

Reconnaissance Investigation of Petroleum Products in Soil and Ground Water at Longmire, Mount Rainier National Park, Washington, 1990

U.S. GEOLOGICAL SURVEY

Open-File Report 94-4030

Water-Resources Investigations Report 94-4030

Prepared in cooperation with

NATIONAL PARK SERVICE



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By S.S. Sumioka

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Tacoma, Washington
1995

U.S. DEPARTMENT OF THE INTERIOR

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U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
inch (in)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer

Temperature: To correct temperature given in this report in degrees Fahrenheit ($^{\circ}\text{F}$), to degrees Celsius ($^{\circ}\text{C}$), use the following equation: $^{\circ}\text{C} = 5/9(^{\circ}\text{F}-32)$

Sea Level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

RECONNAISSANCE INVESTIGATION OF PETROLEUM PRODUCTS IN SOIL AND GROUND WATER AT LONGMIRE, MOUNT RAINIER NATIONAL PARK, WASHINGTON, 1990

By S.S. Sumioka

ABSTRACT

The routine removal of a waste-oil underground storage tank in Mount Rainier National Park at Longmire, Washington, in 1989 led to the discovery that soil surrounding the tank was saturated with unidentified petroleum hydrocarbons. Subsequent investigation by the National Park Service indicated that a petroleum product that smelled like diesel oil was present in the unsaturated zone as far as 120 feet from the tank site. A study was conducted in cooperation with the National Park Service to determine the extent to which the petroleum hydrocarbon(s) have affected the unsaturated zone and ground water in the Longmire area.

Measurements of water levels in wells and of water-surface elevations of the Nisqually River and a wetland west of Longmire indicate that ground water does not flow from the maintenance area to the river or to the wetland. Therefore, it is unlikely that petroleum hydrocarbons affect the Nisqually River near Longmire or the wetland.

Waste oil and diesel oil were detected in soil samples from the site nearest the waste-oil storage tank site. Diesel oil also was detected in samples from a site about 200 feet northwest of the storage-tank site. Organic compounds of undetermined origin were detected in soil samples from all other sites.

Waste oil was not conclusively detected in any of the ground-water samples. Diesel oil was detected in water samples from the well nearest the storage tank and from a well about 200 feet west of the storage-tank site. Ground-water samples from all of the other wells contained organic compounds of undetermined origin.

The findings indicate that diesel oil is the most likely source of most of the organic compounds detected in the soil and ground-water samples; however, a specific source of the diesel oil could not be determined. Although detected in soil samples from the vicinity of the storage tank, waste oil could not be identified as the source of organic compounds in ground water.

INTRODUCTION

Longmire, Wash., located within Mount Rainier National Park, about 50 mi southeast of Tacoma, Wash. (fig. 1), is the site of some National Park Service (NPS) administrative offices, concessionaire offices, maintenance and visitor facilities, and employee housing. The visitor facilities include a visitors' interpretive center, museum, hikers' center, gasoline station, restaurant, gift shop, and lodge. Longmire Meadow, a spring-fed wetland area, is located just west of Longmire. The resident employee population of Longmire ranges from about 40 in winter to about 80 in summer. Many of the approximately 2 million people who visit the park each year use the facilities at Longmire. Drinking water is obtained from springs upgradient from the maintenance area.

In 1989, during the removal of a waste-oil underground storage tank (hereafter referred to as the tank), which served a nearby vehicle and equipment garage in the maintenance area (fig. 1), soil surrounding the tank appeared to be saturated with an oil-like product. The tank itself appeared to be in good condition; the only apparent defect was an improperly installed access plug at the top of the tank. In 1990, NPS investigated further by digging five trenches as much as 22 ft deep within 120 ft of the tank and by collecting soil samples for petroleum-hydrocarbon analyses (fig. 1). Two samples collected from the

northern part of trench 1 and all three samples from trench 5 contained total petroleum-hydrocarbon concentrations ranging from about 110 ppm (parts per million) to about 8,600 ppm. Two samples from the southern part of trench 1 and single samples from trenches 2 and 4 contained total petroleum hydrocarbon concentrations ranging from less than 5 ppm to about 32 ppm. Even though the sample from trench 2 contained the lowest total petroleum hydrocarbon concentration (less than 5 ppm), a hydrocarbon odor (William Oates, National Park Service, written commun., 1990) was noted in this trench. No samples were collected from trench 3, although a hydrocarbon odor was also noticed in this trench. The NPS concluded from its investigation that the area affected by petroleum hydrocarbons extended about 120 ft northwest of the tank site and was about 50 ft wide at its widest point (William Oates, National Park Service, written commun., 1990).

Although the soil surrounding the tank contained high levels of what appeared to be waste oil disposed of in the tank, the product found in the trenches smelled of diesel oil. Many underground and above-ground diesel-oil storage tanks are present in the Longmire area; two are within 40 ft of the tank. The NPS is concerned that the petroleum product has reached, or may reach, the water table and that the quality of ground and surface water in the area has been, or will be, adversely affected. In 1990, the U.S. Geological Survey (USGS), in cooperation with the NPS, conducted a study to address some of these concerns.

Purpose and Scope

This report presents the results of a USGS study with the following objectives: (1) determine the depth to the water table and the direction of ground-water flow; (2) identify the petroleum product(s) found in the soil; (3) determine the source(s) of the product(s); (4) determine the approximate extent of migration of the product(s) in the soil; and (5) determine whether the product(s) have reached the water table, and if so, determine the magnitude of ground-water contamination.

Results of the work, which included drilling five monitoring wells in the maintenance area of Longmire; collecting and analyzing samples of drill cuttings and ground water; and measuring water-level in the wells, the Nisqually River, and a nearby wetland are presented. Data were collected from October 1990 through October 1991.

Acknowledgments

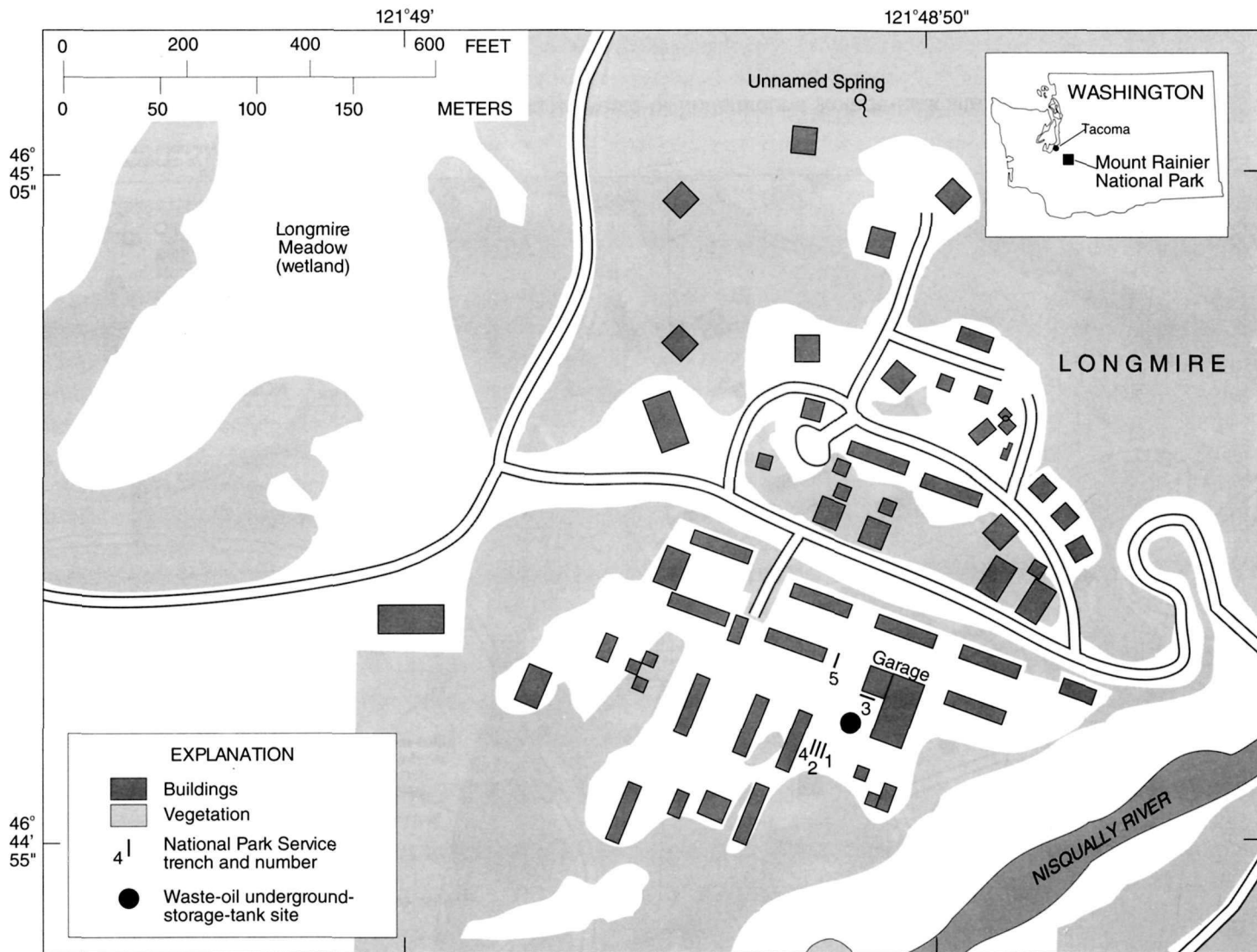
William Oates, National Park Service Civil Engineering Technician, provided much information and field assistance during the course of this study.

HYDROGEOLOGIC SETTING

Longmire, located at an altitude of about 2,760 ft in the foothills of the Cascade Range southwest of Mount Rainier, lies between the Nisqually River to the east and a wetland to the west (fig. 2). The area surrounding Longmire is densely forested with Douglas fir. The average annual air temperature is 43°F. The long-term (1971-91) 12-month average precipitation from November through October at Longmire is about 82 inches.

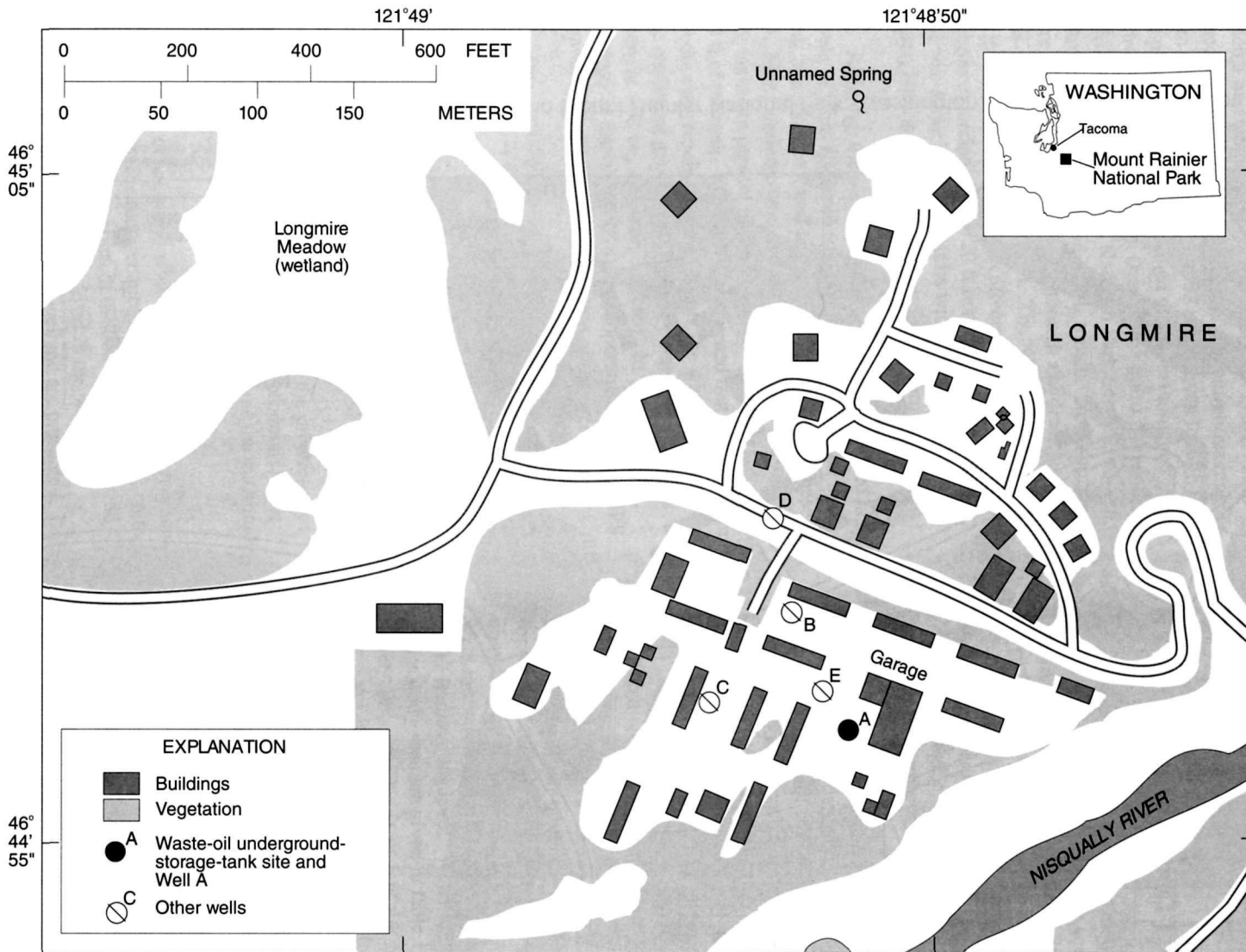
Longmire is underlain by coarse alluvium and glaciofluvial material deposited by the Nisqually River, ranging in size from sand to boulders with little or no silt or clay. The Ohanapecosh Formation, composed of volcanic breccia, sandstone, and siltstone of Eocene Age, is exposed along the banks of the Nisqually River to the northeast of Longmire (Fiske and others, 1963).

The direction of ground-water flow in the Longmire area is generally toward the southwest, determined on the basis of water-table contours shown on figure 3. During the study, the water table was highest at site A (see fig. 2 for well locations), ranging from about 2,734 to 2,738 ft above sea level (table 1). The lowest water-table altitudes were measured at site C, ranging from about 2,724 to 2,732 ft above sea level. Water-table altitudes at all wells in the study area are given in table 1. Hydrographs of water-table altitudes at each of the sites (fig. 4) indicate that water levels rose about 4 to 5 ft during the winter and spring in response to precipitation and snowmelt, then gradually declined during the summer. The water level of the Nisqually River generally is higher than that of the water table immediately to the northwest (table 2), indicating that locally the river is losing water to the ground-water system. A seepage run was not made to confirm this, however. Ground-water flow lines indicate that ground water flowing from the maintenance area does not discharge into the wetland to the west (Longmire Meadow).



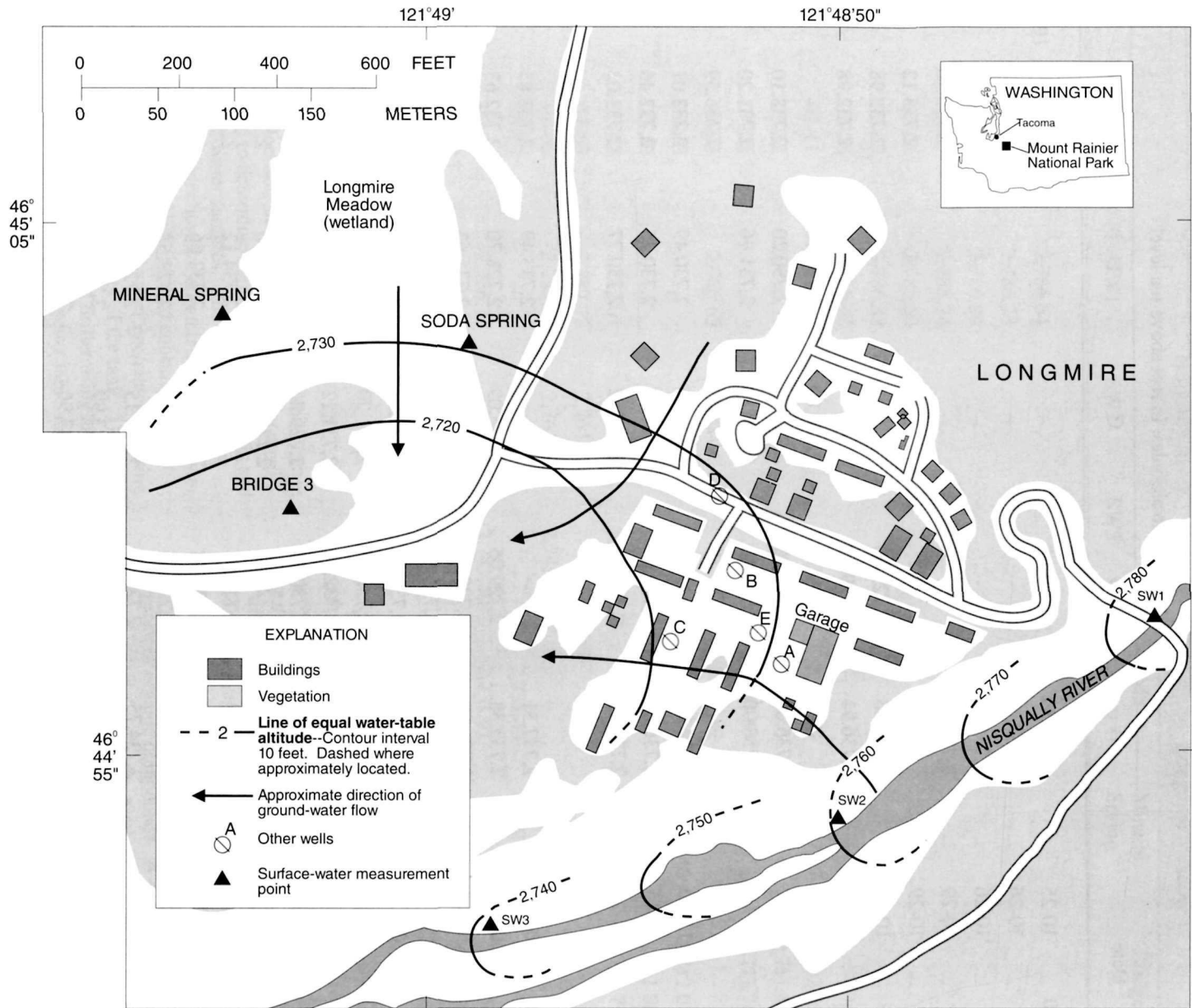
Revised from photomap by U.S. Geological Survey.
Aerial photographs taken July 1982.

Figure 1.--Location of the study area at Longmire in Mount Rainier National Park, Washington, and the trenches dug by the National Park Service in 1990.



Revised from photomap by U.S. Geological Survey.
Aerial photographs taken July 1982.

Figure 2.--Location of vehicle and equipment garage, waste-oil underground storage-tank site, and monitoring wells, Longmire, Washington.



Revised from photomap by U.S. Geological Survey.
Aerial photographs taken July 1982.

Figure 3.--Water-table contours and ground-water flow paths at Longmire, Washington, October 1991.

Table 1.-Water-table altitudes in monitoring wells at sites A, B, C, D, and E at Longmire, Wash.

[--, no measurement]

Date		Water-table altitudes, in feet above sea level				
		A	B	C	D	E
1990	10-25	2,737.89	--	--	--	--
	10-26	2,737.04	--	--	--	--
	¹ 10-26	2,736.98	--	--	--	--
	10-29	2,736.16	--	--	--	2,733.10
	10-29	--	--	--	--	2,733.12
	10-30	2,737.33	2,729.40	--	--	2,732.98
	10-30	2,736.91	2,729.39	--	--	2,732.98
	11-01	--	--	2,726.80	2,730.10	--
	11-02	2,735.60	2,729.80	2,727.00	2,730.20	2,733.10
	11-07	2,738.00	2,731.30	2,730.10	2,731.96	2,731.20
	12-07	--	2,734.39	2,728.95	--	2,736.59
	12-10	2,736.39	2,732.01	2,727.82	2,730.49	2,733.01
	12-15	2,736.45	2,729.64	2,727.25	2,730.25	2,732.46
	12-21	2,736.24	2,729.98	2,727.82	2,730.77	2,733.03
	1991	01-14	2,737.51	--	--	2,733.49
02-01		2,733.38	2,729.05	2,725.09	2,728.70	2,732.63
02-04		2,736.29	2,729.82	2,726.73	2,731.63	2,732.98
02-05		2,737.00	2,731.68	2,729.14	2,732.48	2,733.23
02-06		2,737.54	2,733.05	2,731.51	2,733.44	2,733.83
02-07		2,737.79	2,732.85	2,731.70	--	2,733.69
02-08		2,737.69	2,732.16	2,731.12	2,732.52	2,733.31
02-11		2,737.39	2,730.71	2,729.26	2,731.17	2,733.09
03-12		--	2,729.42	2,726.43	2,729.96	2,732.88
04-08		2,737.79	2,733.97	2,732.88	2,734.12	2,734.69
04-11		2,737.06	2,732.18	2,731.15	2,732.66	2,733.19
05-09		2,734.87	2,729.06	2,724.42	2,728.58	2,732.55
05-22		2,734.75	2,728.02	2,724.15	2,728.32	2,732.35
06-06		2,734.58	2,728.95	2,723.99	2,727.89	2,732.42
07-03		2,734.62	2,728.86	2,723.96	2,727.63	2,732.35
08-06		2,734.28	2,727.12	2,723.91	2,725.78	2,731.41
09-10		2,734.28	2,726.43	2,724.02	2,725.19	2,729.97
10-16	2,734.28	2,725.86	2,723.99	2,725.14	2,729.15	

¹Two measurements about 1 hour apart were made on 10-26, 10-29, and 10-30

Table 2.-Water-surface altitudes in the Nisqually River and in Longmire Meadow at Longmire, Wash.

[SW1, SW2, and SW3, surface-water sites (see fig. 5 for locations); --, no measurement]

Date		Water-surface altitudes, in feet above sea level					
		Nisqually River			Longmire Meadow		
		SW1	SW2	SW3	Soda Spring	Mineral Spring	Bridge 3
1991	01-14	2,786.64	--	--	--	--	--
	02-01	2,786.28	--	--	--	--	--
	02-04	2,786.89	--	--	--	--	--
	02-05	2,786.74	--	--	--	--	--
	02-06	2,786.50	--	--	--	--	--
	02-07	2,786.43	--	--	--	--	--
	02-08	2,786.40	--	--	--	--	--
	02-11	2,786.32	--	2,742.50	2,731.74	2,727.47	2,712.03
	03-12	2,786.71	--	2,742.00	2,731.63	2,727.47	2,711.86
	04-01	--	--	2,742.02	2,731.63	2,727.51	2,711.78
	04-08	2,786.65	--	--	2,731.82	--	--
	04-10	--	--	--	2,730.43	2,727.46	2,712.01
	05-10	--	--	--	2,731.71	2,727.43	2,711.88
	06-05	2,787.01	2,760.82	2,742.54	2,731.59	2,727.49	2,711.77
	07-03	2,787.73	2,761.33	--	--	--	--
	08-06	2,787.43	2,761.08	2,742.03	--	--	--
	08-13	--	--	--	2,731.49	2,727.54	2,711.61
	09-10	2,786.77	2,760.88	2,741.40	2,731.41	2,727.54	2,711.54
	10-08	2,787.09	2,760.78	2,741.40	2,730.69	2,727.51	2,711.53

METHODS OF STUDY

Five boreholes were drilled in the maintenance area at Longmire to collect soil samples and to install the monitoring wells used to determine depth to the water table and to collect ground-water samples. The locations of the boreholes (fig. 2) were chosen after an initial site investigation during which the NPS inferred subsurface flow directions from observations of water encountered during trenching operations in the vicinity of the tank. The boreholes were drilled by a private well driller using air-rotary techniques to a depth 5 ft below the water table and were cased with 2-inch-diameter polyvinyl chloride (PVC) casing. The wells were finished with a 6-ft length of 0.020-inch slotted PVC screen straddling the water table, and the annular space around the screen was backfilled with clean sand. Bentonite clay was used to seal the annular space above the screened interval and cement grout was used as a surface seal.

Samples of soil were obtained from the air exhaust of the drill column every 2 ft during drilling because the coarse nature of the subsurface material prevented the use of a conventional sampling device (split-spoon sampler). (In this report, the term soil is used to refer to the unconsolidated, unsaturated material below land surface.) Two samples from site A, nearest the tank (fig. 2), and one sample each from sites B, C, D, and E were analyzed for the presence of organic compounds. A sample from 19 ft below land surface at site A (about 9 ft above the water table) was chosen for analysis because that depth closely approximates the depth at which the NPS obtained contaminated soil samples from trench 1 (see fig. 1) near the tank site. A sample from 35 ft below land surface at site A (about 7 ft below the water table) was chosen for analysis to determine the vertical extent of migration of the petroleum product near the tank site. Only samples from about 20 ft below land surface at each of the other sites were chosen for analysis because soil at this depth was esti-

mated to be above the seasonal high water-table level and therefore unaltered by contact with ground water. All soil samples were unsaturated except for the sample collected from 35 ft below land surface at site A. Additional samples that were collected but not analyzed during this study were stored for possible future analysis.

A sample of waste oil from the maintenance garage and a sample of diesel oil from one of the storage tanks also were collected and analyzed. These samples were used as reference samples which were compared with the results of the analyses of soil and water samples.

Ground-water flow directions were estimated by using water-level measurements from the monitoring wells and from the water-surface altitudes of the Nisqually River and the wetland (fig. 2). The altitude of the top of the well casings, land surface adjacent to the wells, and reference marks on the banks of the Nisqually River and near the shore of the wetland were determined relative to a USGS vertical benchmark (28 FMK 1971 2757) located near the Longmire Headquarters building. Water levels in the monitoring wells were measured at least monthly for 12 months (November 1990 through October 1991) (fig. 4 and table 1). Water-surface elevations in the Nisqually River and the wetland were determined from measurements made monthly from January 1991 through October 1991 (table 2). Additional measurements were obtained from the wells, the river, and the wetland after rainstorms and snowmelt.

Water samples for chemical analyses were collected from all of the wells with a glass bailer after three to five casing volumes of water had been removed with a PVC bailer. However, prior to purging, a sample from the water surface in each well was collected and visually checked for the presence of a petroleum product. Because the petroleum products are less dense than water, free-product diesel oil or waste oil present in amounts greater than residual saturation (the maximum amount of oil that is retained in the pore spaces of the unsaturated material) appears as a separate layer floating on the water surface. Temperature, specific conductance, pH, alkalinity, and dissolved-oxygen (DO) concentration of water samples were determined on site (table 3). Water for the analysis of selected inorganic constituents and nutrients (listed in table 3) was filtered through a cellulose- acetate membrane with a pore size of 0.45 micrometers. Water collected for organic analysis was not filtered. A water sample also was collected from a spring about 500 ft north of the tank (fig. 2) and was analyzed for organic compounds only. Samples were preserved and shipped according to methods described in Pritt and Jones (1989

and 1990) and Fishman and Friedman (1989). All samples of soil and water selected for hydrocarbon analysis were shipped on ice to the Geological Survey's National Water Quality Laboratory in Arvada, Colo., and were analyzed by methods described by Wershaw and others (1987) and Fishman and Friedman (1989).

Estimates of the concentrations of organic compounds were obtained by gas chromatography/flame-ionization-detector (GC/FID) scans of extracts of water and soil samples. This analysis is a semiquantitative procedure in that the concentrations of unknown organic compounds are compared with the response of a known compound added to the sample at a known concentration.

Gas chromatography is used to separate the components of a mixture of organic compounds; both diesel oil and waste oil are mixtures of many organic compounds. The organic compounds in a water or soil sample are first extracted with an organic solvent and then injected into the gas chromatograph. The gas chromatograph is a long, coiled capillary tube coated on the inside with an organic solvent and enclosed in an oven. Separation of the individual organic compounds from the mixture results from differences in both their boiling points and their affinities for the coating of the column. These differences, enhanced by gradually increasing the oven temperature, cause compounds to travel through the tube at different rates and, therefore, to exit at different times. The compounds then pass through the FID. The elapsed time from the injection of the mixture to the exit from the column is called the retention time (RT) of the compound. The RT of a compound is characteristic of that compound for a given gas-chromatograph setup.

As each compound exits the column, it is ionized by a hydrogen flame in the FID. The ions complete an electrical circuit and the current produced is proportional to the amount of that compound present in the mixture. The results are recorded on a strip chart where pen deflections represent the current from the FID and the area under the deflection is integrated to estimate the amount of the compound. The time of the deflection corresponds to the retention time and is used to tentatively identify the compound.

Because of the small number of water samples (six) analyzed during the study, the scope of the quality-assurance program was limited. Field meters used for pH, specific conductance, and DO measurements were calibrated daily, prior to use, according to manufacturers' specifications; however, no duplicate samples were collected. An aliquot of carbon-free water, used to rinse the glass bailer

following cleaning, was processed in the same manner as a regular sample and was submitted to the laboratory for analysis as an equipment blank. Laboratory quality-assurance procedures (Friedman and Erdmann, 1982) included incorporation of blanks, internal standards, and surrogate compounds into the sample runs. Internal standards are compounds similar in physical and chemical properties to the constituents being analyzed for that are added to the sample just prior to analysis. Internal standards are used to normalize all data to a known amount of a common reference (Wershaw and others, 1987). Surrogate compounds are compounds similar in physical and chemical properties to the constituents being analyzed for that are added to the sample prior to any extraction or other sample processing procedures. Surrogates are used to monitor how well constituents are recovered from the sample matrix (Wershaw and others, 1987).

Results of GC/FID analyses of the equipment blank (fig. 5) and laboratory blanks (fig. 6) indicated that only one compound detected in the equipment blank, tentatively identified by the laboratory as bis (2-ethylhexyl) phthalate (RT = 46.64 minutes), could affect data interpretation. Other compounds detected in the equipment blank also were detected in laboratory blanks, indicating that the presence of these compounds probably is not indicative of their presence in the soil and water samples.

Table 3.--Physical properties and concentrations of selected inorganic constituents in ground water at Longmire, Washington

[°C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25°C; mg/L, milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter]

Site	Date sampled	Water temperature, °C	Specific conductance, ($\mu\text{S}/\text{cm}$)	pH, standard units	Concentration			
					Dis-solved oxygen (mg/L)	Bicar-bonate, as HCO_3 (mg/L)	Ammonia, (mg/L)	Nitrite (mg/L)
A	04-11-91	7.0	83	6.2	2.3	45	0.04	<0.01
E	04-11-91	8.5	87	6.1	4.7	71	<.01	<.01
C	04-10-91	7.5	63	5.9	4.0	34	.03	<.01
B	04-10-91	7.5	67	6.0	.9	36	.04	<.01
D	04-10-91	6.5	79	5.7	8.3	41	.05	<.01

Site	Date sampled	Concentration			
		Nitrite plus nitrate (mg/L)	Sulfate (mg/L)	Iron ($\mu\text{g}/\text{L}$)	Manga-nese ($\mu\text{g}/\text{L}$)
A	04-11-91	0.01	3.3	4,000	380
E	04-11-91	.30	3.6	10	<10
C	04-10-91	.21	4.1	140	90
B	04-10-91	.14	2.7	90	190
D	04-10-91	.35	5.8	90	40

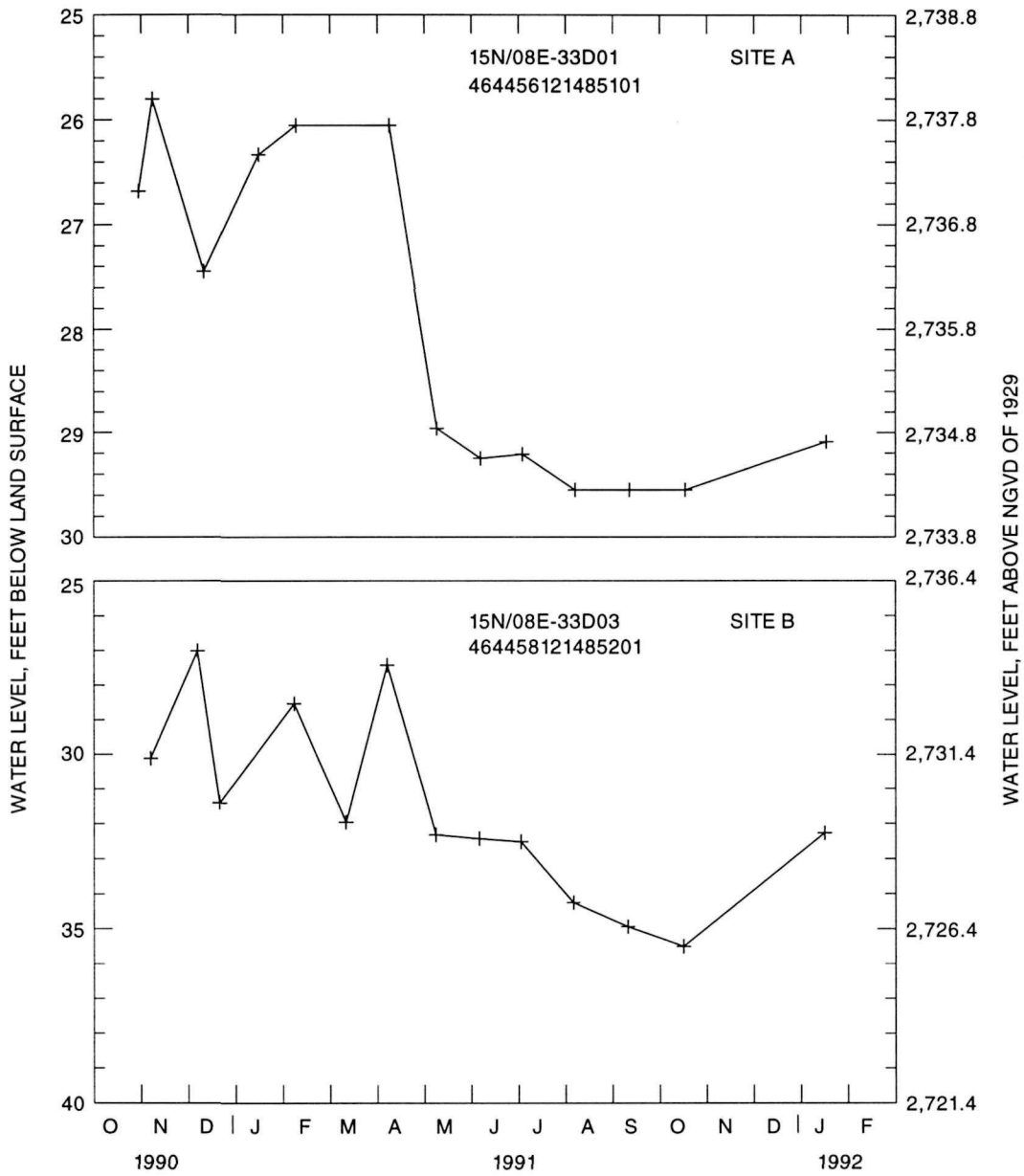


Figure 4.--Water levels in monitoring wells at Longmire, Washington.

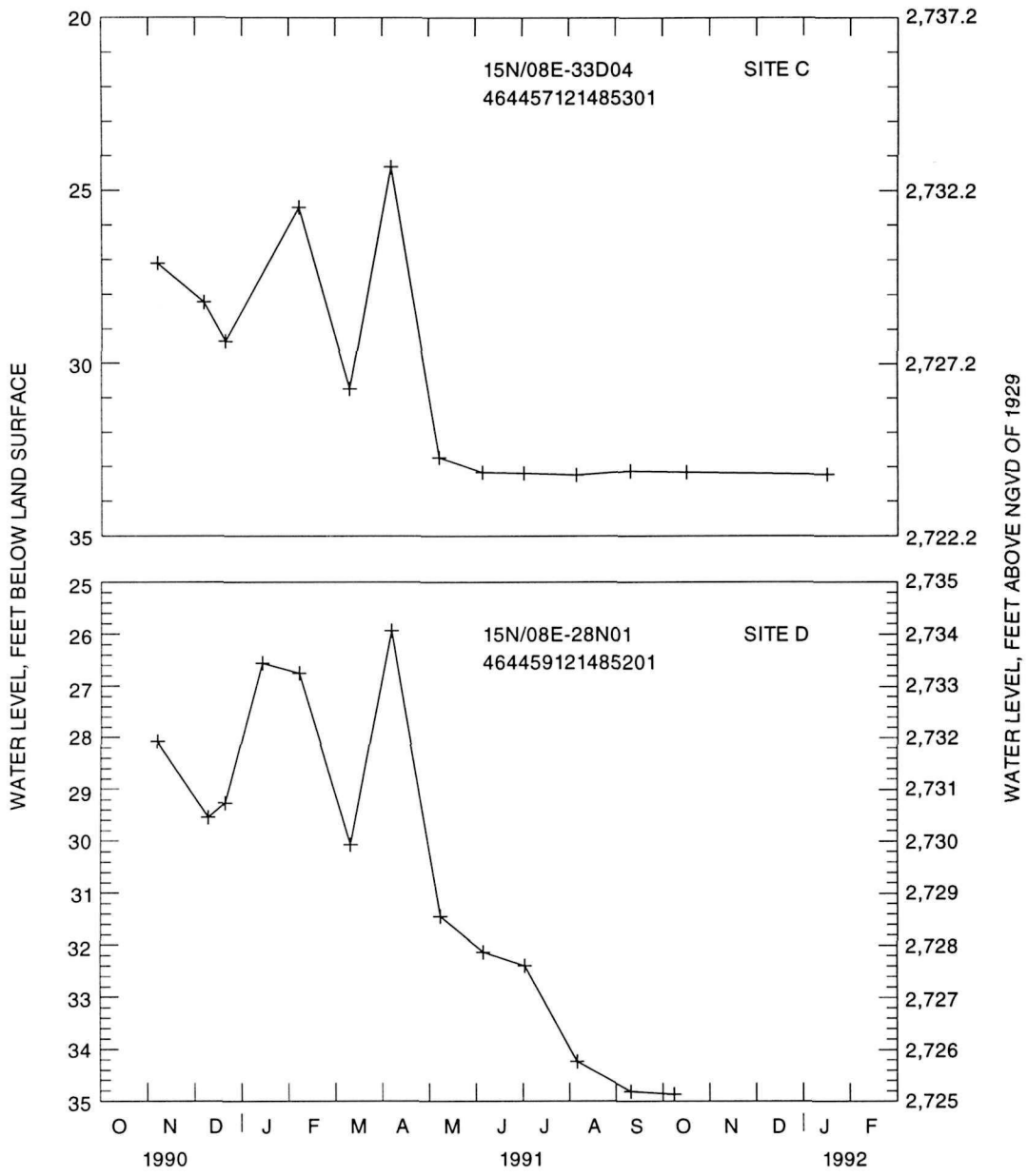


Figure 4.--Continued

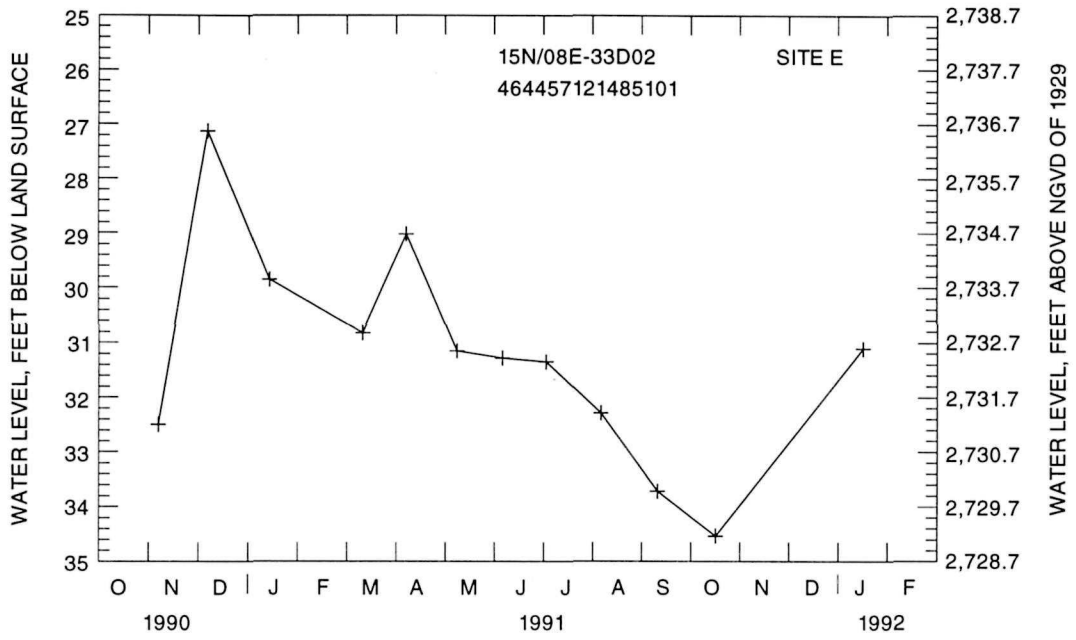


Figure 4.--Continued

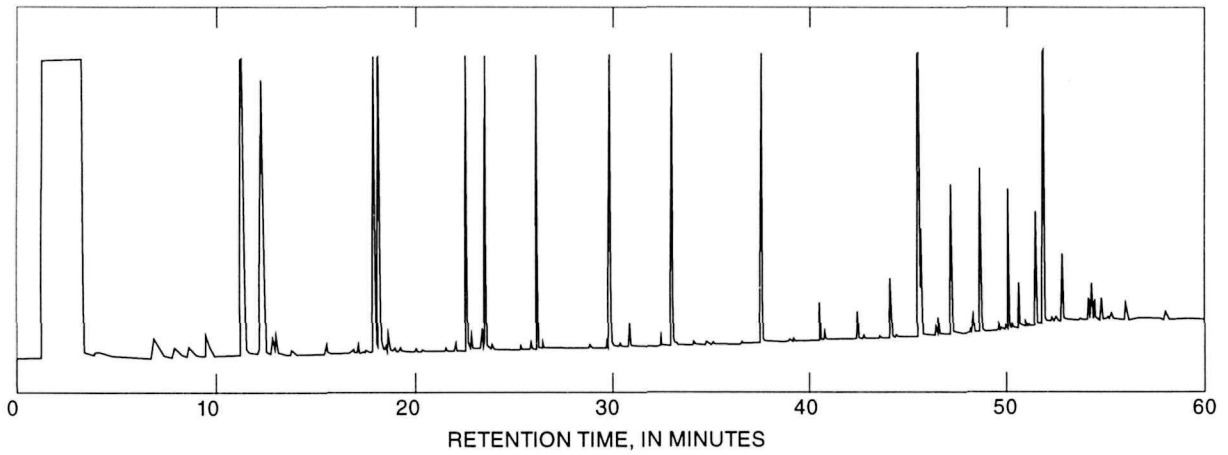


Figure 5.--Chromatogram of an equipment blank of carbon-free water.

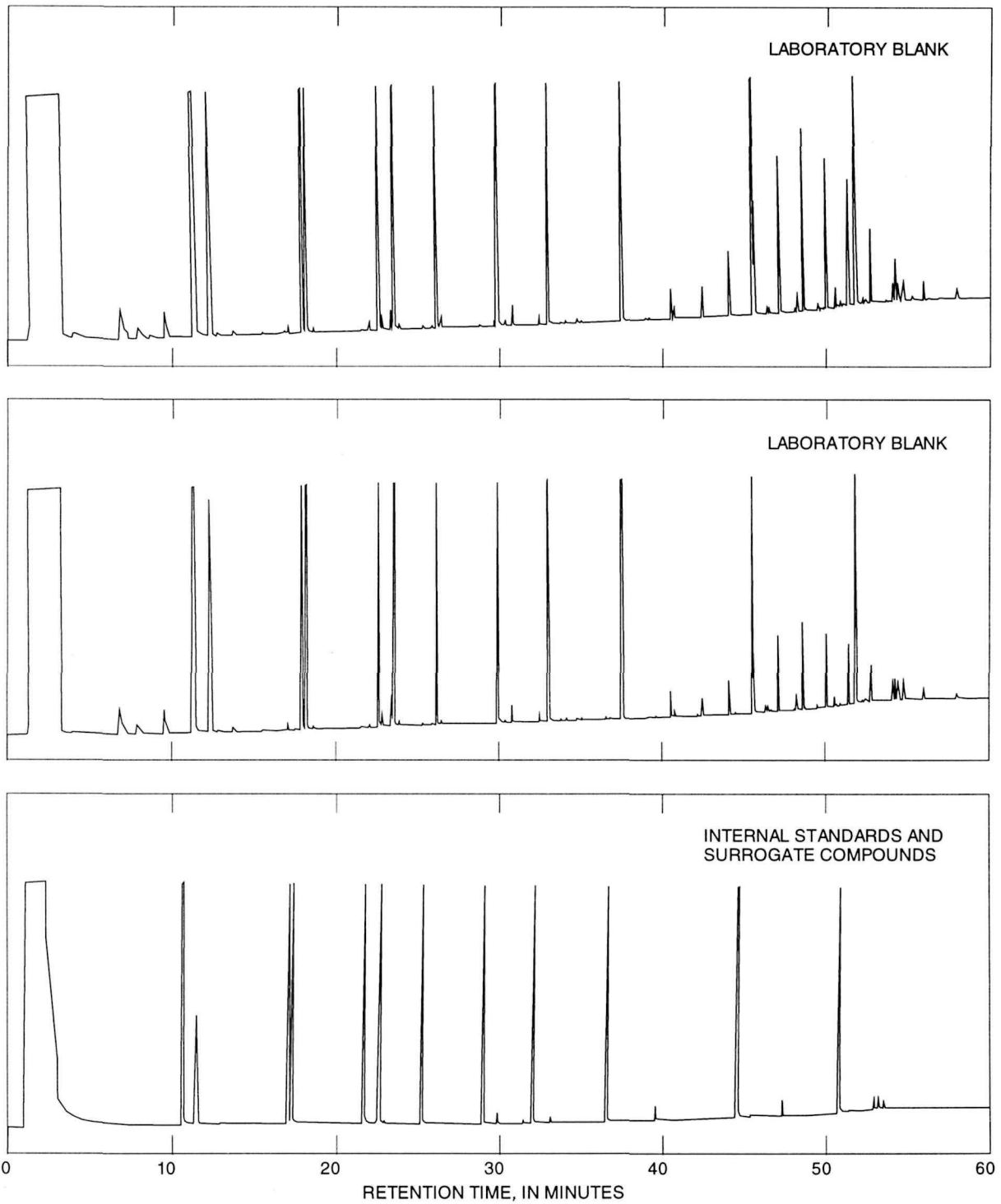


Figure 6.--Chromatogram of laboratory blanks and internal standards and surrogate compounds.

PETROLEUM PRODUCTS IN SOIL

Following the release of a petroleum product (crude oil or its derivatives) at or below land surface, the petroleum product or its hydrocarbon components moves primarily downward in response to gravity. Some lateral movement also occurs because of capillary forces. Depending on the quantity involved and the depth to the water table, petroleum products may reach ground water, and, because they are less dense than water and immiscible in water, may accumulate on top of the water table and move laterally in the direction of ground-water flow (Freeze and Cherry, 1979). In addition, the volatile components of the petroleum product may vaporize, move through soil pore spaces, and recondense or dissolve into soil water at locations some distance from their point of origin (Baehr, 1987).

When the release of the petroleum product has ceased, as it has at Longmire, a significant portion is immobilized in the pore spaces, resulting in a condition termed residual oil saturation (Freeze and Cherry, 1979). This residual oil may undergo further volatilization, microbial degradation, and dissolution into soil water. It also may move vertically as rain and snowmelt percolate through the area or, depending on the distance to the water table, in response to seasonal water-level fluctuations.

Chromatograms of soil samples were compared with chromatograms of waste oil and diesel oil (fig. 7) in order to identify the petroleum products in the soil samples. Both waste oil and diesel oil are mixtures of many organic compounds; 46 compounds were detected in the waste-oil sample and 173 compounds were detected in the diesel-oil sample. (When several compounds in a mixture are characterized by similar RT's and exit together, an upward drift occurs in the pen track on the chromatograms.) Some organic compounds are common to both waste oil and diesel oil (table 5). In general, however, retention times of most of the compounds found in waste oil (about 90 percent) are greater than 35 minutes, whereas retention times of about 75 percent of the compounds found in diesel oil are less than 35 minutes (see fig. 7). The chromatogram of the soil sample from 19 feet below land surface at site A, which smelled of diesel oil, exhibited a baseline drift similar to that of both waste oil and diesel oil (see figs. 7 and 8). The chromatogram of the soil sample from the saturated zone at site A, 35 ft below land surface, produced a chromatogram that indicated that a petroleum product had reached that level. The source of the petroleum product could not be determined conclusively from the chromatogram, but a small baseline drift in the waste-oil region (retention times between 34 and

55 minutes) indicated that waste oil may be present. Many peaks, but only a slight baseline shift, in the diesel-oil region of the chromatogram indicated that diesel oil also may be present. Although the chromatogram of the soil sample from site B did not exhibit a baseline drift, many peaks with retention times of less than 35 minutes indicate that diesel oil may be present in the soil at that location (see figs. 7 and 8).

Organic compounds were detected in all soil samples (table 4 and fig. 8); however, the source (waste oil or diesel oil) of these compounds could not be determined conclusively from the chromatograms. Some of the compounds probably represent the volatile components of waste oil that migrated from the tank site, diesel-oil components from nearby diesel-oil storage tanks, or both. These compounds also may be degradation products of waste oil, diesel oil, or both.

Several of the organic compounds were tentatively identified by the laboratory as phthalate esters. Three compounds were detected in all of the soil samples: diethyl phthalate (RT = 29.06), butyl benzyl phthalate (RT = 43.88), and bis (2-ethylhexyl) phthalate (RT = 46.93). Bis (2-ethylhexyl) phthalate is reported to be present in waste oil (Watts, 1989). Phthalate esters also are produced in the decomposition of naphthalene and naphthalene derivatives (Smith and others, 1988) that are found in diesel oil. However, phthalate esters also are used extensively as plasticizers in products such as plastic pipe, tubing, construction materials, and plastic containers. Therefore, the source of the phthalate esters may be waste oil or diesel oil, but leaching from the PVC pipe used as well casing or contact with the PVC bailer used to purge the wells cannot be ruled out as a source of these compounds. No information was available on the effect of diesel oil or waste oil on the release of phthalate esters from PVC but Miller (1982) found no identifiable organic leachates after soaking PVC in a solution of chromium, lead, and six halogenated hydrocarbons. Curran and Tomson (1983) found that hot (80°C) water spiked with naphthalene leached less than 0.1 ppb (parts per billion) of organic compounds from PVC.

Although the source of the waste oil at site A was most likely the adjacent tank, a single source of the diesel oil is not obvious because of the number of diesel-oil tanks in the area. For example, a possible source of diesel oil at site B is an equipment-refueling station where gasoline and diesel oil are stored and dispensed about 50 ft southwest of site B.

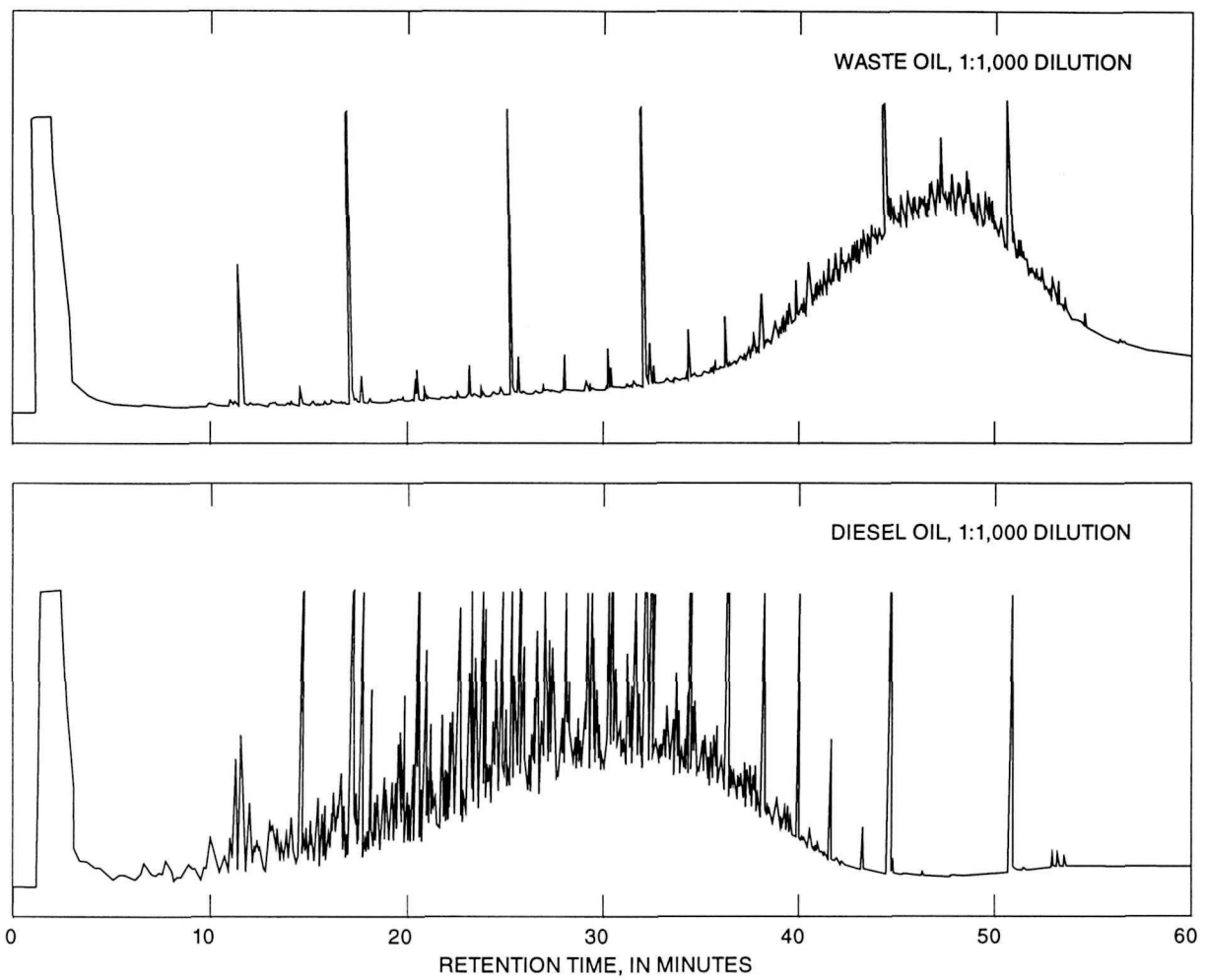


Figure 7.--Chromatograms of waste oil and of diesel oil.

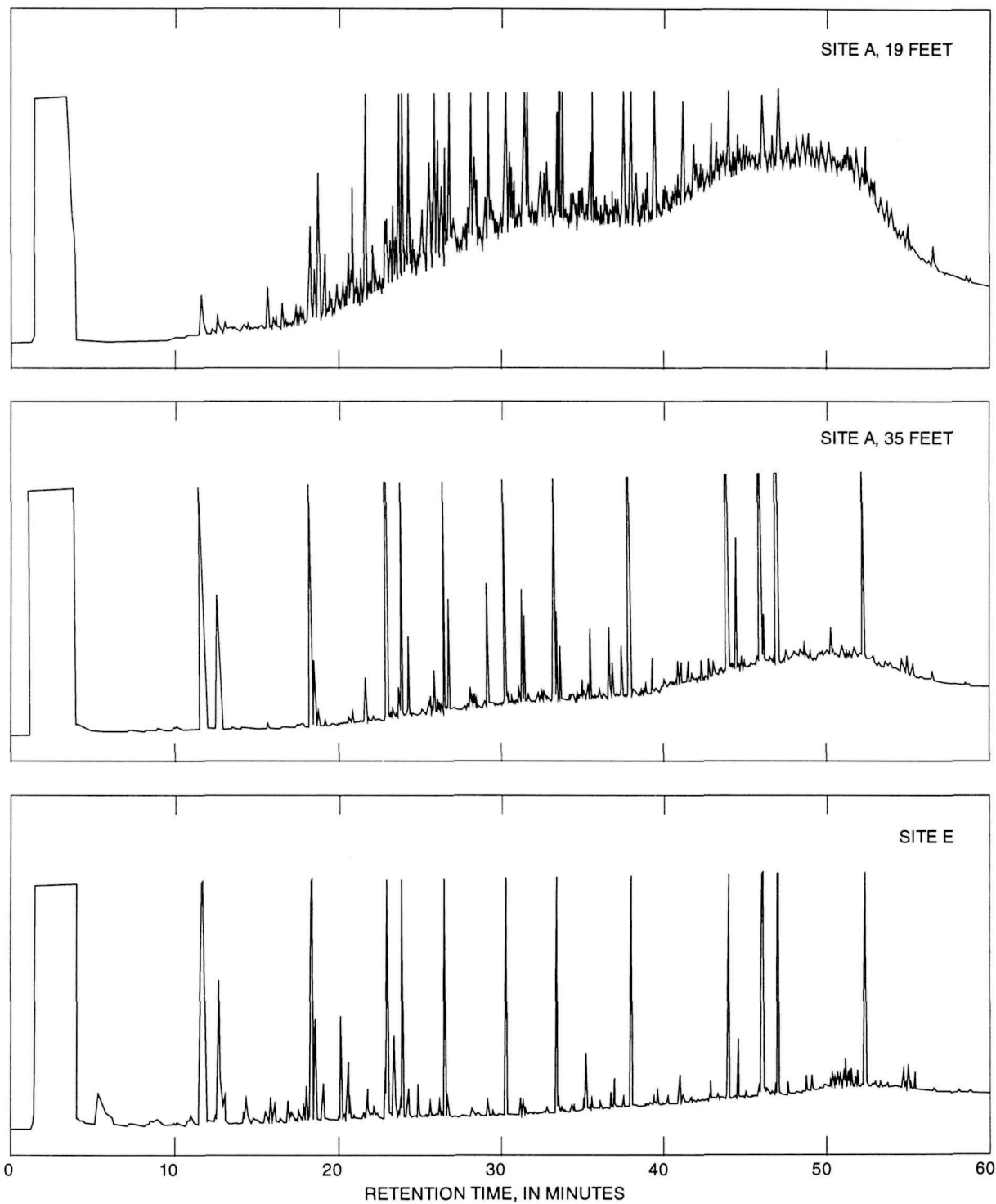


Figure 8.--Chromatograms of soil samples collected during the drilling of the monitoring wells at Longmire, Washington.

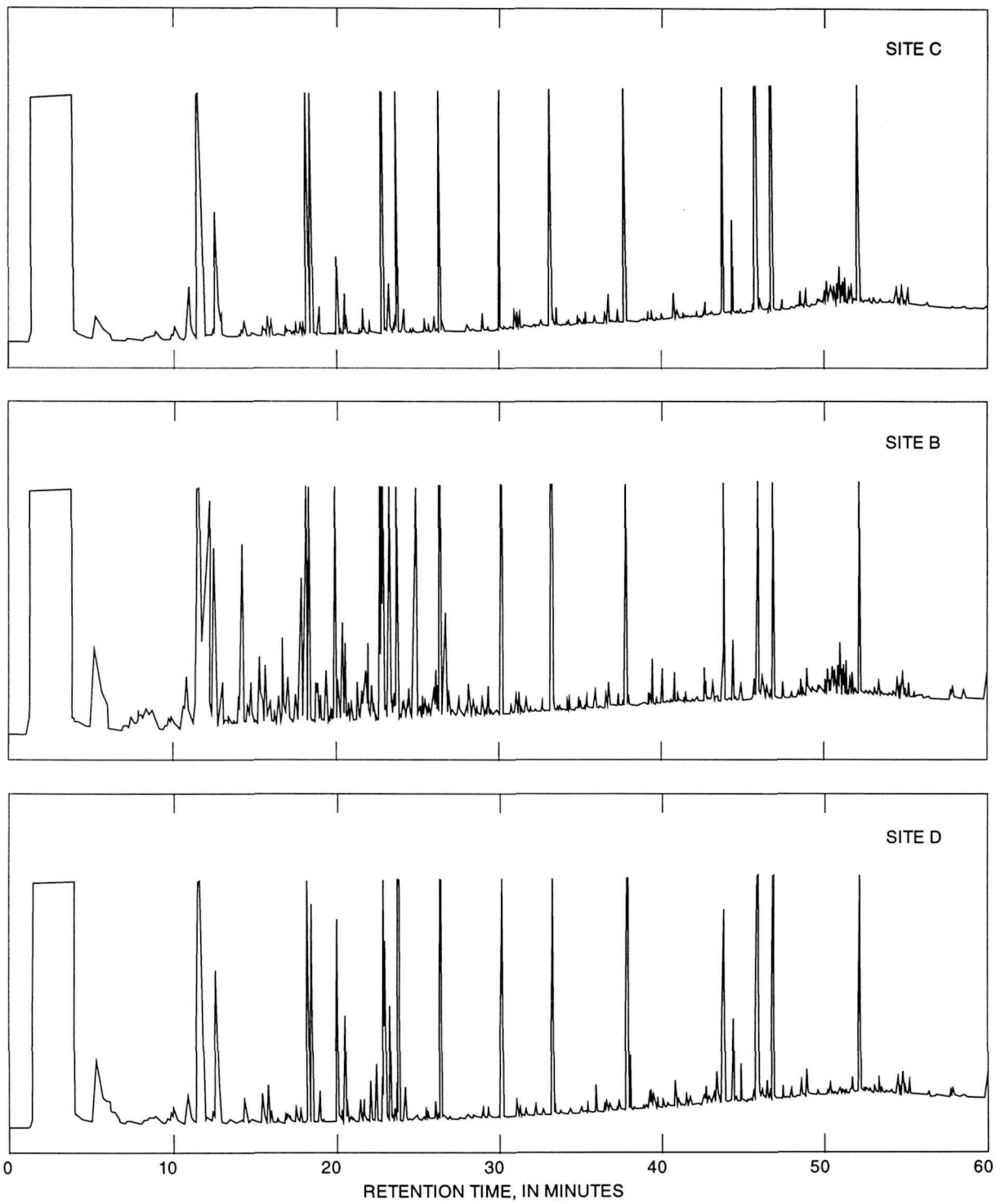


Figure 8.--Continued

Table 4.--Estimated concentrations of total hydrocarbons in soil and ground water at Longmire, Wash.

[µg/kg, micrograms per kilogram; µg/L, micrograms per liter; --, no data]

Site	Total hydrocarbon concentration	
	Soil (µg/kg)	Ground water (µg/L)
A	¹ 470,000 ² 17,000	320
E	3,100	7
C	5,300	34
B	8,700	20
D	3,100	23
Spring	--	1

¹Sample from 19 feet below land surface

²Sample from 35 feet below land surface

PETROLEUM PRODUCTS AND INORGANIC CONSTITUENTS IN GROUND WATER

In general, petroleum products are considered to be insoluble in water; however, most petroleum products are mixtures of many organic compounds, all of which are at least slightly soluble in water. The solubility in water of naphthalene is 34.4 mg/L (milligrams per liter) at 25°C; the solubilities of diethyl phthalate and bis (2-ethylhexyl) phthalate are 896 mg/L and 0.4 mg/L at 25°C, respectively (Smith and others, 1988). Therefore, when waste oil and diesel oil come in contact with ground water, many compounds enter the aqueous phase. Once dissolved in the aqueous phase, these components move in the direction of the hydraulic gradient. Furthermore, small-scale variations in the direction in ground-water flow also cause these components to spread laterally, perpendicular to the general direction of ground-water flow (Ptacek and others, 1987). Usually, the movement of the dissolved components is retarded relative to that of the ground water by adsorption onto aquifer material. The degree of adsorption and, consequently, retardation is proportional to the amount of organic material in the aquifer and inversely proportional to the particle size of the aquifer material (Newsom, 1985). Although the organic content of the

aquifer material at Longmire is not known, a visual inspection of the samples of soil collected during drilling did not reveal significant amounts of organic matter, and the coarse nature of the aquifer material (gravel and cobbles) indicates that little adsorption would be likely to occur.

Another process that may affect the presence of petroleum products in the Longmire area is biodegradation by microorganisms. The most common reactions are oxidative, ultimately resulting in the production of carbon dioxide and water if sufficient oxygen is present (Ptacek and others, 1987). If oxygen is not available or becomes depleted as degradation occurs, degradation may stop or proceed very slowly, leading to the accumulation of intermediate degradation products.

A nonaqueous phase liquid was present on the surface of the water in the well at site A. This liquid formed a layer about 0.25 in. thick, was yellow in color, and smelled like diesel oil. None of the wells at sites B, C, D, or E contained this layer. The presence of this layer at site A indicates the potential for further ground-water transport downgradient. If this petroleum product is diesel oil, it is not known whether its presence is related to the location of the well near the tank site or a coincident spill or leak of diesel oil upgradient. However, the presence of free product in the well at site A does not necessarily mean that the petroleum product has reached the water table. The presence of a nonaqueous-phase liquid may be due to local disturbance of material making up the unsaturated zone, causing a small quantity of residual oil to accumulate in the wells.

The chromatogram of the water sample from site A (see fig. 9) indicates the presence of whole diesel oil, and perhaps some components of waste oil. A baseline drift in the chromatogram between about 11 and 46 minutes is similar to that seen on the diesel-oil chromatogram (see fig. 7). This baseline drift appears to attenuate in the region where waste-oil components were found on the chromatogram of waste oil (see fig. 7). This attenuation may represent low concentrations of waste-oil components that are partly masked by diesel oil, or it may indicate the presence of diesel-oil degradation products. The chromatogram of the water sample from site C (see fig. 9) also exhibits a baseline drift in the diesel-oil range, but to a much lesser degree than from the chromatogram of the sample from site A.

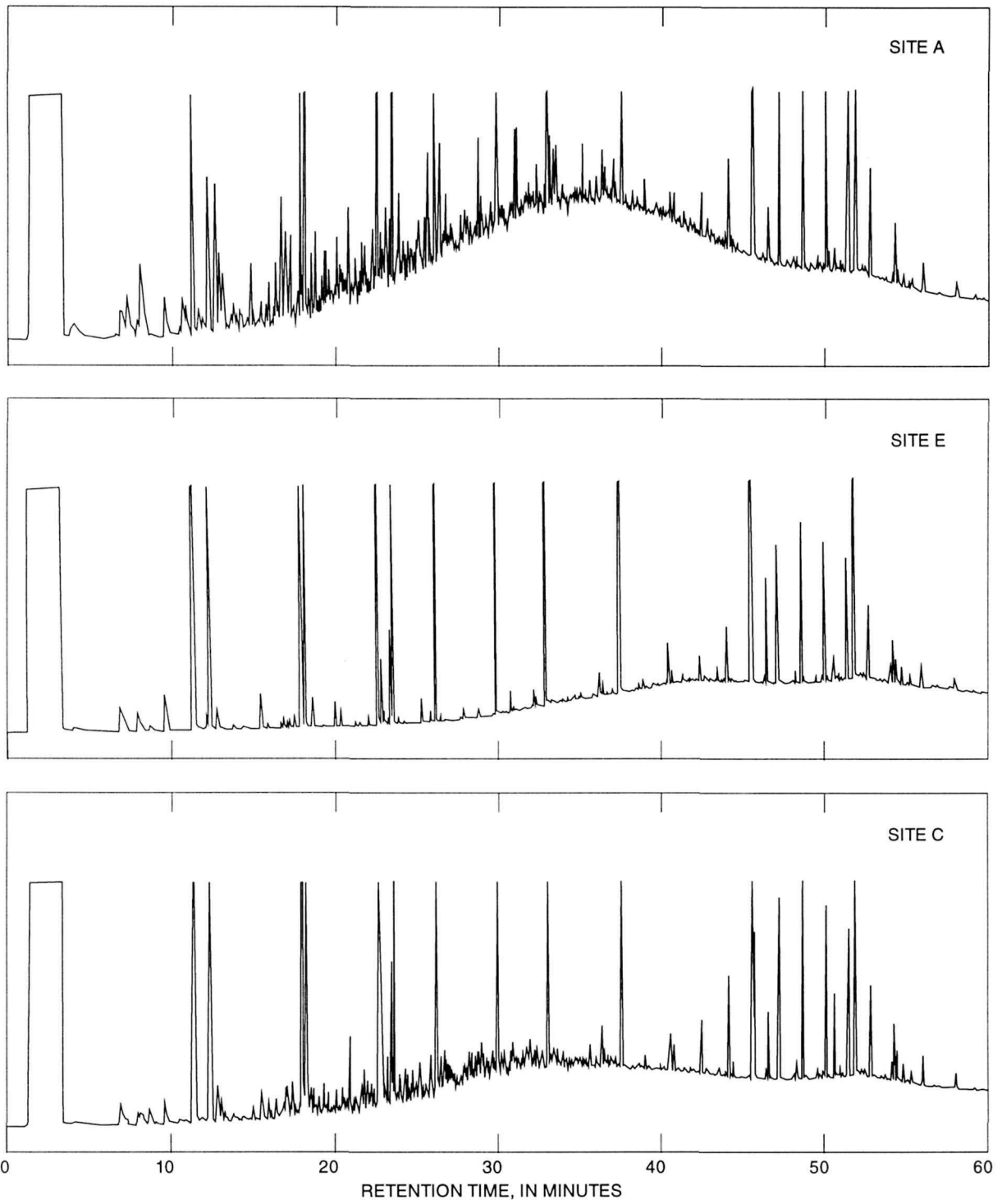


Figure 9.--Chromatograms of ground-water samples from Longmire, Washington.

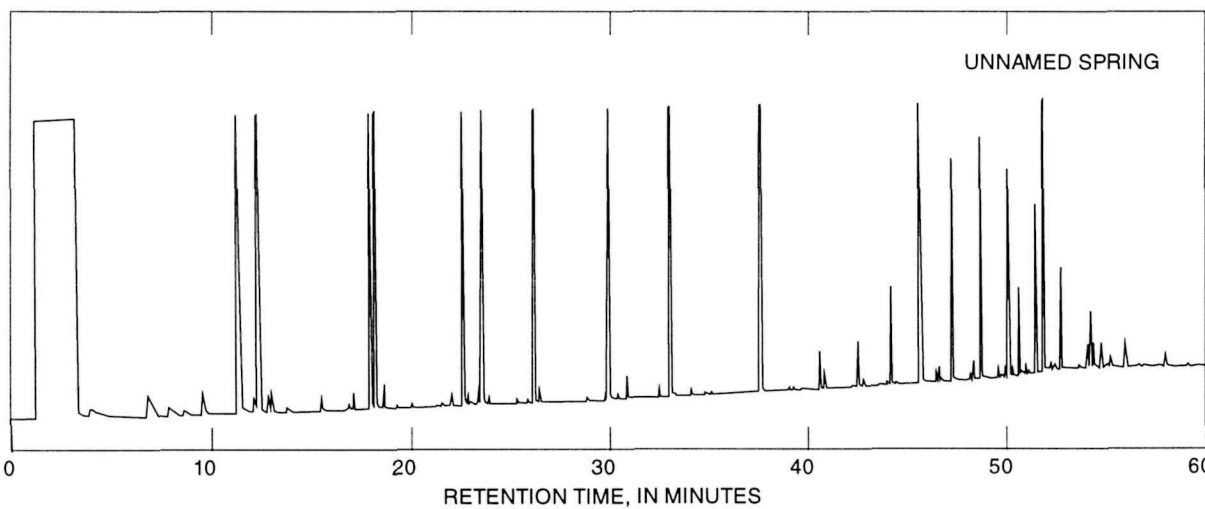
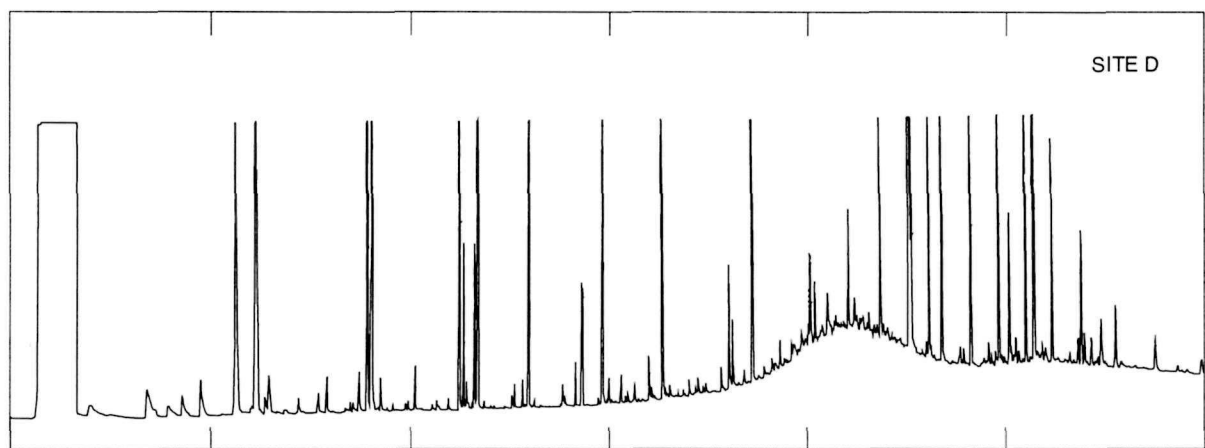
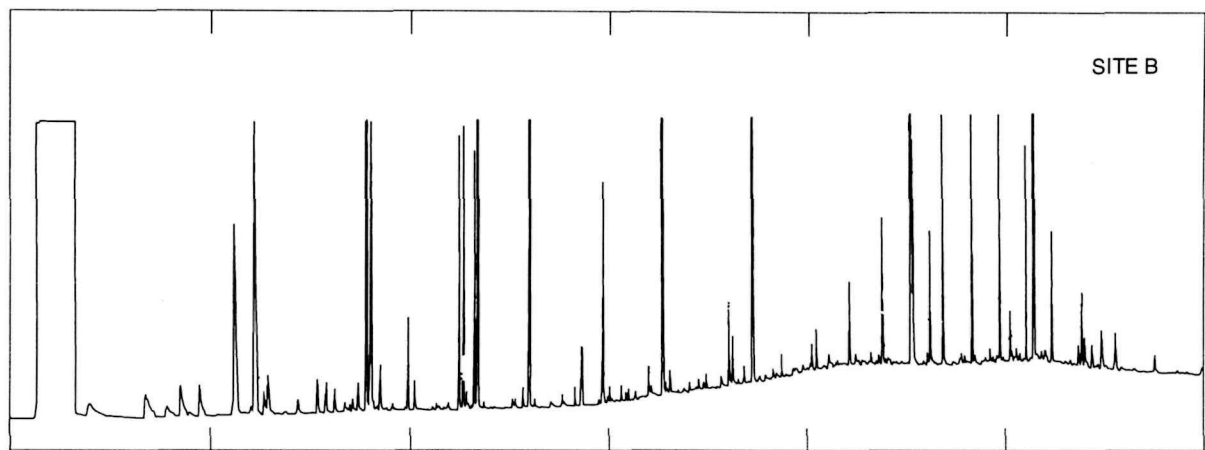


Figure 9.--Continued

The chromatograms of water samples from the other wells also exhibited slight baseline shifts in the waste-oil region. The shift is seen in chromatograms where there is no apparent evidence of diesel oil, as well as in those with peaks in the diesel-oil range. This indicates that soluble waste-oil components may be present in small concentrations in the ground water.

A small displacement of the baseline in the chromatogram of the water sample from site D (see fig. 9) may represent a complex of high-boiling-point components from diesel oil or a complex of low-boiling-point components from waste oil. The source (diesel oil or waste oil) of this complex could not be determined from the available data. Individual peaks representing distinct organic compounds were found in all of the chromatograms. These peaks probably represent the water-soluble fraction or water-soluble degradation compounds of the petroleum product. Some of these peaks were tentatively identified as phthalate esters. Bis (2-ethylhexyl) phthalate was detected in all ground-water samples (RT = 46.64); diethyl phthalate (RT = 28.85) and di-n-butyl phthalate (RT = 36.62) were detected in three samples (from sites A, B, and D); and dimethyl phthalate (RT = 25.47) and butyl benzyl phthalate (RT = 43.62) were detected only at site D. Bis (2-ethylhexyl) phthalate also was detected in the field blank so its presence in the samples may be an artifact of sampling or analysis. Even though the presence of bis (2-ethylhexyl) phthalate in ground-water samples is inconclusive, the presence of the other phthalate esters indicates that ground water is in contact with petroleum products or their residues.

Estimated concentrations of total hydrocarbons in ground-water samples are given in table 4. The largest concentration (320 $\mu\text{g/L}$) was found at site A, nearest the tank site. The smallest concentration (7 $\mu\text{g/L}$) was found at site E, the next nearest well to the tank site. It is not known why the hydrocarbon concentration at site E was so small. On the basis of ground-water flow paths and similar, equal hydrocarbon concentrations in the soil at site E and site D, the concentration in ground water was expected to be similar. Hydrocarbon concentrations at the other sites (B, C, and D) were similar, ranging from 20 to 34 $\mu\text{g/L}$. These data indicate that either ground-water flow paths near site E are more complex than indicated by the water-table altitudes, or biological and (or) chemical processes are reducing the hydrocarbon concentrations in ground water.

The total hydrocarbon concentration in the spring was 1 $\mu\text{g/L}$ and this probably represents naturally occurring concentrations of hydrocarbons in ground water in the Longmire area. No sources of petroleum-derived hydrocarbons are present upgradient of the spring.

Water quality varies among the wells, as indicated by small differences in values of most field measurements and concentrations of some inorganic constituents (temperature, specific conductance, pH, bicarbonate, and sulfate; table 5). These differences are probably due to local, naturally occurring variations in the composition of aquifer materials. Larger differences in DO concentrations and in concentrations of the nitrogen species (ammonia and nitrate), iron, and manganese indicate that petroleum products may be affecting ground-water quality at some of the wells. Dissolved-oxygen concentrations range from a low of 0.9 mg/L at site B to 8.3 mg/L at site D. The DO concentration at site D is almost 60 percent higher than the next highest DO concentration (site E, 4.7 mg/L). The large DO concentration at site D may be caused by small concentrations of oxidizable substances in the ground-water flow path to site D or by the fact that aggregated recharge (rain and snowmelt) enters the ground-water flow system more readily upgradient from site D than from other sites. Much of the area upgradient from the other monitoring wells consists of bedrock or is paved, reducing infiltration and percolation of oxygenated water.

Concentrations of ammonia, nitrate, iron, and manganese (table 5) are affected indirectly by the presence of petroleum products in ground water. As DO is used by microorganisms in oxidizing petroleum products, the reduced forms of compounds are favored (nitrite, ammonia, and soluble iron and manganese) and their concentrations increase. Conversely, the concentrations of oxidized compounds (nitrate and insoluble iron and manganese oxides) decrease. Ground water at site A contained the smallest concentration of nitrate (0.01 mg/L) and the largest concentrations of iron and manganese (4,000 micrograms per liter, and 380 micrograms per liter, respectively). Even though ground water at this location contained measurable DO (2.3 mg/L), the small concentrations of nitrate and the large concentrations of iron and manganese indicate that reducing conditions may exist there as a result of the degradation of the petroleum products by microorganisms.

Table 5.--Organic compounds found in waste oil and diesel oil (from Watts, 1989)

Waste oil	Diesel oil
<u>Aliphatic compounds</u>	
acetone	alkanes, predominantly 10 carbon to 16 carbon chains
methylene chloride	
methylethyl ketone	
1,1,1-trichloroethane	
trichloroethylene	
tetrachloroethylene	
<u>Aromatic compounds</u>	
acenaphthene	anthracene
anthracene	benzene
benzene	ethylbenzene
bis (2-ethylhexyl) phthalate	fluorene
chrysene	naphthalene
ethylbenzene	phenanthrene
fluorene	n-propylbenzene
2-methylnaphthalene	toluene
naphthalene	1,3,5-trimethylbenzene
phenanthrene	xylene
polychlorinated biphenyls	
pyrene	
toluene	
xylene	

SUMMARY AND CONCLUSIONS

In 1989, during the removal of a waste-oil underground storage tank from the maintenance area in Mount Rainier National Park at Longmire, Washington, the soil surrounding the tank was found to be saturated with an unknown petroleum product. A preliminary investigation of the unsaturated zone by the National Park Service concluded that a petroleum product that smelled like diesel oil was present in an area immediately northeast of the tank site, about 120 feet long and about 50 feet wide at its widest point. The U.S. Geological Survey, in cooperation with the National Park Service, conducted a study to determine the identity of the petroleum product, the general ground-water hydrology of the area, the extent of contamination in the unsaturated zone, and the extent to which the petroleum product had affected ground water in the Longmire area.

Ground water flows from the Nisqually River southwestward, generally under the maintenance area. Flow directions inferred from water-table contours indicate that contaminated ground water would not affect the wetland in Longmire Meadow.

Petroleum products found in the unsaturated zone near the tank consisted of both waste oil from the tank and diesel oil. A single source of the diesel oil could not be identified conclusively because there are several diesel-oil storage tanks present in the immediate area, including two that are within 40 feet of the site of the tank. Organic compounds were detected in all of the samples of unsaturated soil, but it was not possible to conclusively identify them as being derived from waste oil or diesel oil. The tentative identity of some of the compounds (phthalate esters) indicates that diesel oil is the major contributor of organic contamination; however, some of the compounds may also be components of waste oil.

Chromatograms of water samples from wells and from a spring upgradient from the tank indicate that ground water in the vicinity of the maintenance area contains elevated concentrations of petroleum-based compounds. Diesel oil was detected at sites A and C. Diesel oil is also the most likely source of the organic compounds detected at the other sites. However, waste oil might also be the source of some of the organic compounds detected at the other sites. Retention times of some of the organic compounds detected at sites B and D are common to both waste oil and diesel oil.

The limited inorganic chemical data obtained from analyses of ground-water samples indicate that, for the most part, variations in water quality among the wells may be due to local variations in recharge and ground-water flow. However, differences in dissolved-oxygen, nitrate, iron, and manganese concentrations may be caused by the presence of a petroleum product at or upgradient from the sampling site. Small concentrations of dissolved oxygen and nitrate in ground water, in association with large concentrations of iron and manganese, usually indicate contact with oxidizable substances: in this case, petroleum hydrocarbons. At site A, where the largest concentration of the product was detected, the concentration of nitrate was smallest and the concentrations of dissolved iron and manganese were largest. The dissolved-oxygen concentration was not the smallest measured, but the presence of soluble iron and manganese indicate that reducing conditions may exist. However, an unexpectedly large dissolved-oxygen concentration at site D may result from oxygenated recharge entering the ground-water flow system upgradient from the site.

These findings indicate that diesel oil is the most likely source of most of the organic compounds detected in the soil and ground-water samples. Waste oil was identified in soil samples collected from the vicinity of the tank but could not be conclusively identified in any ground-water sample.

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NATIONAL PARK, WASHINGTON, 1990