C_e - C)/C_e = \exp(-DA/t/XV) \]

A plot of \( \ln[(C_e - C)/C_e] \) versus \( t \) should give a straight line whose slope, \( m = -DA/XV \), and the diffusion constant \( D = -mXV/A \). In our experiments, the absorbances of the WSF's being proportional to the concentrations were used in the regressions.

For our experimental container \( X = 14.9 \text{ cm}, A = 110.8 \text{ cm}^2 \) and \( V = 1890 \text{ cm}^3 \) giving \( XV/A = 254 \text{ cm}^2 (0.0254 \text{ m}^2) \) so that \( D = -254 \text{ cm}^2 \) times the slope of the plot of \( \ln[(C_e - C)/C_e] \) versus \( t \). The slopes of the regression lines and the dispersion constants are presented in Table VI.

The absorbance of the WSF's increased with time as shown in Figure 2. For the regression, an extrapolated final absorbance was used. This value was frequently lower than the absorbance at 2000 hr and similar to that of the stirred preparation. The higher value at 2000 hr is probably due to some oxidation of components of the WSF.

The time required for 95% saturation (\( t_{95\%} \)) of a quiescent body of water with gasoline can be estimated from

\[ t_{95\%} = -2.996 \, \frac{XV}{DA} \]

\( X = \text{distance from interface to bottom of water in cm} \)
\( V = \text{volume of water in cm}^3 \)
\( A = \text{interfacial area in cm}^2 \)
\( D = \text{diffusion constant in cm}^2/\text{hr} \)
Figure 2. Formation of WSF.

Chevron unleaded.

\[ A_{2000} = 1.020 \]
\[ A_{\text{ext}} = 0.850 \]
\[ A_{\text{stirred}} = 0.790 \]
Table VI. Diffusion constant data for formation of WSF's under static conditions at 18°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope</th>
<th>r</th>
<th>D</th>
<th>n</th>
<th>t_{1/2}</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevron premium</td>
<td>-0.0062</td>
<td>0.997</td>
<td>1.6</td>
<td>24</td>
<td>111</td>
<td>0.70</td>
</tr>
<tr>
<td>Chevron unleaded</td>
<td>-0.015</td>
<td>0.984</td>
<td>3.8</td>
<td>16</td>
<td>45</td>
<td>0.88</td>
</tr>
<tr>
<td>Chevron regular</td>
<td>-0.021</td>
<td>0.988</td>
<td>5.3</td>
<td>16</td>
<td>34</td>
<td>0.66</td>
</tr>
<tr>
<td>Shell premium</td>
<td>-0.0046</td>
<td>0.993</td>
<td>1.2</td>
<td>24</td>
<td>151</td>
<td>0.85</td>
</tr>
<tr>
<td>Shell unleaded</td>
<td>-0.021</td>
<td>0.998</td>
<td>5.3</td>
<td>15</td>
<td>32</td>
<td>1.70</td>
</tr>
<tr>
<td>Shell regular</td>
<td>-0.023</td>
<td>0.994</td>
<td>5.8</td>
<td>16</td>
<td>30</td>
<td>2.00</td>
</tr>
<tr>
<td>Shell diesel</td>
<td>-0.0083</td>
<td>0.994</td>
<td>2.1</td>
<td>8</td>
<td>83</td>
<td>0.44</td>
</tr>
<tr>
<td>Chevron diesel</td>
<td>-0.012</td>
<td>0.993</td>
<td>3.0</td>
<td>8</td>
<td>55</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Slope is the slope of the regression of $\ln[(A_t-A)_{e}/A_e]$ on t
r is the product moment correlation coefficient
D is the diffusion constant in cm$^2$/hr
n is the number of data points
$t_{1/2}$ is the half life in hr for saturation in static conditions used.
$A_{e}$ is extrapolated equilibrium absorbance at $t_{e}$.

Ultraviolet Spectroscopy of the WSF's.

In the determination of the diffusion constants the UV spectra of the WSF's were recorded from 350 to 240 nm. All WSF's exhibited an intense absorption below 250 nm which tailed to higher wavelengths. In the region from 300-250 nm the spectra of the WSF's contained surprisingly different features which are summarized below.

- Chevron premium multiplet @ 248,254,261,268 nm
- Shell premium shoulder @ 268 nm
- Chevron unleaded shoulders @ 253,260,268 nm
- Shell unleaded doublet @ 272,277 nm
- Chevron regular shoulder @ 243 nm
  multiplet @ 260,268,272,276 nm
Shell regular doublet @ 272, 276 nm
Chevron diesel no peaks or shoulders tail to 350 nm
Shell diesel broad peak centered @ 270 nm

Each WSF exhibits a characteristic and distinguishable pattern of peaks and shoulders with the single exception of the Shell regular whose spectrum is qualitatively the same as the Shell unleaded. This finding suggests that the UV spectra of the WSF's can be used in the identification of gasolines in conjunction with the determination of lead content.

DISCUSSION

Gasolines contain a complex mixture of hydrocarbons both saturated and aromatic. The monoaromatic hydrocarbons including benzene and the alkylbenzenes represent a major portion of the gasolines studied. This result agrees with analyses summarized by the National Research Council (National Research Council, 1981) Table VII.

Table VII. Alkylbenzene composition of a Composite Gasoline obtained in the Los Angeles Area*.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wt %</th>
<th>Compound</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.34</td>
<td>Isobutylbenzene</td>
<td>0.08</td>
</tr>
<tr>
<td>Toluene</td>
<td>6.73</td>
<td>sec-butylbenzene</td>
<td>0.09</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>1.71</td>
<td>tert-butylbenzene</td>
<td>0.12</td>
</tr>
<tr>
<td>m- and p-Xylene</td>
<td>6.73</td>
<td>1-Methyl-3-propylbenzene</td>
<td>0.56</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>2.86</td>
<td>1-Methyl-4-isopropylbenzene</td>
<td>0.02</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>0.14</td>
<td>1-Methyl-2-N-propylbenzene</td>
<td>0.15</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>0.61</td>
<td>1,2-Diethylbenzene</td>
<td>0.57</td>
</tr>
<tr>
<td>2-Ethyltoluene</td>
<td>0.96</td>
<td>1,3-Diethylbenzene</td>
<td>0.08</td>
</tr>
<tr>
<td>3- and 4-Ethyltoluene</td>
<td>2.89</td>
<td>1,3-Dimethyl-2-ethylbenzene</td>
<td>0.59</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>3.30</td>
<td>1,2,4,5-Tetramethylbenzene</td>
<td>0.37</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>1.15</td>
<td>1,2,3,5-Tetramethylbenzene</td>
<td>0.15</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>0.44</td>
<td>Naphthalene</td>
<td>0.46</td>
</tr>
</tbody>
</table>

| Total                  | 32.10 (a) |
| Total Saturates        | 65        |

* From Mayrsohn et al., 1978.
(a) Unidentified alkylbenzenes would probably raise this figure to approximately 35%.
When gasoline contacts water several processes occur. The gasoline may become emulsified or dispersed in the water. The more soluble components may dissolve forming what is referred to as the water soluble fraction (WSF). The more volatile components may evaporate. In a spill situation where the gasoline is in contact with both air and water evaporation will exceed dissolution as a result of the more rapid mass transfer to the vapor phase. In addition, in this case, the evaporation of the WSF, as described by Henry's Law, is rapid; therefore little accumulation of gasoline components is expected. However, in a spill situation underground, where the gasoline is mostly in contact with water, considerable transfer of the components of the WSF may occur. The potential for groundwater contamination by underground spills has received less attention in the literature but may be equally important.

The WSF's of the gasolines analyzed were enriched considerably in total aromatic hydrocarbons and especially in benzene and toluene. A body of water in equilibrium with gasoline (9:1) may contain benzene levels as high as 40 mg/L and toluene levels from 9 to 76 mg/L based on the laboratory equilibrations (Table II-III). The differences in determination of the aromatic hydrocarbons by headspace analysis and pentane extraction are minor and result from differences in extraction efficiency.

The actual concentrations obtained in an environmental situation depend on a variety of factors. The laboratory derived equilibrium values represent a maximum obtainable concentration. These equilibrium values exceed the EPA ambient water quality values (U.S. Environmental Protection Agency, 1979a, 1979b, 1981) for benzene and toluene:

<table>
<thead>
<tr>
<th></th>
<th>24-hr avg.</th>
<th>Max. Limit</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>3.100 mg/L</td>
<td>7.000 mg/L</td>
<td>Freshwater</td>
</tr>
<tr>
<td></td>
<td>0.920 mg/L</td>
<td>2.100 mg/L</td>
<td>Saltwater</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>Human Health</td>
</tr>
<tr>
<td>toluene</td>
<td>2.300 mg/L</td>
<td>5.200 mg/L</td>
<td>Freshwater</td>
</tr>
<tr>
<td></td>
<td>0.100 mg/L</td>
<td>0.230 mg/L</td>
<td>Saltwater</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.4 mg/L</td>
<td>Human Health</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td></td>
<td>1.1 mg/L</td>
<td>Human Health</td>
</tr>
</tbody>
</table>

Unless the criterion for benzene is relaxed, gasoline contamination of water will result in a level of benzene greater than the zero value for the human health criterion. In extreme situations the criteria for aquatic life may be exceeded also.
Reviews of the effects of benzene, toluene, ethylbenzene, and the alkylbenzenes are available (U.S. Environmental Protection Agency, 1979a, 1979b, 1981). The criteria above reflect these data. However, virtually no attention has been paid to the \( C_4 \) to \( C_6 \) hydrocarbons. Their toxicity is not known at present. One study (Hutchinson et al., 1979) with the marine algae, Chlorella vulgaris and Chlamydomonas angulosa, suggests that the toxicity of hydrocarbons is a function of their solubility in water (Table VIII). Hexane was found to be about 10 times more toxic than benzene. If this phenomenon is general, then the saturated hydrocarbons will exhibit toxicities to aquatic life greater than toluene and benzene (compare solubilities Table VIII.). The toxicity of the WSF's of gasoline may be the result in large part from the toxicity of saturated compounds in the WSF's. and will require further study for adequate assessment.

Table VIII. Solubilities of Hydrocarbon constituents of the water soluble fraction of gasolines (McAuliffe, 1966).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility mg/L</th>
<th>Compound</th>
<th>Solubility mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>61.4</td>
<td>Benzene</td>
<td>1780</td>
</tr>
<tr>
<td>Isobutane</td>
<td>48.9</td>
<td>Toluene</td>
<td>515</td>
</tr>
<tr>
<td>Pentane</td>
<td>38.5</td>
<td>o-Xylene</td>
<td>175</td>
</tr>
<tr>
<td>Isopentane</td>
<td>47.8</td>
<td>Ethylbenzene</td>
<td>152</td>
</tr>
<tr>
<td>2,2-dimethylpropane</td>
<td>33.2</td>
<td>1,2,4-Trimethylbenzene</td>
<td>57</td>
</tr>
<tr>
<td>Hexane</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>18.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The dispersion constants (Table IV) indicate that dissolution in a quiescent situation is rather slow. The half-life for saturation of a 15 cm deep water layer varied from 30 to 151 hr. The reason for the variation in diffusion constant from 1.2 to 5.8 cm²/hr is unknown. It may result from effect of various additives.

The characterization of the WSF's herein focused on the major soluble and volatile components as determined by gas chromatography. The characterization of additives of low volatility and high aqueous solubility, i.e. those not extracted by pentane, was not attempted.
Monoaromatic hydrocarbons, including benzene, toluene, and the xylenes, constitute an important fraction of gasoline (23-55%) and the major components of the water soluble fraction (42-74%). Benzene, which is enriched by a factor of ten in the water soluble fraction, is important as an environmental contaminant because of its link to leukemia. Under conditions where evaporation is suppressed, benzene and the alkyl aromatic hydrocarbons may pose a threat to aquatic life. The importance of the C\textsubscript{4} to C\textsubscript{6} saturated hydrocarbons cannot be assessed; however, these compounds may exhibit considerable toxicity to aquatic organisms.
BIBLIOGRAPHY and REFERENCES

1. Chemical Composition of Gasoline


2. Aquatic Toxicology

2a. Gasoline


2b. Benzene

Benville, P.E., Jr., and S. Korn. 1977. The acute toxicity of six monocyclic aromatic crude oil components to striped bass (Morone saxatilis) and bay shrimp (Crano franciscorum). Calif. Fish Game. 63:204.

Caldwell, R.S., et al. 1977. Effects of a seawater soluble fraction of Cook Inlet crude oil and its major aromatic components on larval stages of


2c. Toluene

Benville, P.E., Jr., et al. 1977. The acute toxicity of six monocyclic aromatic crude oil components to striped bass (Morone saxatilis) and bay shrimp (Craco franciscorum). Calif. Fish & Game. 63:204.


2d. Others


3. Mammalian Toxicology and Human Health

3a. Benzene


3b. Toluene


4. Occurrence and Fate in Aquatic Environment

4a. Gasoline


4b. Benzene


4c. Toluene


4d. Others


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APPENDIX of CHROMATOGRAMS

Figure legends.

Figure A1. Gas chromatogram of Brand A premium gasoline.
Figure A2. Gas Chromatogram of Brand B premium gasoline.
Figure A3. Gas Chromatogram of Brand A unleaded gasoline.
Figure A4. Gas Chromatogram of Brand B unleaded gasoline.
Figure A5. Gas Chromatogram of Brand A regular gasoline.
Figure A6. Gas Chromatogram of Headspace of WSF of Brand A premium.
Figure A7. Gas Chromatogram of Headspace of WSF of Brand B premium.
Figure A8. Gas Chromatogram of Headspace of WSF of Brand A unleaded.
Figure A9. Gas Chromatogram of Headspace of WSF of Brand B unleaded.
Figure A10. Gas Chromatogram of Headspace of WSF of Brand A regular.
Figure A11. Gas Chromatogram of Headspace of WSF of Brand B regular.
Figure A12. Gas Chromatogram of Headspace of WSF of Brand A diesel.
Figure A13. Gas Chromatogram of Headspace of WSF of Brand B diesel.
Figure A14. Gas Chromatogram of Pentane Extract of WSF of Brand A premium gasoline.
Figure A15. Gas Chromatogram of Pentane Extract of WSF of Brand B premium gasoline.
Figure A16. Gas Chromatogram of Pentane Extract of WSF of Brand A unleaded gasoline.
Figure A17. Gas Chromatogram of Pentane Extract of WSF of Brand B unleaded gasoline.
Figure A18. Gas Chromatogram of Pentane Extract of WSF of Brand A regular gasoline.
Figure A19. Gas Chromatogram of Pentane Extract of WSF of Brand B regular gasoline.
Figure A20. Gas Chromatogram of Brand A Diesel Fuel.
Figure A21. Gas Chromatogram of Brand B Diesel Fuel.
Fig. A9

Headspace

WSF shelf unloaded

benzene

toluene

xylenes
Pentane Extract

WSP Shell Super

- Toluene
- Xylenes

C₃ - Benzene

NO. LNR 81004333
Pentane Extract
HSF Chevron Unleaded
Figure A19

Graph showing the comparison of Pentane Extract and WSF Shell Regular.

Chemicals identified:
- Benzene
- Toluene
- C12 Std
- C3 Benzene

Graph axes indicate measurements along the vertical and horizontal axes.