THE EVAPORATION of BENZENE and a SERIES of ALKANES from CRUDE OIL

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Abstract

The concentrations of benzene, pentane, hexane, heptane, and octane evaporating from a large, open pan of fresh crude oil were measured over a 7-hour period. Results of these measurements indicated that the maximum benzene concentration 19 millimeters above the fresh oil was 90 parts per million by volume and decreased quickly as the oil weathered.

Introduction

During accidental oil spills, emergency response and remediation workers often work near freshly spilled oil. Benzene is a highly volatile component of crude oils and many refined petroleum products. Consequently, significant airborne concentrations can be expected above and downwind of spills and might pose a health hazard to these workers. This report describes the measurement of the airborne concentrations of benzene and a series of alkanes evaporating from an oil spill under one set of well-characterized conditions.

Methods

In situ measurements of the airborne concentration of a series of hydrocarbons were made over a 7-hour period above a large pan of freshly poured crude oil. Two gas chromatographs were used to sample and analyze the air for volatile organic compounds at two vertical positions above the center of the pan. Wind velocity, air temperature, relative humidity, solar energy flux, and oil temperature were measured to characterize the environmental factors affecting evaporation and transport.

The measurements were made on May 29, 1991, at Little Sand Island in Mobile Bay, a site managed by the United States Coast Guard Fire and Safety Test Detachment.

During the experiment, the oil was in a large, square, double-walled steel pan. The inside pan dimensions were 15.5 meters (m) by 15.5 m by 0.6 m deep. The outer wall enclosed a water filled moat that was approximately 1 m wide (the moat was designed for cooling water during oil burning experiments and did not affect the present measurements). The pan was aligned 12 degrees relative to true north. The area surrounding the pan for 30 m or more consisted of sandy soil with short, sparse grasses. The southern bank of the island was 60 m south of the pan. To reduce turbulence near the upwind edge of the pan, sheets of plastic 1.2 m wide were stretched tight from the top of the southern wall of the pan to the ground. Before introducing the oil, the inner pan was filled to a depth of 0.50 m with water pumped from Mobile Bay. Wooden booms were used to make a smaller square area, 6.10 m

on a side, in the northwest corner of the pan. At 8:00 A.M. local time, a Louisiana crude oil supplied from the Exxon refinery in Baton Rouge was pumped into the water in the reduced area to a depth of 62 millimeters (mm), the filling process took 13 minutes (min).

Samples of the oil were taken 5 min and 465 min after the oil was introduced into the pan; care was taken to minimize the headspace in the bottles containing the samples. Within 3 days of the experiment, these samples were analyzed for benzene, toluene, and xylenes using a Hewlett Packard 589 ™ gas chromatograph coupled with a Hewlett Packard 5970 Mass Selective Detector™ (Getty, 1991).

Shortly after introducing the oil, the air sampling procedure began. Air was continually sampled at two positions above the center of the oil spill, 19 mm and 95 mm above the surface of the oil. Since the oil level was continually dropping due to evaporation, the positions of these sampling points relative to the oil's surface increased to 24 mm and 100 mm by the end of the experiment. By sampling in the center of the oil, variations in fetch across the oil upwind of the sampling point were minimized; the fetch across the oil varied from 3.0 to 4.3 m. The air was sampled using two Teflon sampling tubes, 3.2 mm inside diameter and 7.6 m long, attached at one end to a steel rod placed on a stand in the oil and sampling pumps on the other end. A flow rate of 500 milliliters (ml) min^{-1} was maintained. Three ml of the air stream were diverted from each sample line to the gas chromatographs for analysis at 10-min intervals during the first 3 hours of the experiment and at 20-min intervals thereafter.

Samples were analyzed using two Micromonitor M200™ dual gas chromatographs operated isothermally at 40°C. Carrier gas velocities were, as specified in the standard operating procedure developed at Louisiana State University, 0.50 m sec^{-1} for the nonpolar OV-73 column (Column A) and 0.57 m sec^{-1} for the moderately polar OV-1701 column (Column B). Injection times were 255 milliseconds (ms) (corresponding to approximately 100 nanoliters). Concentrations were calculated by the M2001 software for benzene and four normal alkanes based on authentic 100 parts per million by volume (ppmv) standards. The detection limit was approximately 1 ppmv, and the systematic error limit was estimated to be less than 5 percent. Benzene, the principle component of interest, was not resolved from cyclohexane on the OV-73 column but was resolved on the OV-1701 column.

Oil temperature measurements were made with an array of 11 low resolution (± 2°C) thermocouples located at various depths within the oil. These 11 measurements were averaged to obtain a mean oil temperature. The initial volume of the oil was measured using a flow meter in the oil supply pipe; however, inconsistencies between this measurement and other indications of initial oil volume suggested a malfunction in the flow meter. The fluid level relative to the top of the pan was measured before introducing the oil, immediately after the oil was introduced, and then hourly during the experiment. Two measurements of the oil thickness were made during the last hour of the experiment using a dip stick coated

with an indicator that changes color when immersed in water. This method was reproducible to ± 2 mm.

Air temperature and wind velocity were measured at an elevation of 2 m about 10 m south of the pan using a Campbell Scientific Weather Station interfaced to an Apple Macintosh computer. Relative humidity was measured with a sling psychrometer hourly about 20 m west of the pan. The instantaneous solar energy flux was measured at ground level about 20 m west of the pan with two solar pyranometers.

Results

The API gravity of the freshly spilled crude oil was measured to be 35.6 (Walton, 1991). No other characterizations beyond analysis for benzene, toluene, and xylenes were made.

An initial oil thickness of 62 mm ± 6 mm was derived from the measured oil and water levels and the relative densities of the oil and water[1]. Near the end of the experiment, 465 minutes after it began, the oil's thickness was 53 mm ± 2 mm. The oil's thickness as a function of time was calculated from these two measurements using an evaporation model (Jones, 1992). Since the distillation data for the oil was not available, distillation data for Louisiana crude oil with the same density was used to initialize the model. The calculated thickness is presented graphically in Figure 1.

Measurements of airborne concentrations were initiated at 8:18 A.M. local time and were completed 7 hours later. During this period, air temperatures ranged from 26° to 28°C. Relative humidity decreased from 91 to 78 percent. Winds were initially out of the southeast at about 2 m s^{-1} and gradually shifted to the southwest and increased to 5 m s^{-1}. Except for a brief period during the mid morning, the skies were clear. The average oil temperature rose from about 27 to 50°C. Table 1 contains measured oil temperatures, air temperature, wind speed, wind direction, and fetch over the oil. The oil temperature was averaged over 5 min; the wind speed was scalar averaged over 2 min; the wind direction, air temperature, and fetch over the oil were averaged over 2 min. Figures 2 and 3 show the measured wind speed and solar energy flux.

The concentration of benzene in the oil 5 min after the oil was introduced into the pan was 996 ppm by mass. After an additional 460 min of weathering, the concentration dropped to below 200 ppm by mass, the detection limit of the analytical method.

The measured airborne concentrations of benzene and four normal alkanes are presented in tabular and graphical form in Tables 2 through 6 and Figures 4 through 8. The airborne concentrations at 19 mm of the hydrocarbons decreased with time; pentane concentrations dropped most rapidly, followed by hexane, benzene, heptane, and octane. The measurements made at 95 mm exhibited large fluctuations

over the first 3 hours of the experiment; after 200 minutes, declining concentrations were observed. At 19 mm, the measured concentration of benzene, the chemical associated with the greatest health risk, ranged from 90 ppmv to 8 ppmv. At 95 mm, the concentration of benzene dropped to less than 10 ppmv after about 3 hours.

Conclusions

The evaporative mass flux is the rate at which a chemical is introduced into the air and is central to determining the airborne concentration at any point above or downwind of the oil. The evaporative flux is primarily a function of chemical's vapor pressure, its concentration in the surface layer of the oil, and the wind speed. Wind velocity and turbulence also have pronounced effects on airborne concentrations. Wind and turbulence affect the evaporation and transport of all the measured chemicals in approximately the same way. At any given time and height, the differences between the chemicals can be attributed to the differences in vapor pressures and concentrations in the oil.

Measurements of all the hydrocarbons at 95 mm exhibited a similar pattern of wide fluctuations in concentration over the first 3 hours of the experiment. These fluctuations were attributed to the effects of thermally induced turbulence. The turbulence at this height was dominated by buoyant forces resulting from temperature differences between the oil's surface and the air. In contrast, at 19 mm above the oil's surface, turbulence was induced primarily by mechanical means, for example, frictional effects at the surface. The integration time of the sampling procedure (>250 ms) was sufficiently large to average out any of these faster fluctuations in the measured concentrations.

The concentrations of benzene and alkanes measured in this study are not generally representative of concentrations expected near spills of different oils or under different conditions. However, this study did provide a limited data set that can be used to test evaporation models. The authors believe that both modeling and further experimentation are needed to adequately address the air quality issues associated with oil spills.

Endnotes

1. Since the thickness derived from the flow meter measurement was judged unreliable, a less direct method was used to calculate the initial thickness of the oil using hydrostatic principles:

$$H = \Delta Z[1 - (\frac{R_A R_D}{1 + R_A})]^{-1},$$

where   H = initial thickness of the oil,

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$\Delta Z =$ difference between the water level prior to filling
and the level of the oil after introducing the oil to
the pan,

$R_A =$ (area covered by water)/(area covered by oil),

$R_D =$ (density of oil)/(density of water).

Acknowledgments

References

Getty, S. 1991. Personal communication, analysis performed by Roy F. Weston Inc. as part of Project No. 3327-21-01-3484 under EPA Contract No. 68-03-3482.

Jones, R. 1992. Personal communication, an oil weathering model in development by the National Oceanic and Atmospheric Administration was used to compute evaporation rates.

Walton, D. 1991. Personal communication, measurements were conducted by the National Institute of Standards and Technology, Gaithersburg, MD.

Table 1. Environmental conditions.

time	elapsed time (minutes)	oil temperature (centigrade)	air temperature (centrigrade)	wind speed (m/s)	wind direction (degrees)	fetch over oil (meters)
8:18	0	27.29	25.87	2.54	138	3.75
8:28	10	27.05	26.01	2.41	141	3.91
8:39	21	29.55	26.06	2.08	147	4.30
8:50	32	31.43	26.33	1.64	160	3.58
9:00	42	31.76	26.08	1.65	153	3.92
9:11	53	32.17	26.54	1.61	165	3.41
9:21	63	33.19	26.78	1.93	163	3.49
9:32	74	34.32	27.05	1.55	170	3.30
9:42	84	36.43	27.25	1.43	151	4.05
9:53	95	38.01	27.31	1.33	185	3.07
10:04	106	39.91	27.59	1.50	203	3.11
10:14	116	44.20	27.37	2.26	204	3.12
10:25	127	45.60	27.67	2.64	193	3.05
10:35	137	45.76	27.50	3.22	192	3.05
10:46	148	46.22	27.74	3.16	188	3.06
10:57	159	47.38	27.82	3.30	177	3.16
11:07	169	47.79	27.68	3.35	184	3.08
11:18	180	48.01	27.76	3.79	186	3.06
11:28	190	47.72	27.96	3.98	188	3.06
11:39	201	47.95	28.01	3.74	172	3.24
12:01	223	50.54	27.88	3.79	170	3.28
12:21	243	55.68	27.92	3.81	178	3.14
12:42	264	54.73	27.85	4.47	189	3.05
13:02	284	56.07	27.95	4.88	182	3.10
13:23	305	52.50	28.28	4.41	170	3.28
13:43	325	52.91	27.99	5.00	185	3.08
14:04	346	54.38	28.17	5.53	178	3.14
14:25	367	48.02	28.41	5.01	157	3.72
14:45	387	50.51	28.08	5.45	163	3.48
15:06	408	51.22	28.20	5.33	180	3.12

Table 2.   Benzene concentrations in ppmv.

elapsed time (minutes)	column B at 19 mm	column B at 95 mm
0		4
10		10
21	90	6
32	88	4
42	74	2
53	56	
63	47	
74	40	18
84	36	5
95	33	17
106	31	5
116	28	9
127	29	11
137	27	7
148	26	9
159	25	8
169	25	13
180	26	9
190	29	15
201	29	6
223	33	5
243	23	5
264	24	4
284	20	2
305	20	2
325	16	3
346	13	1
367	12	1
387	10	
408	8	1

Table 3.   Pentane concentrations in ppmv.

elapsed time (minutes)	col.A at 19 mm	col.B at 19 mm	average at 19 mm	col.A at 95 mm	col.B at 95 mm	average at 95 mm
0				53	50	52
10				127	102	114
21	2605	>2000		70	52	61
32	2335	>2000		32	24	28
42	1555	>1500		19	14	17
53	1001	1190	1095			
63	686	805	745			
74	499	571	535	144	122	133
84	375	420	397	31	25	28
95	291	317	304	121	87	104
106	239	253	246	31	17	24
116	212	223	218	58	54	56
127	197	205	201	81	74	77
137	185	191	188	41	32	37
148	174	176	175	45	51	48
159	166	167	167	51	38	44
169	173	175	174	76	58	67
180	183	189	186	43	26	35
190	181	187	184	83	57	70
201	170	172	171	29	22	26
223	132	131	131	18	11	14
243	116	109	112	14	9	11
264	99	88	93	12		
284	82	72	77	5		
305	66	55	61	4		
325	52	40	46	6		
346	40	27	33	2		
367	31	21	26	1		
387	25	15	20	1		
408	20	11	15			

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Table 4.   Hexane concentrations in ppmv.

elapsed time (minutes)	col.A at 19 mm	col.B at 19 mm	average at 19 mm	col.A at 95 mm	col.B at 95 mm	average at 95 mm
0						
10						
21	916	911	913	25	25	25
32	882	877	880	68	58	63
42	631	627	629	38	31	35
53	440	441	440	20	20	20
63	331	330	331	11	12	11
74	264	262	263			
84	220	218	219			
95	190	193	191	110	95	102
106	172	171	171	25	27	26
116	163	163	163	101	80	91
127	157	157	157	27	22	24
137	151	150	150	43	47	45
148	140	140	140	60	62	61
159	133	133	133	34	34	34
169	139	138	138	36	47	41
180	148	149	148	42	39	40
190	155	154	154	71	66	69
201	152	152	152	45	39	42
223	135	134	134	87	73	80
243	123	122	123	30	33	32
264	113	112	112	26	26	26
284	100	99	100	19	22	20
305	85	84	85	19	16	18
325	73	69	71	9	9	9
346	57	57	57	9	7	8
367	47	47	47	11	12	11
387	39	38	38	3	3	3
408	32	31	31	2	2	2

Table 5.   Heptane concentrations in ppmv.

elapsed time (minutes)	col. A at 19 mm	col. B at 19 mm	average at 19 mm	col.A at 95 mm	col.B at 95 mm	average at 95 mm
0				9	12	11
10				30	31	31
21	269	272	270	18	17	17
32	294	296	295	11	13	12
42	230	235	233	5	6	6
53	180	182	181			
63	146	148	147			
74	126	128	127	70	73	72
84	115	116	116	17	21	19
95	110	111	111	69	68	69
106	108	109	109	21	20	21
116	109	111	110	24	32	28
127	110	110	110	34	45	39
137	106	109	107	23	28	25
148	98	101	100	21	31	26
159	95	95	95	27	28	28
169	95	96	95	47	54	51
180	99	100	100	35	35	35
190	105	108	107	65	67	66
201	108	109	109	21	28	25
223	100	105	103	26	31	28
243	100	102	101	19	26	22
264	99	100	99	22	23	23
284	94	95	94	15	16	15
305	86	88	87	16	15	15
325	79	80	80	17	22	19
346	71	72	71	6	7	7
367	63	64	63	4	5	5
387	57	56	57	3	3	3
408	49	49	49	5	7	6

Table 6.   Octane concentrations in ppmv.

| elapsed time (minutes)	col.A at 19mm	col.B at 19 mm	average at 19 mm	col.A at 95 mm	col.B at 95 mm	average at 95 mm
0				4	3	3
10				14	13	13
21	56	65	61	10	7	8
32	77	90	84	6	6	6
42	72	86	79	4	3	3
53	62	70	66			
63	56	62	59			
74	48	75	62	46	39	43
84	48	58	53	12	13	12
95	48	56	52	46	43	44
106	52	59	55	19	14	17
116	54	62	58	14	15	15
127	61	63	62	20	22	21
137	59	67	63	16	15	15
148	55	66	60	14	15	14
159	55	63	59	15	16	15
169	55	61	58	27	27	27
180	57	60	58	22	22	22
190	59	61	60	41	39	40
201	59	69	64	13	13	13
223	58	82	70	23	18	21
243	59	67	63	16	16	16
264	59	68	63	17	17	17
284	58	67	63	19	11	15
305	63	66	65	19	18	18
325	59	62	61	18	22	20
346	55	62	58	10	10	10
367	55	63	59	6	6	6
387	51	61	56	9	5	7
408	50	50	50	11	8	10
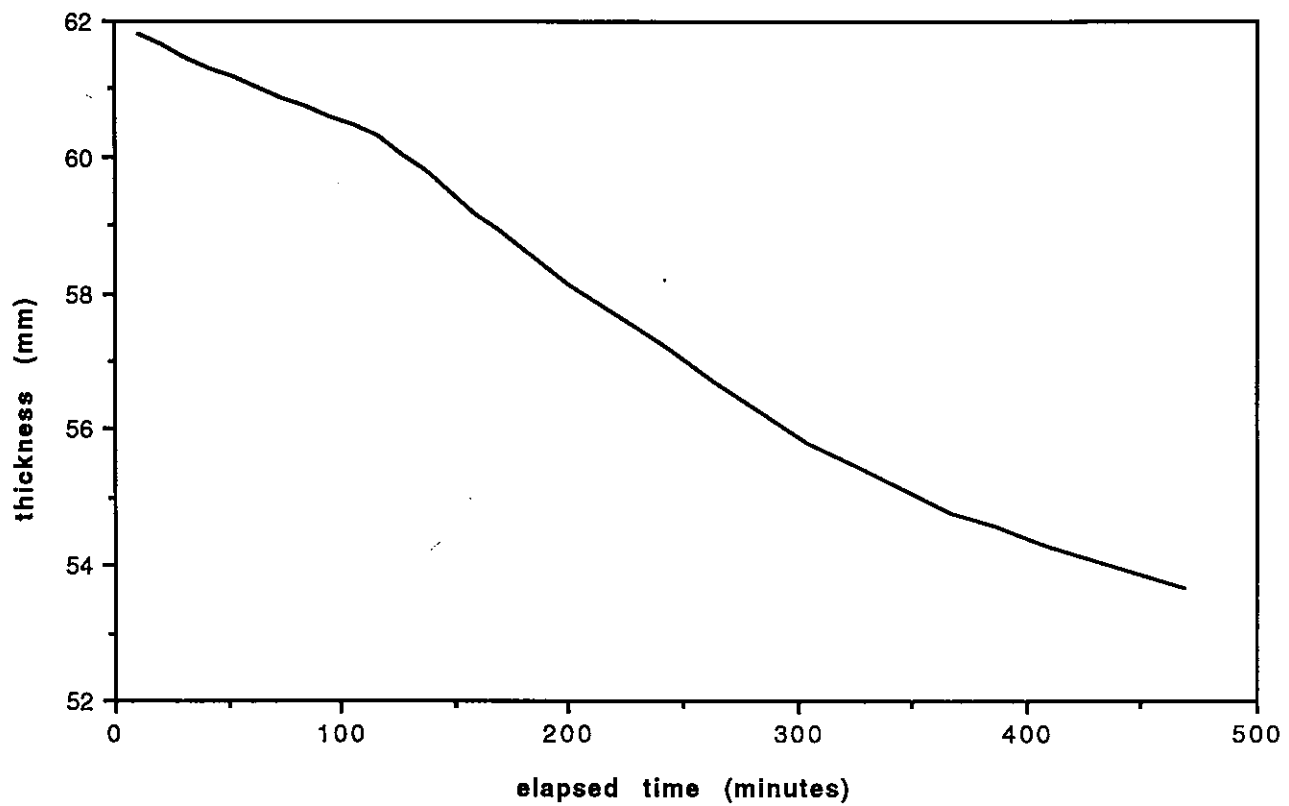
Figure 1. Calculated oil thickness.
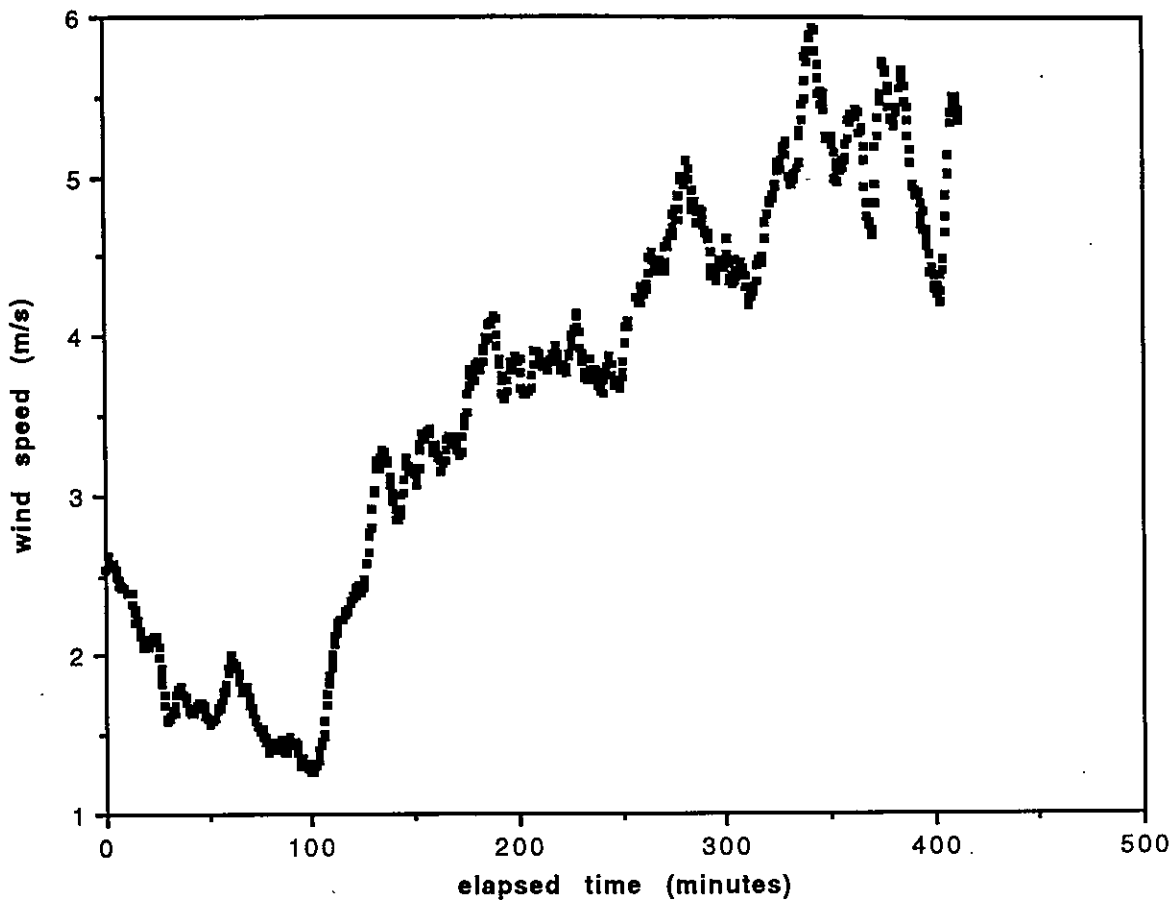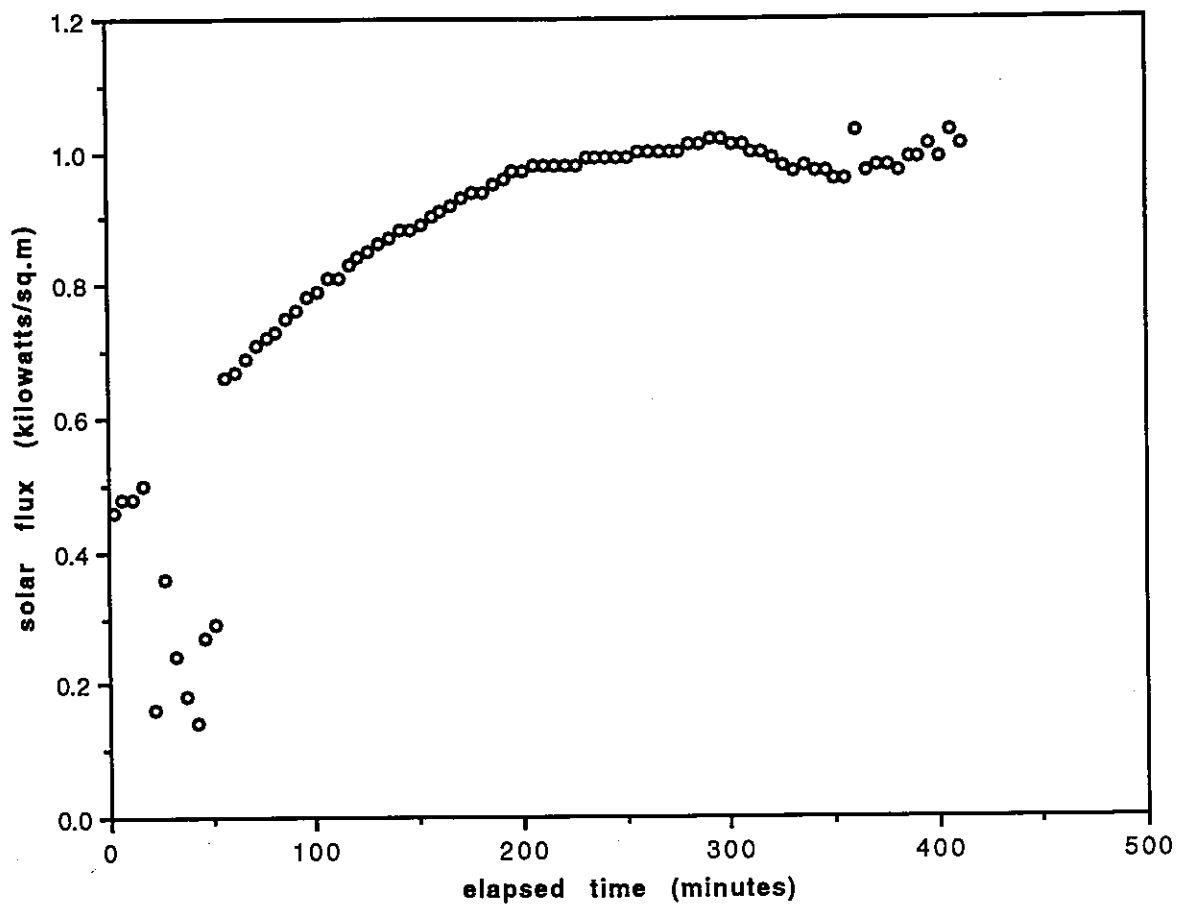
Figure 2. Wind speed.
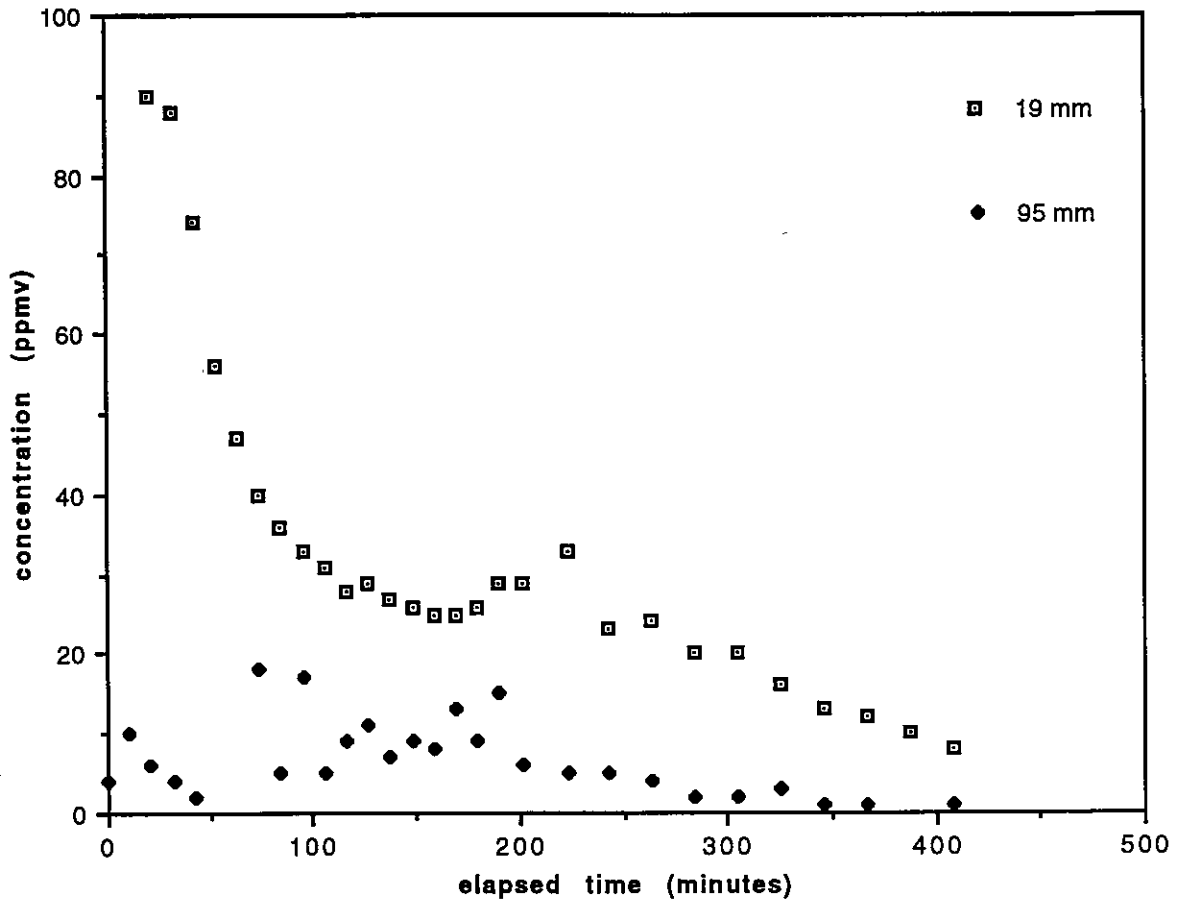
Figure 3. Solar radiation.

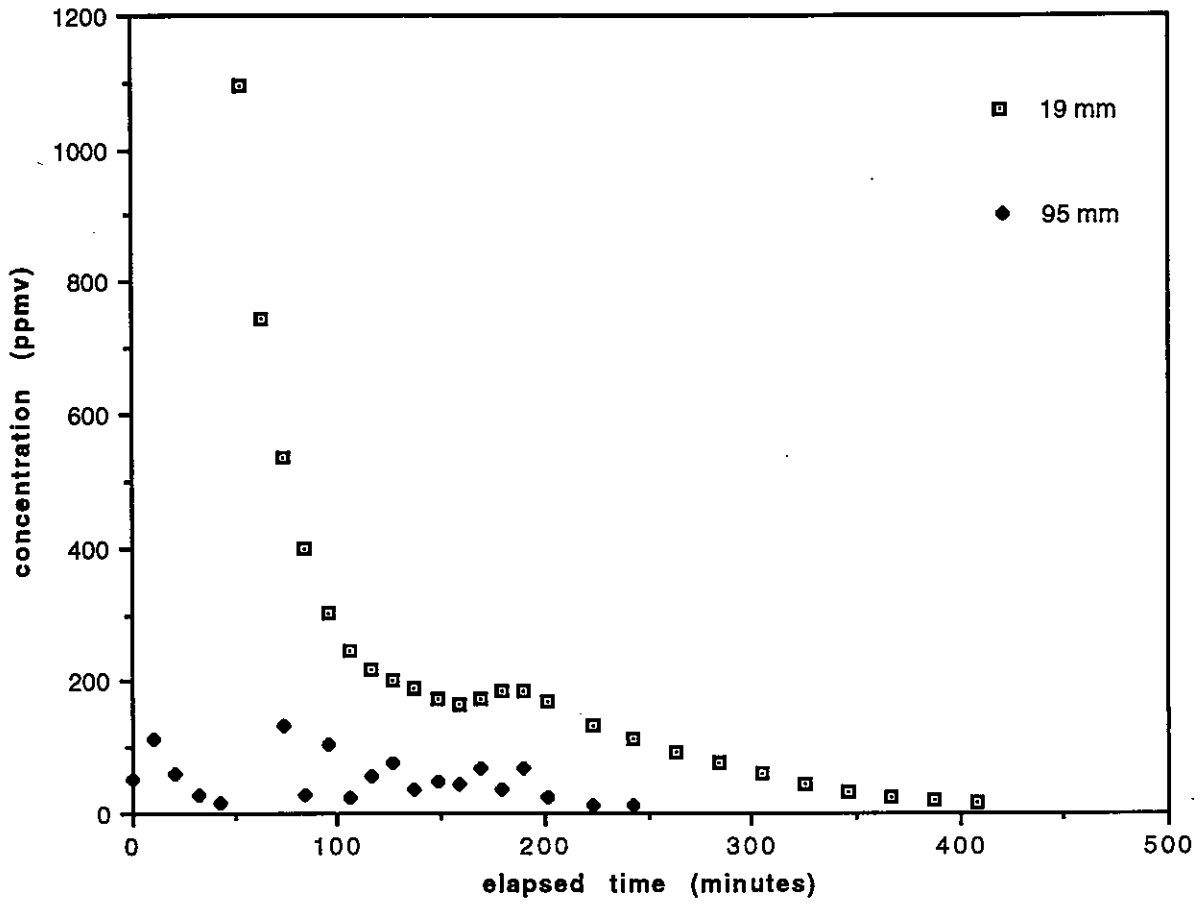Figure 4. Benzene concentrations.
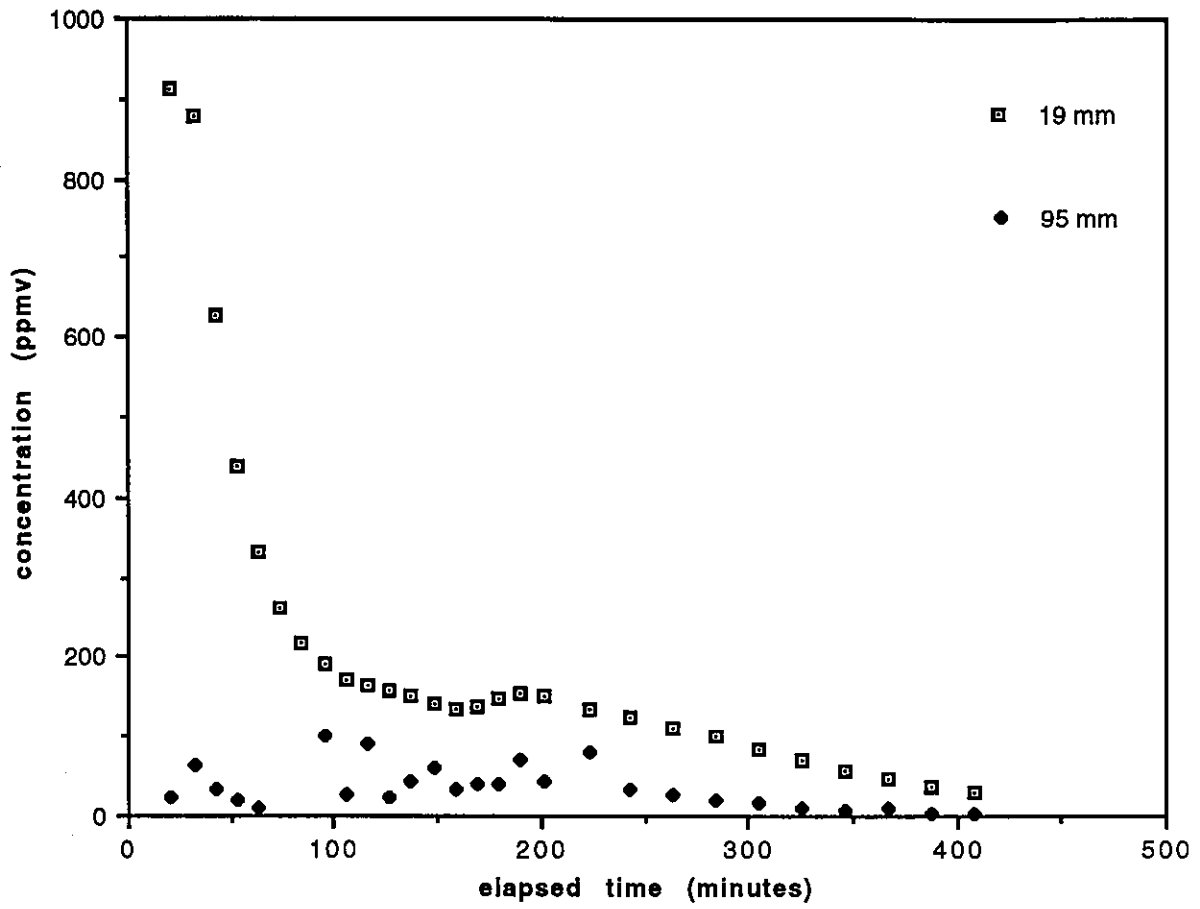
Figure 5. Pentane concentrations.
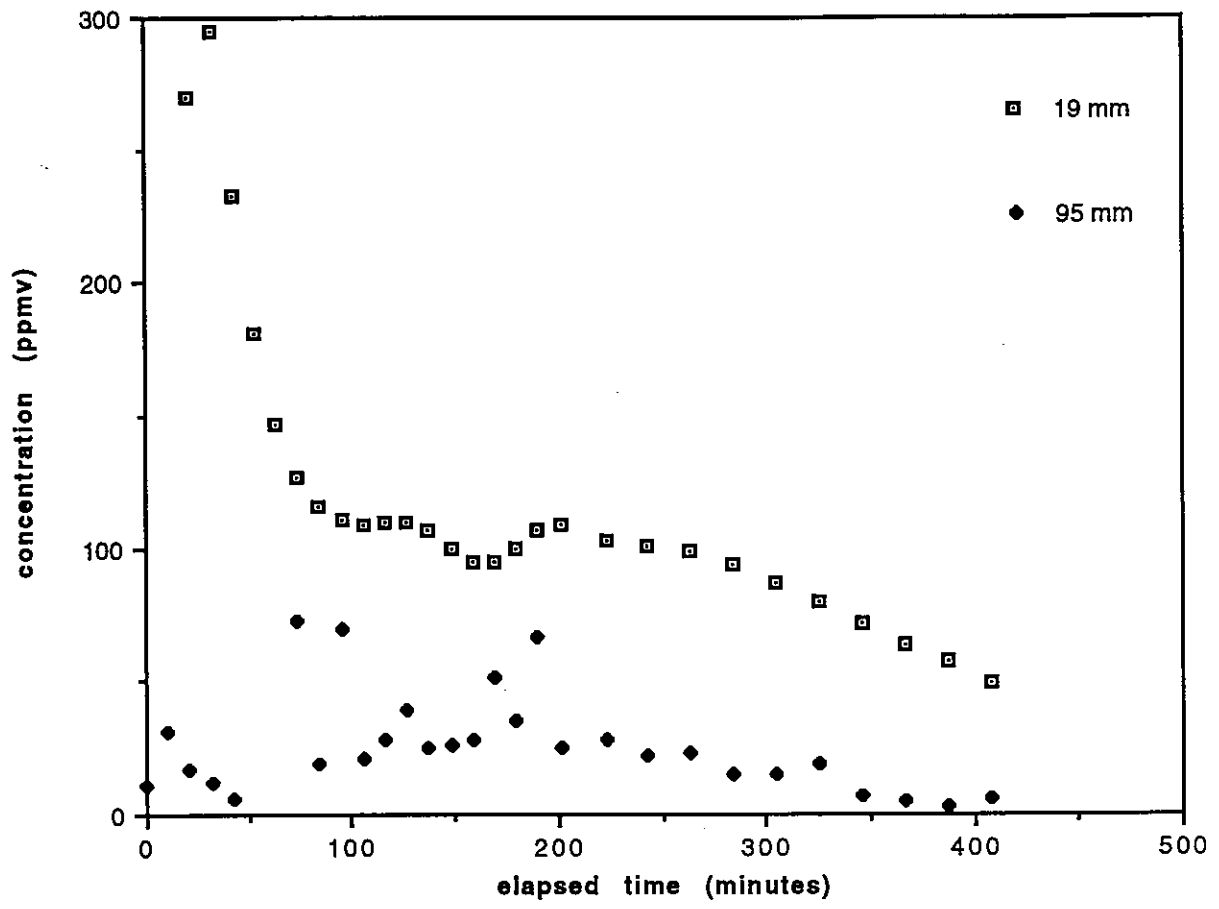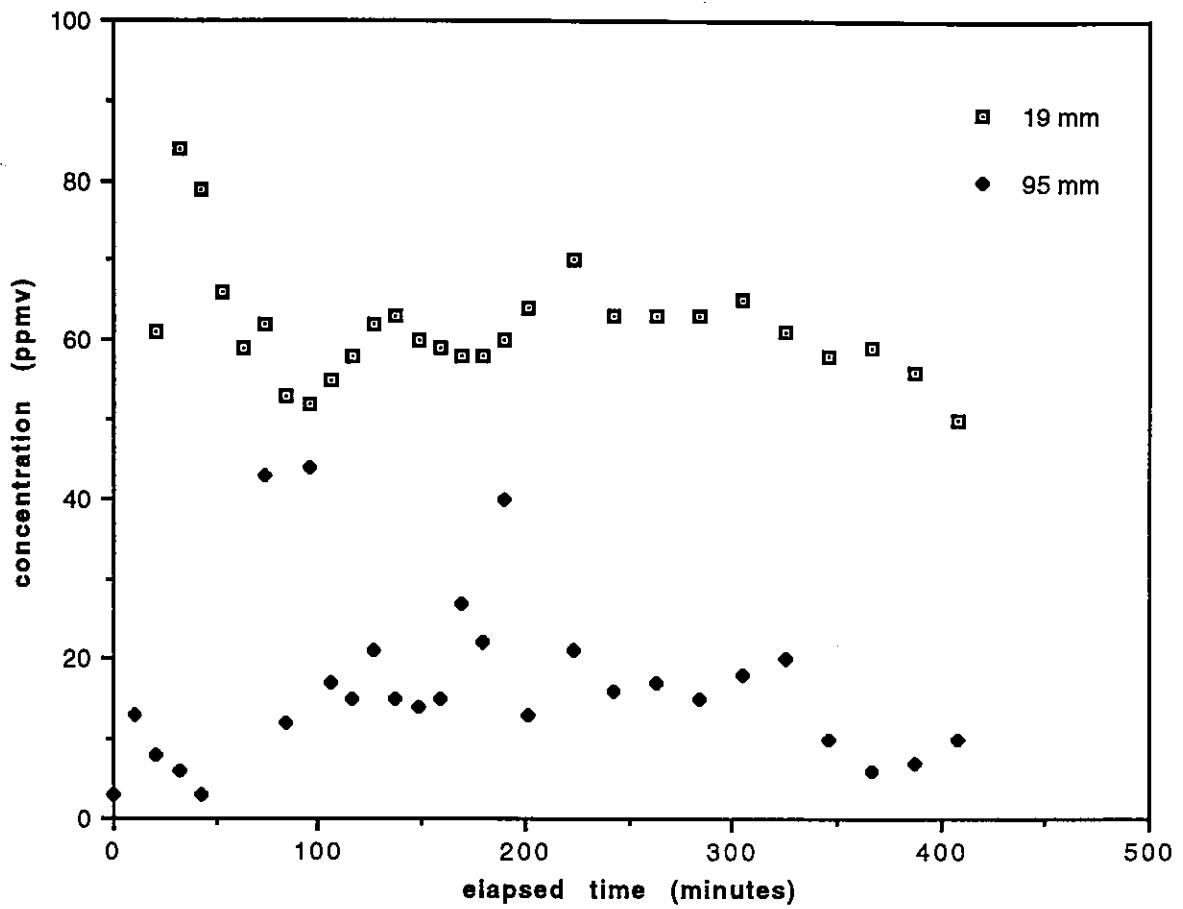
Figure 6. Hexane concentrations.

Figure 7. Heptane concentrations.

Figure 8. Octane concentrations.