

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 LNAPL 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 gasoline was difficult because of the large ranges of initial BTEX values.

Key words: *weathering, JP-4, LNAPL's*

INTRODUCTION

Little information has been available regarding rates of natural weathering of BTEX components from mobile fuel LNAPL's. Because of this, reduction rate source terms in groundwater models are 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 has been the fuel type most widely spilled at Air Force bases; and for jet fuels, it has the highest initial BTEX fractions.

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.

LITERATURE REVIEW

The search did not identify any field studies to evaluate BTEX reductions within mobile LNAPL's 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.

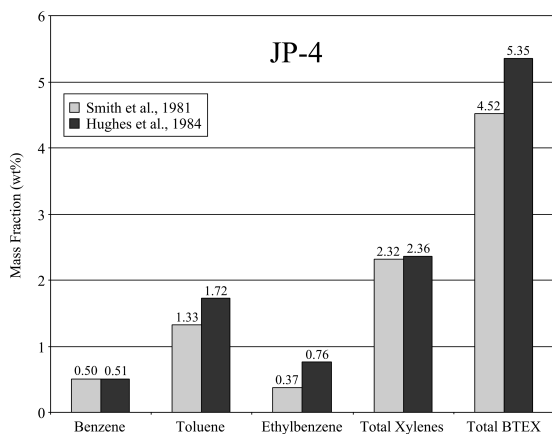


Figure 1. BTEX Concentrations in Fresh Fuels—Fuel Weathering Study

DISSOLUTION AND WATER SOLUBILITY

Dissolution is the 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 determining the fate and transport in the subsurface. Water solubility and effective solubility of JP-4 and

gasoline are listed in Table 1. 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

Five JP-4 fuel release sites were selected for the study and are listed in Table 2. Both soil and groundwater samples were collected. The samples were analyzed using standard analytical methods involving gas chromatographic/mass spectrometry techniques.

Table 1. Dissolved Concentrations of BTEX

Compound	Water ^{a/} Solubility	Water Concentrations in Contact with Fuel (effective solubility) at a 1:10 ratio	
		JP-4 ^{b/}	Gasoline ^{c/}
mg/L			
Benzene	1750	9.8	58.7
Toluene	524	8.5	33.4
Ethylbenzene	187	0.7	4.3
o-Xylene	167	1.2	6.9
m-Xylene	157	2.0	11.0
p-Xylene	180	0.4	4.4
Total Xylenes	168	3.6	22.3

^{a/} Solubilities at 25^o C (Montgomery, 1996)

^{b/} Smith et al., 1981

^{c/} American Petroleum Institute, 1985

DATA ANALYSIS

LNAPL weathering was determined by a 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 2. Highest rates for BTEX weathering were measured at Shaw AFB

where the zero-order and first-order weathering are shown in Table 2. 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.

Table 2. BTEX Weathering Rates 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
DFSP-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

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

Figure 2 shows a compilation of the five average total BTEX concentrations into one weathering plot. 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 predominantly a dissolution function. As concentrations in the mobile LNAPL decrease, depletion rates

also decrease, which occurs as the age of spill is increased. Considering the plots of Figures 2 and 3 in the first-order curves provided reasonable estimates of total BTEX and benzene weathering. The overall 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

Table 2, cont. BTEX Weathering Rates in JP-4 Mobile LNAPL

Site Analyte	Spill Age	Initial Conc. ^{a/}	Remaining Conc.	Zero-Order	First-Order
		wt %		Average % Reduced/Year	
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

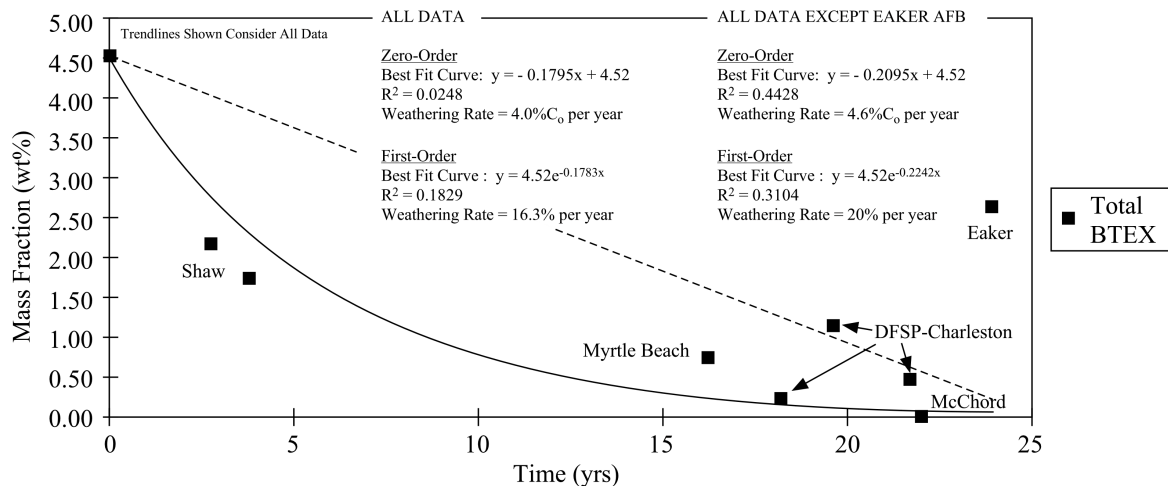


Figure 2. Total BTEX Weathering, Considering Average Data from the JP-4 Release Sites—Fuel Weathering Study

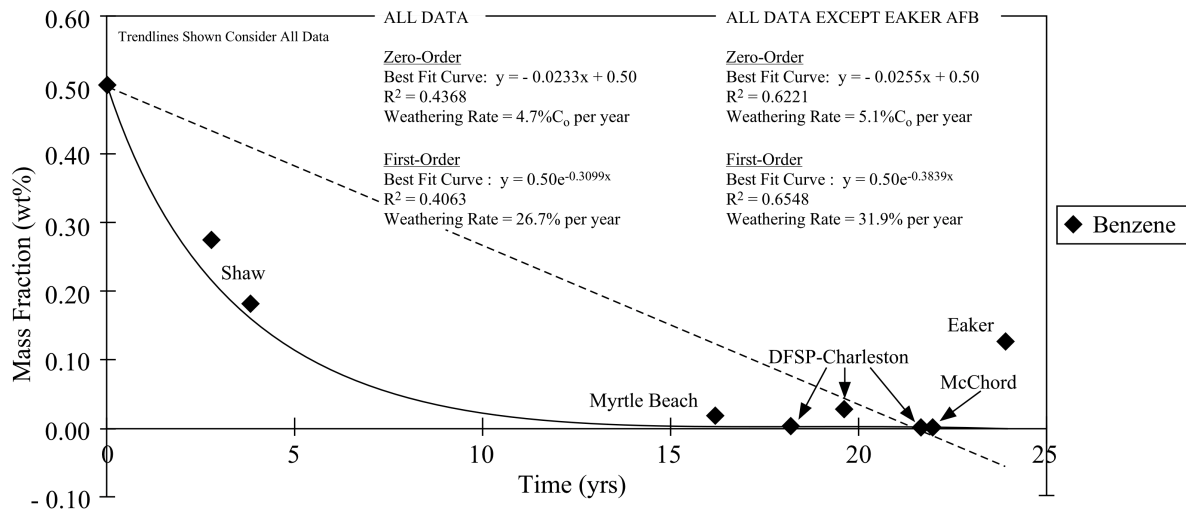


Figure 3. Benzene Weathering, Considering Average Data from the JP-4 Release Sites—Fuel Weathering Study

- varied for the five fuel release sites as influenced by factors of spill age, relative solubilities, subsurface moisture, and soil texture.
- 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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