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Cover Page Footnote

Development of the research report into a manuscript for publication was done by Kathy Tynsky of Computer Sciences Corporation. The research reported has not been subjected to a USEPA review process so official endorsement should not be inferred.

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LIGHT NONAQUEOUS-PHASE LIQUID HYDROCARBON WEATHERING AT SOME JP-4 FUEL RELEASE SITES

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ABSTRACT

A fuel weathering study was conducted for database entries to estimate natural light, nonaqueous-phase liquid weathering and source-term reduction rates for use in natural attenuation models. A range of BTEX weathering rates from mobile LNAPL plumes at eight field sites with known release dates was documented. Free-phase fuel BTEX weathering rates varied among sites and were influenced by many factors. First-order weathering rate for five JP-4 fuel sites was 16%/year. Benzene and toluene exhibited higher weathering rates than ethylbenzene and xylene, as expected, because of higher water solubility. The primary weathering mechanism of mobile LNAPL was dissolution. Meaningful determination of mobile LNAPL weathering rates for BTEX in the fuels was difficult because of the large ranges of initial BTEX values.

Keywords: *weathering, JP-4, LNAPL*

INTRODUCTION

Little information has been available regarding rates of natural weathering of BTEX components from mobile fuel, light nonaqueous-phase liquid. Because of this, reduction rate source terms in groundwater models is often an overly conservative estimate. This approach can result in adverse forecasts of monitored natural attenuation performance at field sites. The main emphasis of the study was for JP-4 jet fuel because it had been the primary fuel type used at Air Force bases until 1994. Consequently, the majority of accidental spills at these bases involved JP-4. For jet fuels, JP-4 has the highest initial BTEX fractions. The study was conducted to improve the scientific basis and defensibility for determining natural LNAPL weathering rates to evaluate contaminant fate and transport for natural attenuation remediation. This report summarizes the initial assessment of some site-specific mobile LNAPL weathering rates. Presently data is being collected and evaluated for a final technical report. The report will incorporate more data collection sites and a detailed statistical analysis of the data.

OBJECTIVE

The study was done to document a range of BTEX weathering rates for mobile LNAPL fractions from some JP-4 release locations with LNAPL plumes and known release dates. The weathering rates are to be used for more accurate natural attenuation input parameters.

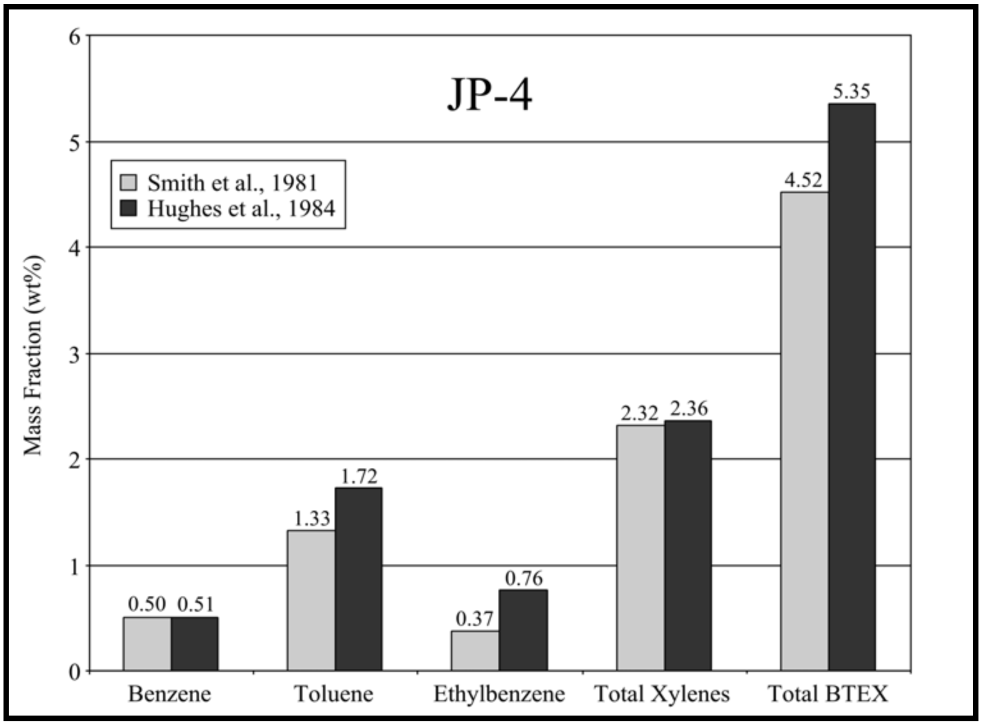

Figure 1. BTEX Concentrations in Fresh Fuels--Fuel Weathering Study.

LITERATURE REVIEW

The search did not identify any field studies to evaluate BTEX reductions within mobile LNAPL at fuel release sites. Frequently a default value of five percent per year has been used, but no field studies were known to exist to support this assumption.

JP-4 BTEX COMPOSITION

The initial concentration of BTEX in the original JP-4 fuels was not known. It was estimated using fresh fuel compositional values reported by Smith et al. (1981) and Hughes et al. (1984) as shown in Figure 1. Mass fractions were obtained using a density value of 802 mg/mL for JP-4.

Table 1. Site Summary

Site	Amount Released (gallons)	Soil Type	Depth to Water Table (feet, bgs)	Product Thickness
Shaw AFB, SC	Unknown	Sand	30	2.5
Myrtle Beach AFB, SC	123,000	Clay/Sand	5	3.8
Defense Fuel Supply Point, SC	83,000	Clay/Sand	20	1.8
Eaker AFB, AR	Unknown	Sandy Silt	11	1.2
McChord AFB, WA	100,000	Silty Gravel	13	0.14

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DISSOLUTION AND WATER SOLUBILITY

Dissolution is partitioning of BTEX from LNAPL into groundwater and most likely the major mechanism of BTEX depletion in mobile LNAPL. Water solubility of the BTEX components is an important factor in determining the fate and transport in the subsurface. Water solubility and effective solubility of JP-4 and gasoline are listed in Table 2. BTEX compounds are more soluble in fuel than water and tend to remain in the fuel.

VOLATILIZATION AND BIODEGRADATION

Contaminant volatilization for subsurface releases through a porous medium is usually restricted by soil moisture and fine soil texture. Effective biodegradation is limited because of a hostile fuel environment and restricted access to nutrients, electron acceptors, etc,. in the LNAPL pool.

COLLECTION OF SITE DATA

Eight JP-4 fuel release points were selected at five different bases for the study and are listed in Table 3. The sites were selected as the only known locations available for the study. Both soil and groundwater samples were collected. The soil samples were used to determine contamination and physical characteristics at the capillary fringe depth.

ANALYTICAL METHOD

Analytical protocol for the free product was an adaptation of USEPA SW8270. Samples for analysis were 1:20 methylene chloride dilutions of the JP-4 product. Water was removed from the dilutions using a narrow column of sodium sulfate. 0.45 mL of sample extract was mixed with fluorobenzene internal standard for a concentration of 10 µg/mL. One µL of the sample mix was injected into a Hewlett-Packard 5890 Series II gas chromatograph with a 5971 Series Mass Selective detector. The column used was a 30M long x 0.25mM ID Restek Stabilwax column with

Table 2. Dissolved Concentrations of BTEX.

Compound	Water[a/] Solubility	Water Concentrations in Contact with Fuel (effective solubility) at a 1:10 Ratio	
		JP-4[b/] mg/L	Gasoline[c/]
Benzene	1750	9.8	58.7
Toulene	524	8.5	33.4
Ethylbenzene	187	0.7	4.30
o-Xylene	167	1.2	6.90
m-Xylene	157	2.0	11.0
p-Xylene	180	0.4	4.40
Total Xylenes	168	3.6	22.3

[a/] Solubilities at 25°C (Montgomery, 1996).
[b/] Smith et al., 1981.
[c/] American Petroleum Institute, 1985.

Table 3. BTEX Weathering Rages in JP-4 Mobile LNAPL.

Site Analyte	Spill Age	Initial Conc.[a/]	Remaining Conc.	Zero-Order	First-Order
		wt %		Average % Reduced/Year	
Shaw AFB, SC	4 years				
Benzene		0.50	0.23	17	22
Toluene		1.33	0.48	20	28
Ethylbenzene		0.37	0.16	17	23
Total Xylenes		2.32	1.07	17	22
Total BTEX		4.52	1.94	18	23
Myrtle Beach AFB, SC	16 years				
Benzene		0.50	0.02	5.9	19
Toluene		1.33	0.00	6.2	36
Ethylbenzene		0.37	0.17	3.4	5.3
Total Xylenes		2.32	0.57	4.7	8.9
Total BTEX		4.52	0.76	5.1	11
Defense Fuel Supply Point (DFST), Charleston, SC	22 years				
Benzene		0.50	0.00	4.8	35
Toluene		1.33	0.01	4.8	25
Ethylbenzene		0.37	0.10	3.6	8.7
Total Xylenes		2.32	0.44	3.9	9.3
Total BTEX		4.52	0.55	4.3	11
Eaker AFB, AR	24 years				
Benzene		0.50	0.13	3.1	12
Toluene		1.33	0.04	4.0	31
Ethylbenzene		0.37	0.47	-	-
Total Xylenes		2.32	2.03	0.5	1.3
Total BTEX		4.52	2.67	1.7	2.9
McChord AFB, WA	22 years				
Benzene		0.50	0.00[b/]	4.5	42
Toluene		1.33	0.00	4.5	44
Ethylbenzene		0.37	0.00	4.5	41
Total Xylenes		2.32	0.00	4.5	43
Total BTEX		4.52	0.00	4.5	43

[a/] Based on assumed analyte concentrations in fresh JP-4 fuel.

[b/] Nondetect values.

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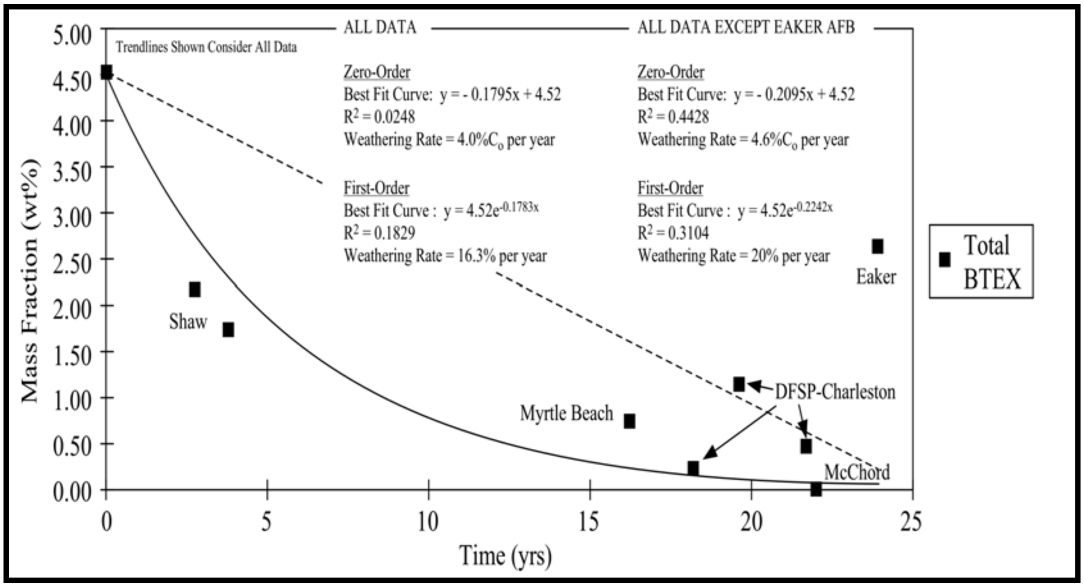

Figure 2. Total BTEX Weathering Considering Average Data from the JP-4 Release Sites--Fuel Weathering Study

a 5M x 0.25mM ID uncoated, deactivated guard column. Column oven temperature was 32°C for four minutes, then 4°C per minute to 70°C, and 20°C per minute to 200°C, hold one minute. Quantitation standards ranged from 0.025 to 250 µg/mL. Density of the product was determined by weighing a known volume.

DATA ANALYSIS

LNAPL weathering was determined by mass fraction reduction of BTEX as compared to assumed initial BTEX levels. Average annual contaminant reduction rates for both zero-order and first-order weathering are shown in Table 3. Highest rates for BTEX weathering were measured at Shaw AFB where the zero-order and first-order rates were 18%/yr. and 23%/yr., respectively. Lowest rates occurred at Eaker AFB and were 1.7%/yr. and 2.9%/yr., respectively.

Figure 2 shows a compilation of the five average total BTEX concentrations into one weathering plot. Zero-order weathering assumed that concentration of a contaminant was depleted at a constant rate regardless of concentration, while first-order rates used nondetect values for C. R^2 indicated the variance between the data and predictive trend lines. Generally, the zero-order curve underestimates total BTEX depletion. The first-order curve provided a more reasonable approximation of BTEX depletion. Also in Figure 3, the first-order curve for benzene alone is a more reasonable approximation of benzene weathering in mobile LNAPL at the five JP-4 sites.

The JP-4 site data indicated that BTEX mobile LNAPL weathering is predominately a dissolution function. As concentrations in the mobile LNAPL decrease, depletion rates also decrease, which occurred as the age of spill increased. Considering the plots in Figures 2 and 3, in the first-order curves provided reasonable estimates of total BTEX and benzene weathering. The overall

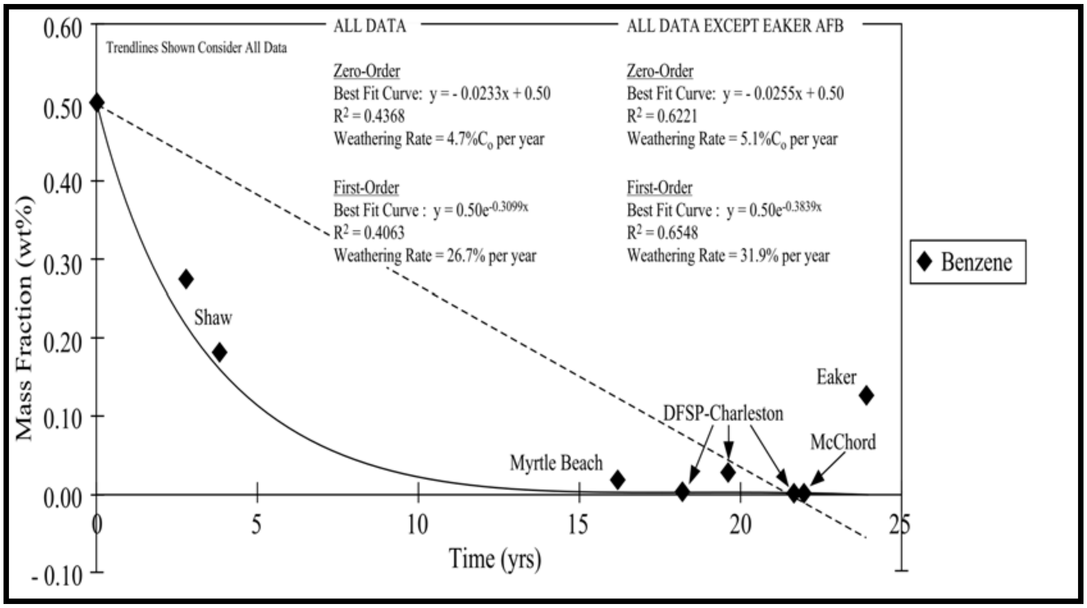

Figure 3. Benzene Weathering Considering Average Data from the JP-4 Release Sites--Fuel Weathering Study

first-order rate for total BTEX weathering from JP-4 mobile LNAPL was near 16%/yr. Reduced chemical concentrations in mobile LNAPL indicated that dissolution was the predominant weathering mechanism and was dominated by benzene.

CONCLUSIONS

- Free-phase fuel BTEX weathering rates varied for the five fuel release sites as influenced by factors of spill age and relative solubilities.
- Dissolution was the primary weathering mechanism that influenced mobile LNAPL rates.
- The average total BTEX for five JP-4 release sites based on first-order weathering was near 16%/year.
- The average benzene first-order weathering rate for the five sites was near 26%/year.
- As expected, benzene exhibited a higher weathering rate than the other BTEX components.

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