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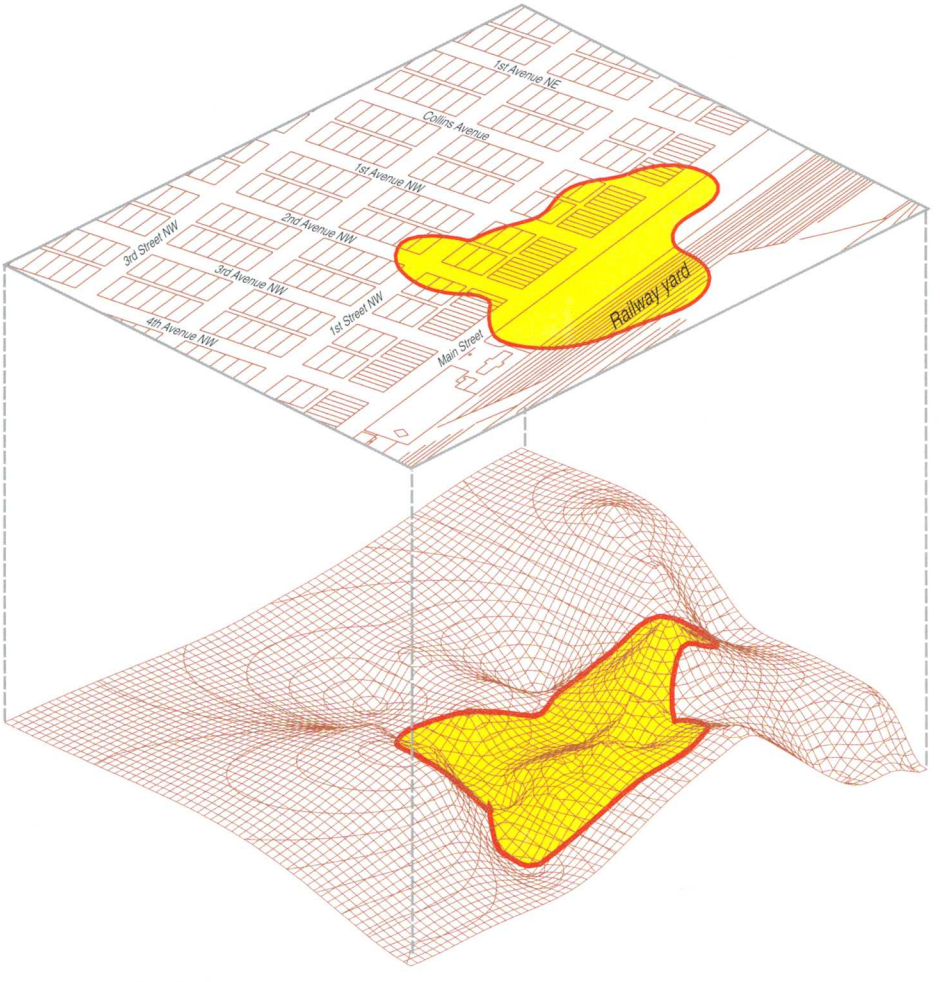
HYDROLOGIC SETTING AND GEOCHEMICAL CHARACTERIZATION OF FREE-PHASE HYDROCARBONS IN THE ALLUVIAL AQUIFER AT MANDAN, NORTH DAKOTA, NOVEMBER 2000

Water-Resources Investigations Report 01-4108



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By Frances D. Hostettler, Colleen E. Rostad, Keith A. Kvenvolden, Geoffrey N. Delin, Larry D. Putnam, Jonathan J. Kolak, Brian P. Chaplin, and Bryan D. Schaap

Water-Resources Investigations Report 01-4108

In cooperation with the North Dakota Department of Health

Bismarck, North Dakota
2001

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Hydrologic Setting and Geochemical Characterization of Free-Phase Hydrocarbons in the Alluvial Aquifer at Mandan, North Dakota, November 2000

By Frances D. Hostettler, Colleen E. Rostad, Keith A. Kvenvolden, Geoffrey N. Delin, Larry D. Putnam, Jonathan J. Kolak, Brian P. Chaplin, *and* Bryan D. Schaap

Abstract

Free-phase hydrocarbons are present in the alluvial aquifer at Mandan, North Dakota. A large contaminant body of the hydrocarbons [light nonaqueous phase liquid (LNAPL)] floats on the water table about 20 feet below land surface. The main LNAPL body is about 6 feet thick, and the areal extent is about 657,000 square feet. A study was conducted to describe the hydrologic setting and characterize the geochemical composition of the free-phase hydrocarbons in the alluvial aquifer.

Most of the study area is underlain by alluvium of the Heart River Valley that ranges in thickness from about 25 to 109 feet. The alluvium can be divided into three stratigraphic units--silty clay, silty sand, and sand--and is underlain by shales and sandstones. Monitoring wells were installed prior to this study, to an average depth of about 29 feet.

Regional ground-water flow in the Heart River aquifer generally may be from west-northwest to east-southeast and is influenced by hydraulic connections to the river. Hydraulic connections also are probable between the aquifer and the Missouri River. Ground-water flow across the north boundary of the aquifer is minimal because of adjacent shales and sandstones of relatively low permeability. Recharge occurs from infiltration of precipitation and is spatially variable depending on the thickness of overlying clays and silts. Although the general water-table gradient may be from west-northwest to east-southeast, the flow directions can vary depending on the river stage and recharge events. Any movement of the LNAPL is influenced by the gradients created by changes in water-level altitudes.

LNAPL samples were collected from monitoring wells using dedicated bailers. The samples were transferred to glass containers, stored in the dark, and refrigerated before shipment for analysis by a variety of analytical techniques. For comparison purposes, reference-fuel samples provided by the refinery in Mandan also were analyzed. These reference-fuel samples included a current diesel fuel, a closely related but slightly broader refinery-cut fuel, a crude-oil composite, unleaded regular gasoline, and additives.

Four principal analytical techniques were used for geochemical characterization: Purge-and-trap gas chromatography/mass spectrometry (volatile components); capillary gas chromatography/mass spectrometry (semivolatile components); isotope ratio mass spectrometry (carbon isotopes; whole oils); and liquid chromatography/mass spectrometry with electrospray ionization (additives and other organic components). Volatile analytes included solvents, disinfection byproducts, halogenated hydrocarbons, and alkylbenzenes, including benzene, toluene, ethylbenzene, and *meta*-, *para*-, and *ortho*-xylenes. Semivolatile analytes included *n*-alkanes, isoprenoid alkanes, cycloalkanes, and polycyclic aromatic hydrocarbons and related compounds (naphthalenes, phenanthrenes, and dibenzothiophenes and their alkylated derivatives). Of the additives, only the diesel-fuel additive with the red dye marker was amenable to electrospray ionization.

Results indicate the LNAPL consists of closely correlatable diesel fuel at various stages of degradation. All LNAPL samples contained the red dye marker for diesel fuel. None of the samples contained chlorinated solvents associated with industries such as drycleaning or automotive maintenance. Solvents such as acetone, dimethyl ether, and methylene chloride and the gasoline additives methyl-t-butyl ether (MTBE), ethyl-t-butyl

ether (ETBE), and t-amyl-methyl ether (TAME) were not found. With one possible exception, no evidence of a different diesel or other hydrocarbon fuel contribution was identified. At one site near the north edge of the main LNAPL body, evidence exists for traces of possible gasoline components in addition to the diesel fuel. The geochemical analysis of the LNAPL and correlations with other fuel products and additives strongly suggest episodic releases of a single, local-source, diesel fuel into the aquifer over an extended period of time.

INTRODUCTION

Ground-water contamination by crude oil and other petroleum-based hydrocarbons such as diesel fuel and gasoline is a widespread problem. Understanding the nature, transport, and fate of these organic contaminants is necessary to design appropriate, cost-effective remedial solutions at contaminated sites. Such understanding includes geochemical characterization of the specific contaminants involved as well as assessment of the hydrogeologic setting that affects their emplacement and transport.

Free-phase hydrocarbons related to petroleum are present in the subsurface at Mandan, N. Dak., in the Heart River Valley (ThermoRetec Consulting Corporation, 1999) (fig. 1). A large contaminant body of the hydrocarbons [also referred to in this report as light nonaqueous phase liquid (LNAPL)] exists beneath a railway yard and parts of the downtown area. The main free-phase body is about 6 feet thick and is floating on the water table about 20 feet below land surface.

Although the possibility of multiple input sources exists for any contaminant body, known input sources to at least part of the LNAPL body at Mandan are diesel-fuel spills from the railway yard and fueling areas south of Main Street (fig. 2) (Roberts, 2001). Chronic spillage of diesel fuel, thought to have occurred from 1953 to 1991, has resulted in an estimated subsurface accumulation of 1.5 to 3 million gallons of diesel product; recent recovery efforts by the railway have reclaimed about 0.5 million gallons (Roberts, 2001). Other possible, but currently unsubstantiated, sources include gasoline, perhaps leaking from underground tanks at local consumer gasoline stations, and commercial solvents from a variety of local businesses. The commercial solvents may include automobile parts degreasers such as methylene chloride and trichloroethylene (TCE) or drycleaning solvents such as perchloroethylene (tetrachloroethylene) and 1,1,2-trichloro-1,2,2-trifluoroethane (Occupational Safety and Health Administration, 2001).

The Mandan site provides an opportunity for the U.S. Geological Survey to add to knowledge gained in previous studies of hydrocarbons in the subsurface. For example, long-term interdisciplinary research sponsored by the U.S. Geological Survey Toxic Substances Hydrology Program began in 1983 at a crude-oil spill site near Bemidji, Minn. That research focuses on physical, chemical, and biological processes controlling the migration and fate of petroleum hydrocarbon contaminants in a glacial outwash setting. This study at Mandan, conducted during 2000-01 by the U.S. Geological Survey in cooperation with the North Dakota Department of Health, focused on similar processes but involved hydrogeologic conditions in an alluvial setting.

The purposes of this study were to describe the hydrologic setting and characterize the geochemical composition of the free-phase hydrocarbons in the alluvial aquifer at Mandan. The study included descriptions of the hydrologic setting, the spatial extent of the LNAPL contaminant body, and the geochemical composition of the LNAPL. Any possible chemical contributors to the LNAPL body, consistent with possible local input sources, were considered in the analyses. Hydrocarbon compositions were differentiated insofar as possible between diesel fuel or fuels and gasoline components on the basis of guidelines in peer-reviewed literature. The study focused on the downtown area, including the railway yard and the east and west fueling areas (fig. 2). Most of the hydrogeologic data used for the study were collected during 1991-2000; LNAPL samples were collected in November 2000. The locations of monitoring wells in the study area are shown in figures 2 and 3, and the locations of monitoring wells from which LNAPL samples were collected are shown in figure 4. This report presents the results of this study.

The authors thank John Enz, North Dakota State Climatologist, and his assistant, Barbara Mahoney, who provided Mandan precipitation data. Thanks to Roger Schmid, Water Supply, Inc., Bismarck, N. Dak., for providing geologic logs and aquifer-test results for monitoring wells in the downtown Mandan area; Donna Rose, U.S. Geological Survey National Water Quality Laboratory, Denver, Colo., for analytical work and additional interpretation; and James Wald, Robert Lundgren, and Wayne Berkas, U.S. Geological Survey, for providing assistance with sampling and report preparation. Thanks also to Debbie Ludwick, Brian Blee, Drazen Samardzic, and Jeff Denmen, ThermoRetec Consulting Corporation,

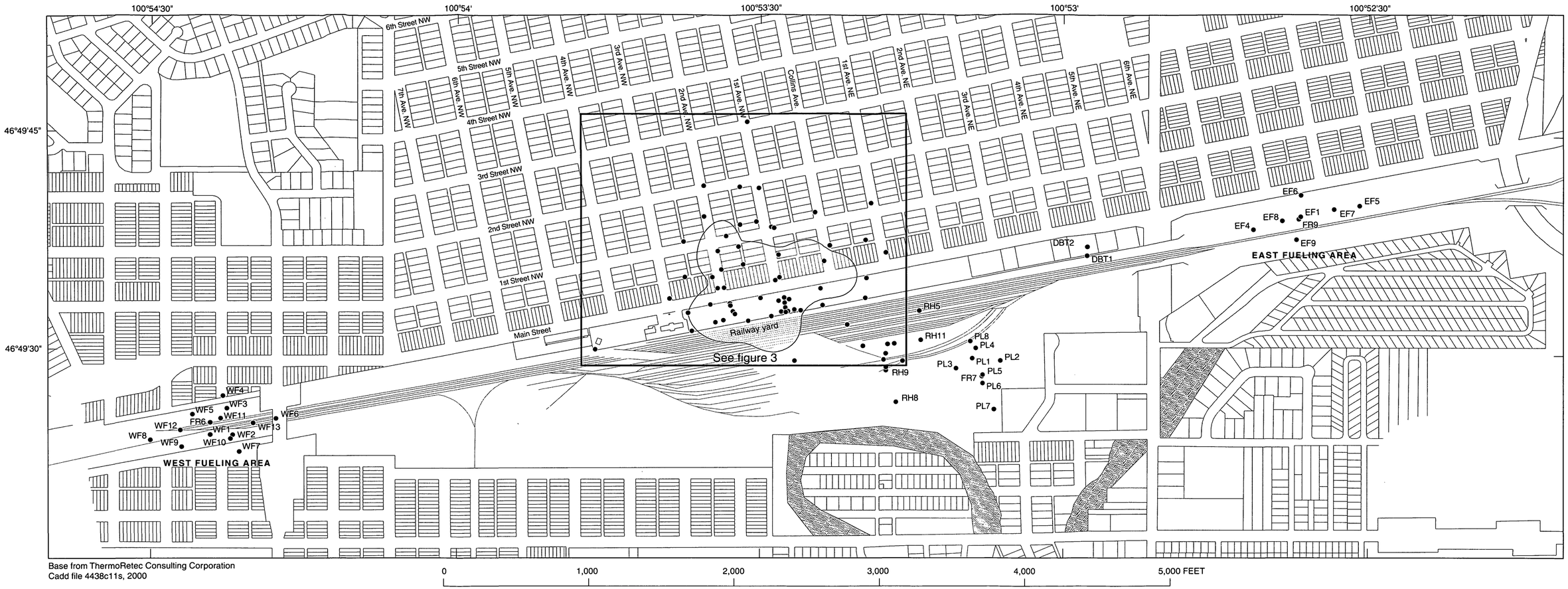

Figure 2. Locations of monitoring wells in study area, Mandan, North Dakota.

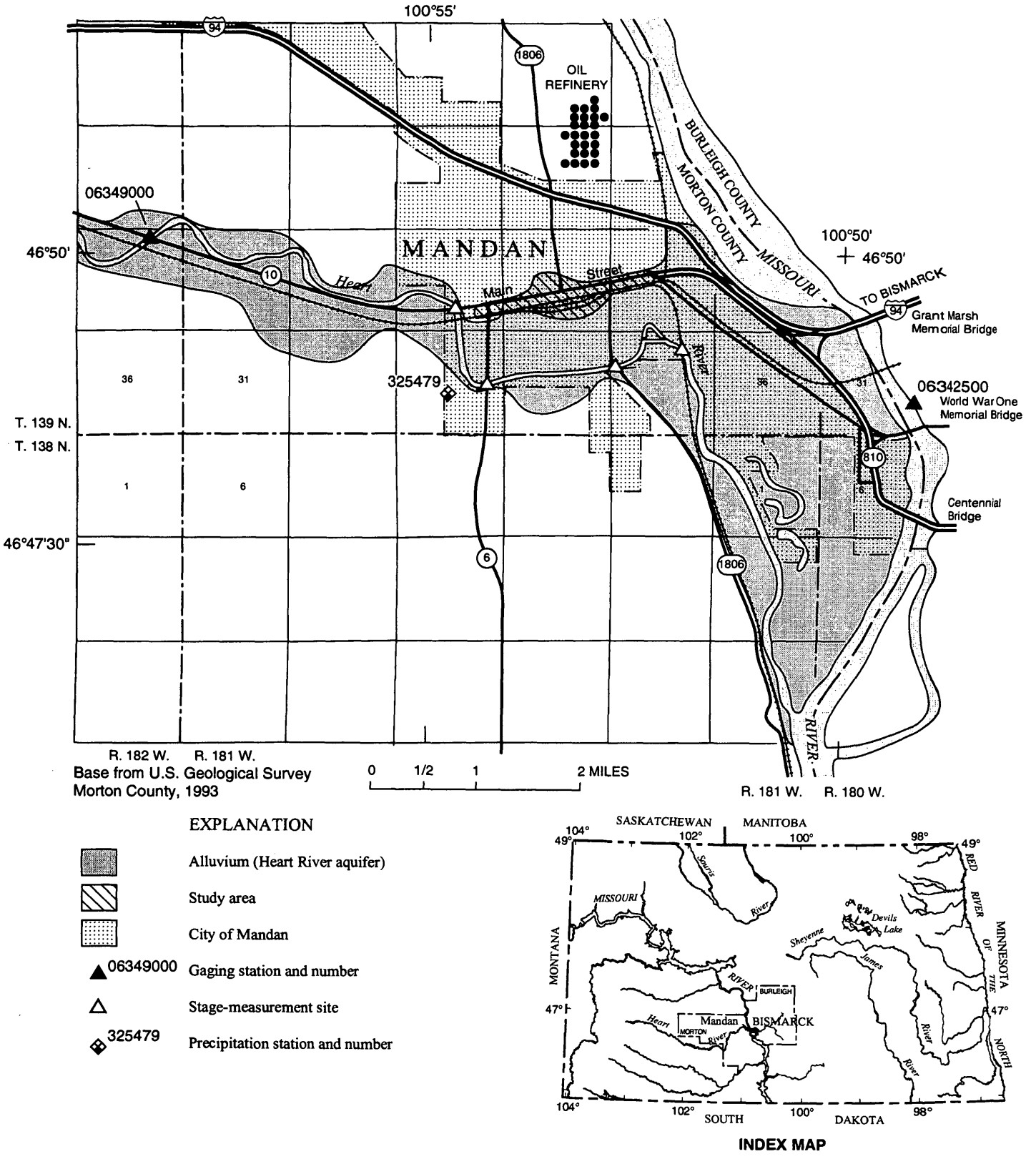

Figure 1. Locations of study area, gaging stations, stage-measurement sites, and precipitation station, Mandan, North Dakota.

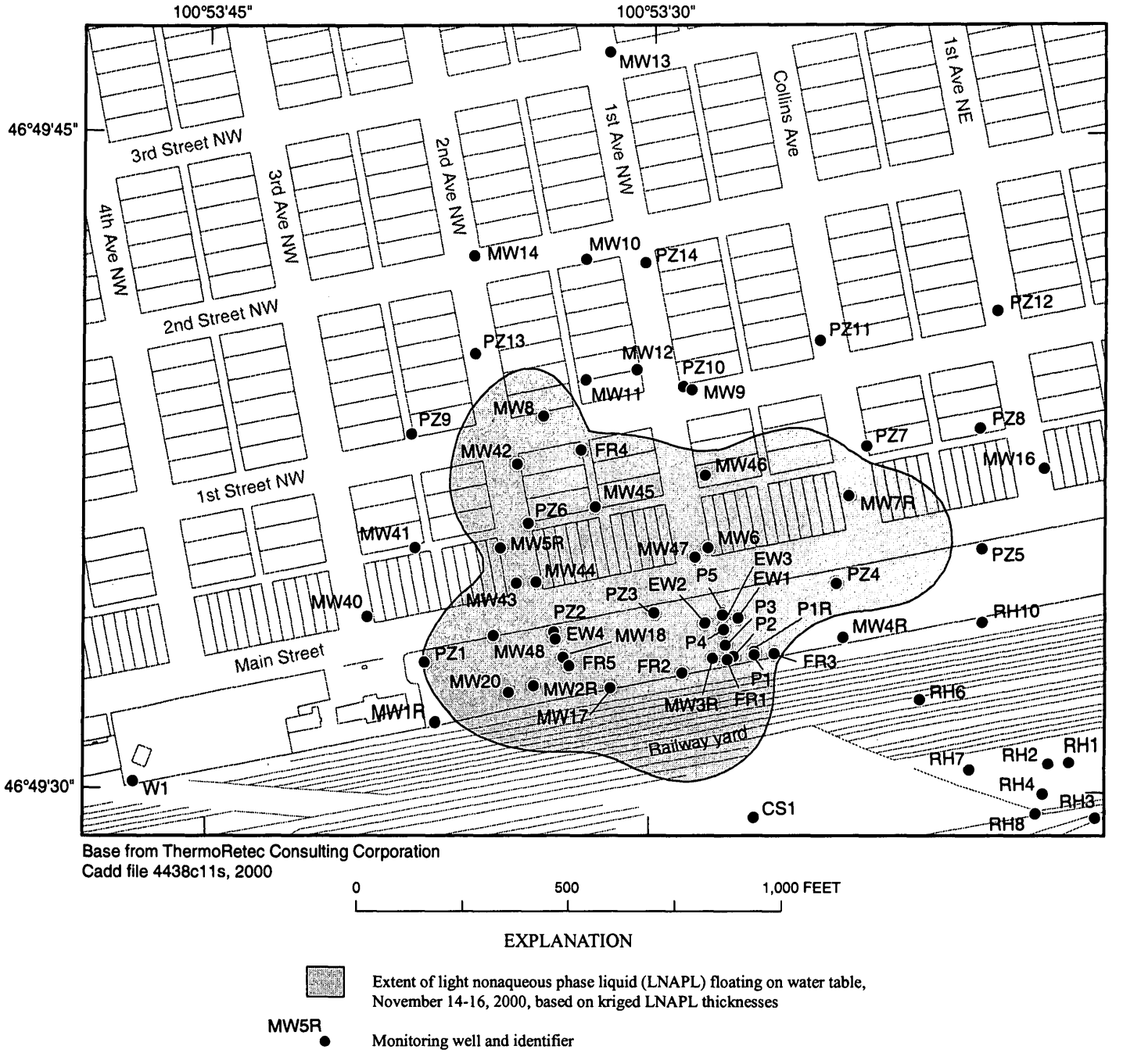

Figure 3. Locations of monitoring wells in downtown area, Mandan, North Dakota.

Mandan, for their assistance in locating and sampling wells and for providing safety training. Burlington Northern Santa Fe Railway, Mandan, allowed access to their property; and BP Amoco Mandan Refinery, Mandan, provided samples of reference fuels and additives.

HYDROLOGIC SETTING

Climate

The semiarid climate of the study area includes large variations in temperature and precipitation. Temperatures range from summer highs of near 100°F (degrees Fahrenheit) to winter lows of -30°F. Soils begin to freeze in November, remain

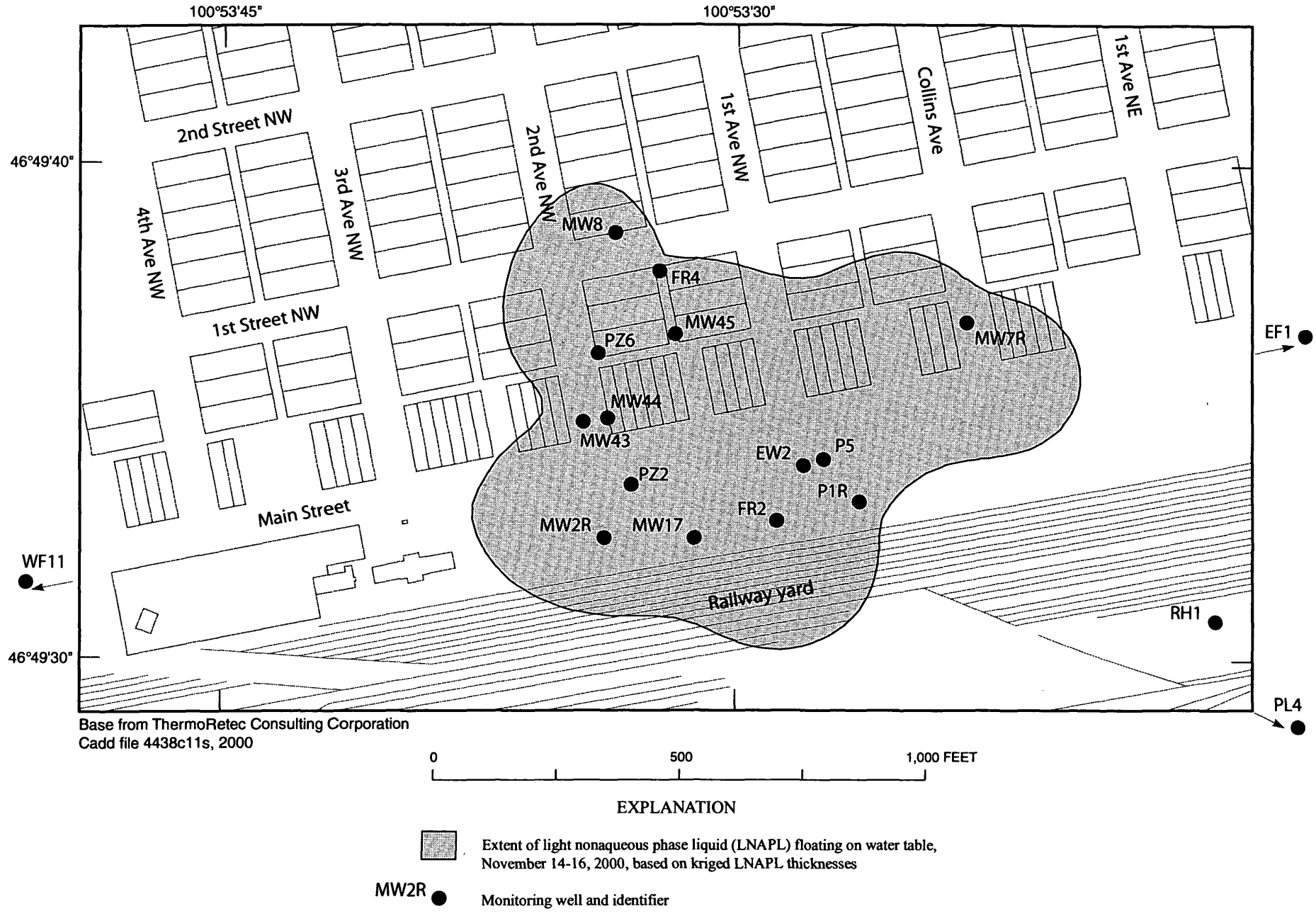

Figure 4. Locations of monitoring wells from which light nonaqueous phase liquid samples were collected, Mandan, North Dakota.

frozen from December through February, and begin to thaw in March. The hottest temperatures occur in July and August. For the 50 years from 1951 through 2000, the mean annual precipitation at the Mandan Experiment Station (U.S. Department of Commerce, Station #325479) (fig. 1), located about 1 mile southwest of the study area, was 16.61 inches (table 1). The minimum annual precipitation of 9.74 inches was recorded in 1973, and the maximum annual precipitation of 26.33 inches (about 2.7 times the 1973 total) was recorded in 1993. During 1991-2000 when most of the hydrogeologic data used in this study were collected, annual precipitation was about 3.4 inches above average. Monthly precipitation statistics for 1951-2000 (table 2) show the large variation that can occur in precipitation, especially in the early spring and summer.

Table 1. Mandan annual precipitation, 1951-2000

[Based on information from J. W. Enz and B. A. Mahoney, North Dakota State Climatologist office, written commun., 2000, 2001]

Years	Mean (inches)	Minimum (inches)	Maximum (inches)
1951-60	16.24	10.29	21.76
1961-70	16.00	12.12	23.34
1971-80	15.00	9.74	19.06
1981-90	15.77	9.83	25.52
1991-2000	20.05	14.19	26.33
1951-2000	16.61	9.74	26.33

Table 2. Mandan monthly precipitation, 1951-2000

[Based on information from J. W. Enz and B. A. Mahoney, North Dakota State Climatologist office, written commun., 2000, 2001]

Month	Mean (inches)	Minimum (inches)	Maximum (inches)
January	0.38	0.01	0.96
February	.37	.01	1.62
March	.53	0	2.02
April	1.44	0	6.36
May	2.38	.28	6.81
June	3.32	.71	6.56
July	2.67	.20	13.43
August	2.10	.11	6.09
September	1.47	.19	4.67
October	1.10	0	5.81
November	.53	0	1.96
December	.33	.01	.82

Hydrogeologic Units

Most of the study area is underlain by alluvium of the Heart River Valley (fig. 1) that ranges in thickness from about 25 to 109 feet (Ackerman, 1980). This alluvium is about 1 mile wide from south to north near the study area and becomes wider toward the Missouri River. The alluvium is underlain by shales and sandstones and in some areas is overlain by fill material. The alluvium can be divided into three stratigraphic units--silty clay, silty sand, and sand (fig. 5). The monitoring wells in downtown Mandan were installed prior to this study (data from several contractors), to an average depth of about

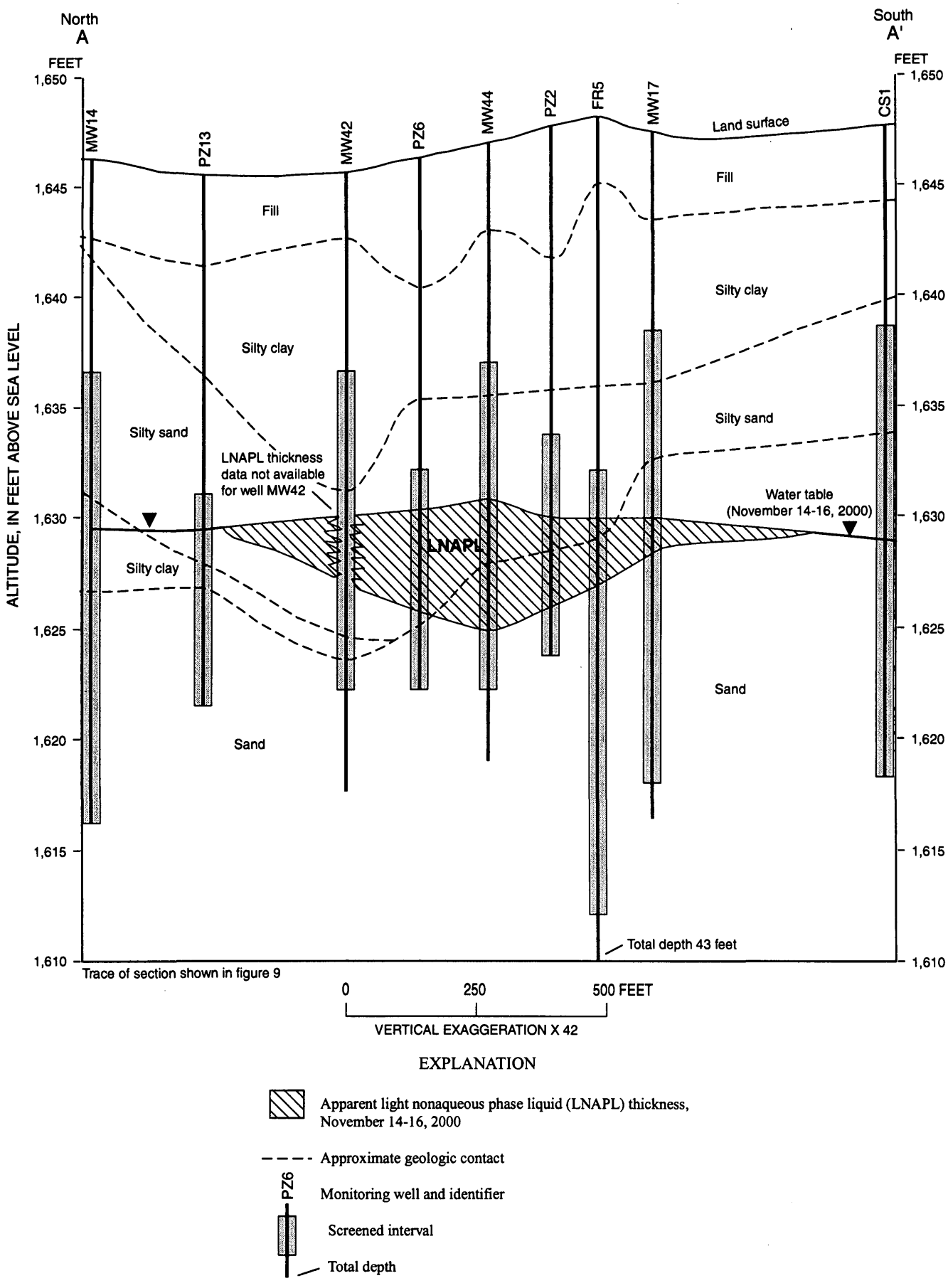

Figure 5. Hydrogeologic section A-A', Mandan, North Dakota.

29 feet below land surface (appendix A) using various methods. Because many geologists logged the wells, determining the continuity of geologic strata is tenuous.

The uppermost 0 to 6 feet of material is asphalt, concrete, or fill that consists of a heterogeneous mixture of gravel, sand, and silt. Underlying the fill is a silty clay unit that ranges in thickness from 2 to 21 feet. Average thickness of the unit is about 12 feet. Within the silty clay unit are very fine to medium-grained silty sand lenses that are as much as 8 feet thick. Many areas of the unit also have a fine sand fraction. Underlying the silty clay unit is a discontinuous fine to very fine silty sand unit that has an average thickness of about 6 feet where present. Interbedded within the silty sand unit are sand lenses that are as much as 4 feet thick and clay lenses that are 1 to 2 feet thick. This unit is most noticeably present beneath the area of Main Street, specifically near wells MW42, MW44 (fig. 5), MW5R, MW43, and MW45 (fig. 3), but is absent throughout about half the downtown area. Underlying the silty sand unit is a very fine to coarse-grained sand unit that ranges in thickness from 3 to 32 feet. The average thickness is about 13 feet, but many of the wells do not penetrate the entire thickness. Deeper parts of the unit consist of fine to coarse gravel.

The geologic contact between the bottom of the silty clay or silty sand unit and the top of the sand unit is shown in figure 6. Depth to the top of the sand unit ranges from less than 14 feet at wells CS1, MW13, MW40, MW41, PZ2, PZ4, PZ6 through PZ9, and PZ11 to greater than 20 feet at wells FR8, MW1R, MW5R, MW16, MW42, MW43, MW45 through MW48, RH1, RH2, and W1. The less-than-14-feet zones are illustrated in figure 6 as relatively high areas and the greater-than-20-feet zones as relatively low areas. Superimposed on the wire-frame diagram is the extent of the LNAPL floating on the water table and the extent of the LNAPL in the silty sand unit.

Unconfined conditions are presumed to prevail in most of the alluvial aquifer. Results of aquifer tests in the study area indicated the transmissivity of the sand unit ranges from 900 to 3,200 feet squared per day and the storage coefficient is 0.03 (Soil Exploration Company, 1985; Roger Schmid, Water Supply, Inc., written commun., 2001). Based on a saturated thickness of 30 feet, the hydraulic conductivity ranges from about 30 to 110 feet per day. The upper value is similar to the value of 130 feet per day based on ground-water-flow model analyses (ThermoRetec Consulting Corporation, 1999). Based on sieve analyses, the hydraulic conductivity of the silty sand and sand units ranges from 0.1 to 7 feet per day (Soil Exploration Company, 1985). Estimates of specific yield for the sand unit range from 0.008 (ThermoRetec Consulting Corporation, 1999) to 0.38 (Soil Exploration Company, 1985). Based on regional data for the sand unit (Ackerman, 1980), the transmissivity ranges from 100 to 10,000 feet squared per day, the hydraulic conductivity ranges from 10 to 400 feet per day, and the storage coefficient is 0.0005 where the unit is confined by silty clay and 0.2 where the unit is unconfined. Hydraulic information is not available for the silty clay unit in the study area, but the typical range of hydraulic conductivity for silty clays is 0.001 to 10 feet per day (Freeze and Cherry, 1979).

Ground-Water Flow

Regional ground-water flow in the Heart River aquifer generally is reported to be from west-northwest to east-southeast (Ackerman, 1980) and is influenced by hydraulic connections to the river. Hydraulic connections also are probable between the aquifer and the Missouri River, located about three-fourths mile east of the study area. Ground-water flow across the north boundary of the aquifer probably is minimal because of adjacent shales and sandstones of relatively low permeability.

Recharge occurs from infiltration of precipitation and is spatially variable depending on the thickness of overlying clays and silts. Less overlying clay and silt allows more infiltration of precipitation. Recharge to the aquifer from the Heart and Missouri Rivers and discharge from the aquifer to the rivers depends on the relation between the altitudes of water levels in the aquifer and of stage in the rivers.

Water levels in the aquifer (Roger Schmid, Water Supply, Inc., written commun., 2001; Nic Winslow, ThermoRetec Consulting Corporation, written commun., 2001) change seasonally in response to river stages and precipitation. In the early spring, snowmelt runoff causes the stage in the Heart River to rise above the water level in the aquifer. Measurements made at highway bridge sites (fig. 1) during 1987 through 2000 indicate the stage can rise as much as 20 feet during peak spring runoff (James D. Wald, U.S. Geological Survey, written commun., 2001). Because the Heart River is to the west and south of the study area, the water level in the aquifer begins to rise to the west and south in response to rise in river stage. During the spring and early summer, when precipitation is highest, the water level in the aquifer rises as a result of

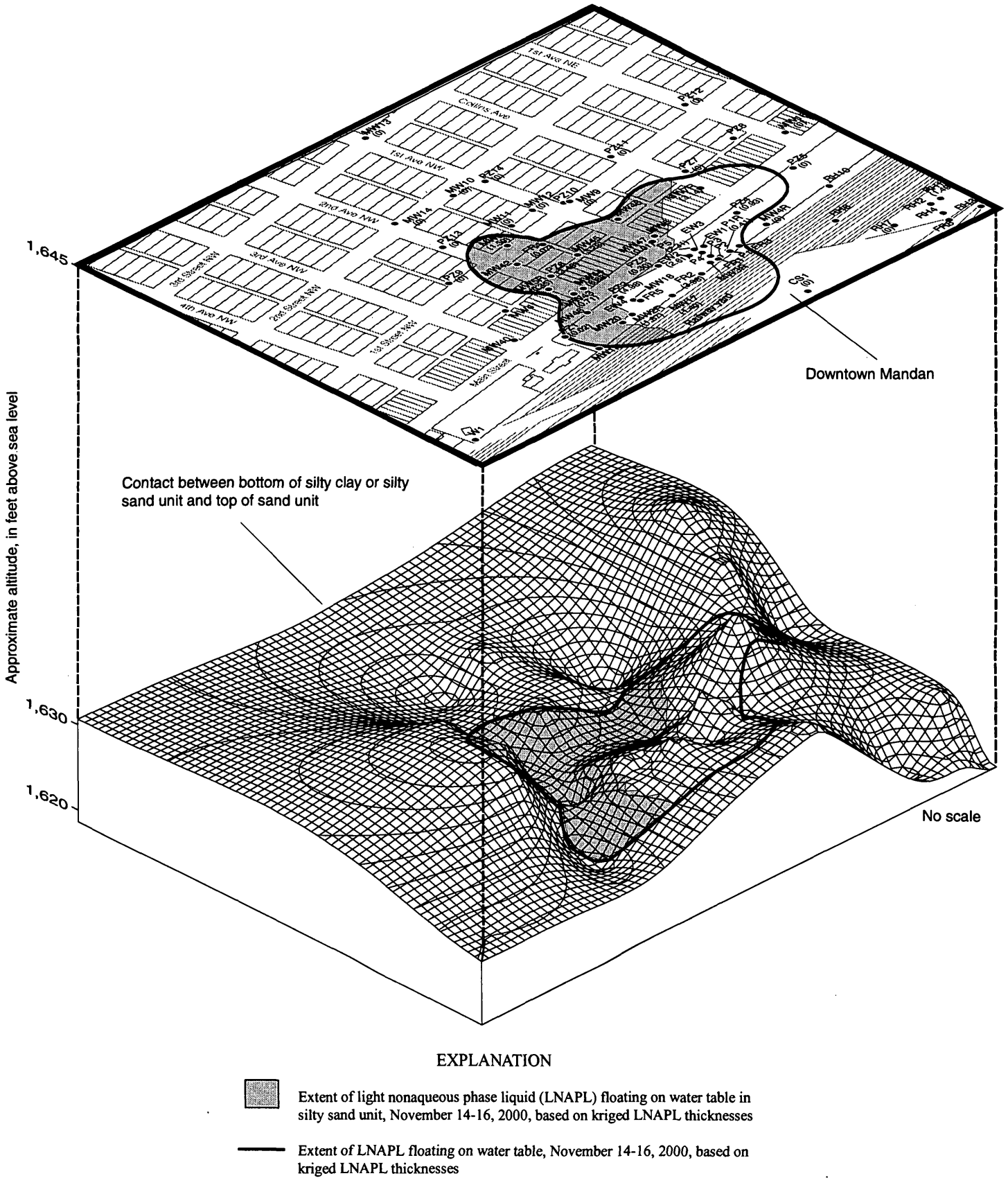

Figure 6. Geologic contact between bottom of silty clay or silty sand unit and top of sand unit, Mandan, North Dakota.

infiltration of precipitation. Greater infiltration of precipitation may occur in the south-central and southeast parts of the study area when runoff collects in abandoned oxbows and stream meanders (fig. 2).

Although the general water-table gradient may be from west-northwest to east-southeast (Radian International, 1999), the flow directions vary depending on the river stage and recharge events. Observed water-table altitudes shown in figure 7 reflect the complex ground-water-flow system. On June 29, 1992, the water levels in the east and west fueling areas were at about the same altitude, and the water levels surrounding the LNAPL did not indicate flow directions that were clearly toward the east-southeast. Some of the monitoring wells in the south part of the study area had higher water-level altitudes than those in the north part of the study area.

Hydrographs for wells CS1, MW14, and MW16 (fig. 8), which are located southeast, northwest, and northeast of the LNAPL, respectively (fig. 7), show typical transient response in water levels. The water levels (1992-95) in well CS1 on the south are greater in the spring and summer than those in wells MW14 and MW16 on the north. The increase in water levels coincides with an increase in monthly precipitation (fig. 8). Precipitation during 1992 was slightly below average, and precipitation during 1993-95 was above average. The response to recharge from precipitation at the wells north of the LNAPL lags behind the response at the well south of the LNAPL, and the peak is somewhat less. The recharge response at well CS1 occurs before that in the north wells, possibly indicating more effective recharge to the south. In the winter, as recharge from infiltration decreases and stage in the Heart River declines, the water level at well CS1 declines, and ground-water-flow directions presumably trend more toward the east-southeast.

The transient response in aquifer water levels in the study area also is affected by the stage of the Missouri River in relation to the stage of the Heart River (U.S. Geological Survey, 1955-2000). Typically, peaks in streamflow in the Missouri River, which is controlled by releases from an upstream dam, do not coincide with spring runoff. This results in smaller differences between the stages of the Heart River near Mandan and the Missouri River at Bismarck during part of the year, most likely late summer and fall. When streamflow in the Missouri River is near 40,000 cubic feet per second, the stage of the river is about 1,630 feet above sea level[1], which is about the same as the stage of the Heart River near the Highway 6 bridge when streamflow there is about 50 to 100 cubic feet per second. The stage record for October 1994 through December 1995 (fig. 8) for the two rivers shows the relation between the stages during a period with above-average precipitation. The highest stage of the Heart River occurred in the early spring, but small rises also occurred as a result of storm events. The highest stages of the Missouri River generally coincide with the lowest stages of the Heart River. When differences between the river stages at the Highway 6 bridge and the Bismarck gage become less, the gradients that cause ground water to flow regionally toward the east-southeast are diminished.

A statistical summary of water-level altitudes (1990-2000) in selected monitoring wells surrounding the LNAPL (table 3) shows small differences in mean values. Seasonal changes in recharge and river stage likely produce seasonal variations in local ground-water-flow directions. The change in water level during the 1990's ranged from about 5 to 10 feet and averaged about 7 feet for most wells. The mean water-level altitude ranged from 1,629.3 to 1,631.3 feet above sea level and, for most wells, was between 1,630.1 and 1,630.5 feet above sea level. The mean water-level altitudes in the three wells southeast of the LNAPL were greater than the mean for the well northeast of the LNAPL. Mean water-level altitudes for February generally were lower on the south and east sides of the LNAPL than on the north and west sides of the LNAPL. However, mean values for July were highest for the three wells southeast of the LNAPL. Water-level altitudes, responding to changes in recharge and river stage, reflect a complex, temporally variable ground-water-flow pattern near the LNAPL.

SPATIAL EXTENT OF FREE-PHASE HYDROCARBONS

U.S. Geological Survey, ThermoRetec Consulting Corporation, and North Dakota Department of Health personnel measured LNAPL thicknesses in selected monitoring wells in downtown Mandan on November 14-16, 2000, using an

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[1]**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.

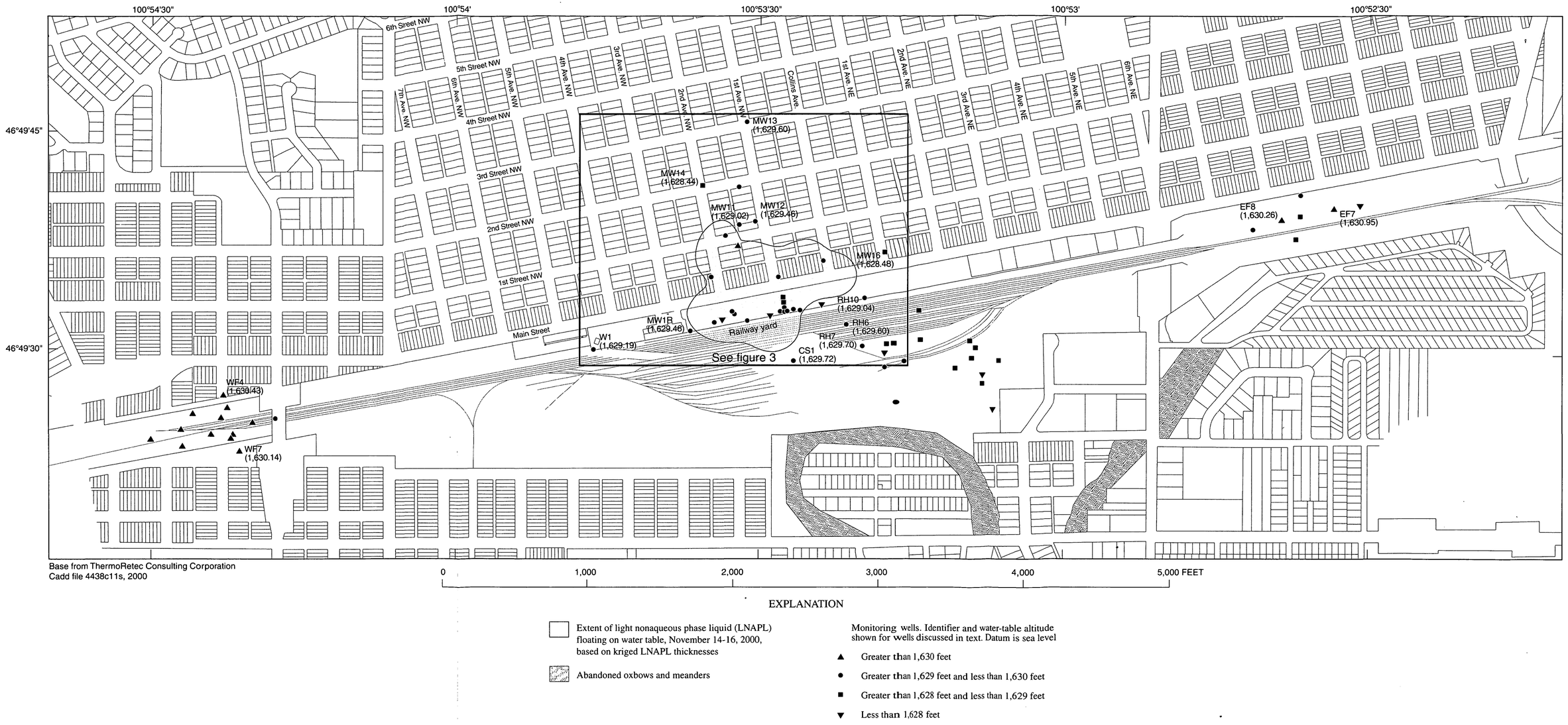


Figure 7. Water-table altitude, Mandan, North Dakota, June 29, 1992.

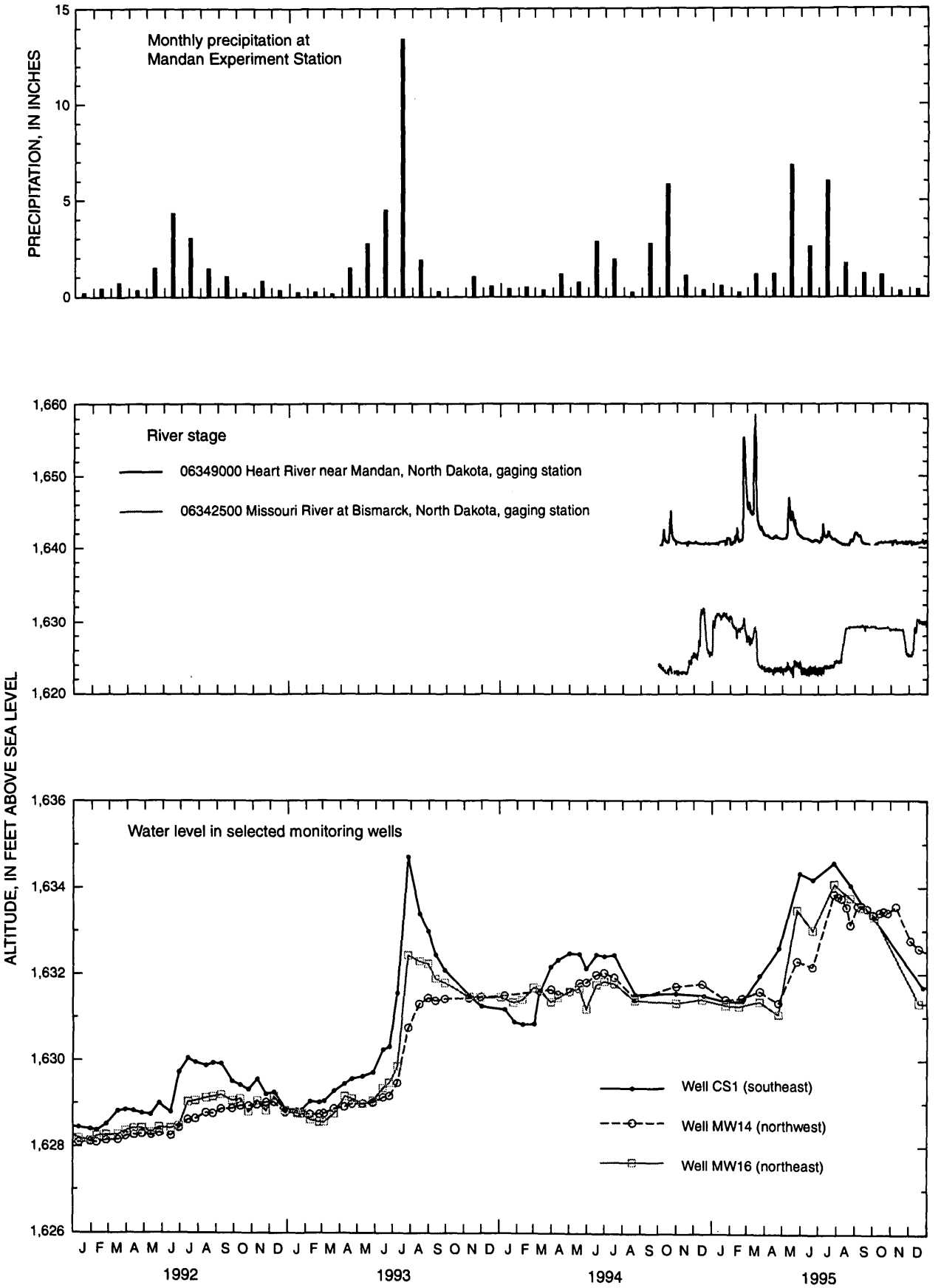


Figure 8. Monthly precipitation, river stage, and water level in selected monitoring wells.

Table 3. Statistical summary of water-level altitudes (1990-2000) in selected monitoring wells surrounding light nonaqueous phase liquid

[LNAPL, light nonaqueous phase liquid]

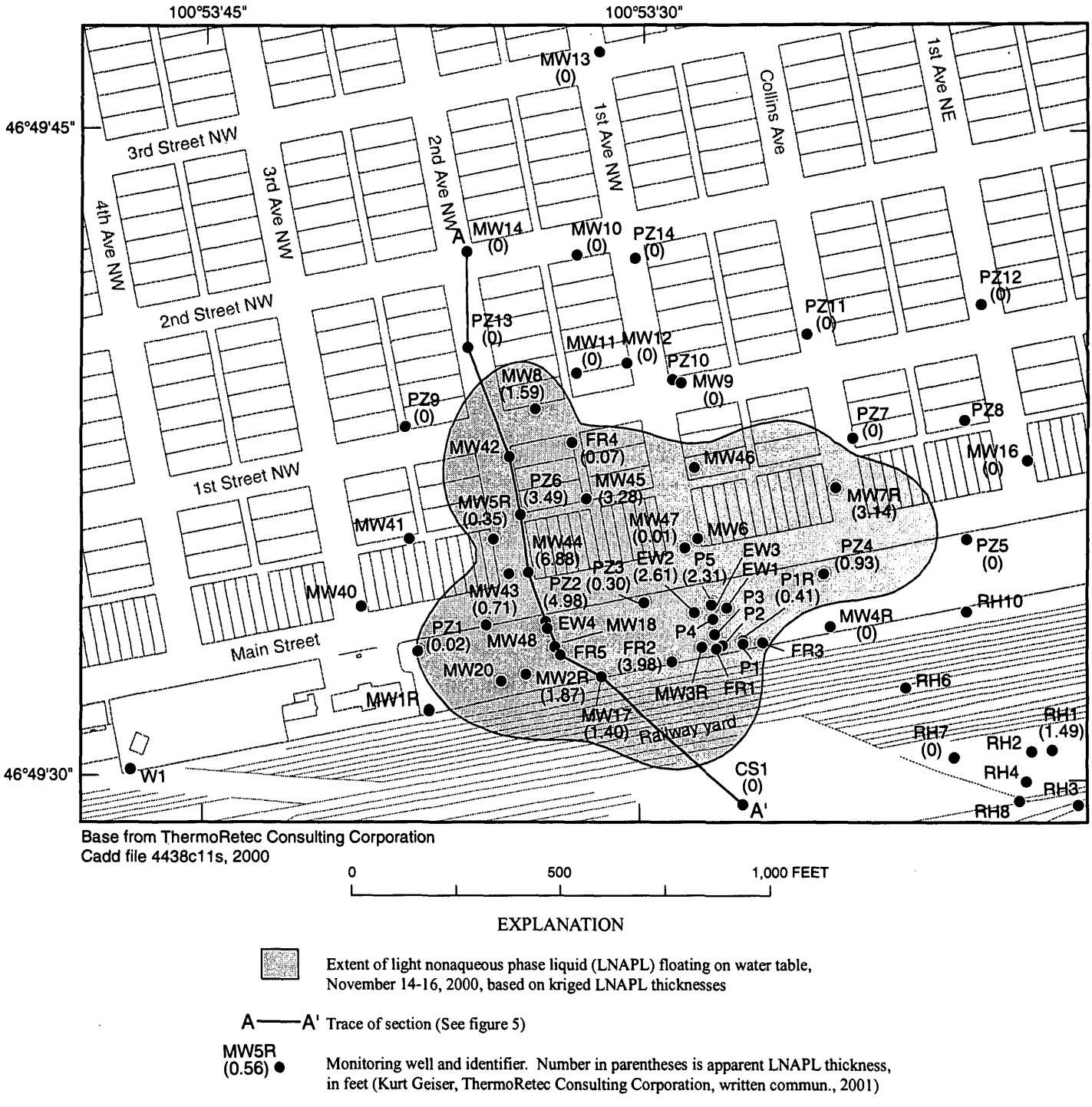
Well identifier	Yearly mean (feet above sea level)	February mean (feet above sea level)	July mean (feet above sea level)	Maximum (feet above sea level)	Minimum (feet above sea level)	Change (feet)	Beginning date of record	Ending date of record	Number of measurements
Monitoring well southwest of LNAPL									
W1	1,630.4	1,630.3	1,630.6	1,634.9	1,628.2	6.7	12/05/91	6/16/00	130
Monitoring wells southeast of LNAPL									
CS1	1,630.1	1,629.6	1,630.8	1,634.7	1,627.7	7.0	4/18/90	6/16/00	139
RH6	1,630.3	1,629.1	1,631.6	1,634.0	1,628.8	5.2	12/26/91	3/01/00	62
RH7	1,631.3	1,629.9	1,633.4	1,638.2	1,628.1	10.1	12/05/91	6/16/00	93
Monitoring wells north or northwest of LNAPL									
MW9	1,630.1	1,629.8	1,629.7	1,634.1	1,627.3	6.8	1/10/90	6/17/00	166
MW10	1,630.5	1,630.1	1,630.8	1,634.7	1,627.8	6.9	1/10/90	6/17/00	133
MW11	1,630.2	1,629.7	1,630.6	1,634.4	1,627.4	7.0	1/10/90	6/16/90	194
MW14	1,629.7	1,629.4	1,629.7	1,633.8	1,627.1	6.7	4/17/90	6/16/00	146
Monitoring well east of LNAPL									
RH10	1,630.2	1,629.1	1,630.0	1,634.1	1,628.3	5.8	12/26/91	6/16/00	76
Monitoring well northeast of LNAPL									
MW16	1,629.3	1,628.8	1,629.7	1,634.7	1,627.1	7.6	4/18/90	6/16/00	136

electric measuring device. The apparent LNAPL thickness in a well generally was different from the actual thickness in the aquifer (van Dam, 1967; Lenhard and Parker, 1990). The LNAPL in the aquifer is present not only as a lens of LNAPL-saturated sediment but is spread over a thicker mixing zone that contains air, LNAPL, and water in the pores. If the water level rises, the apparent thickness in the well is likely to decrease. If the water level declines, the apparent thickness in the well is likely to increase. Although the apparent thickness in the well fluctuates, the total amount of LNAPL in the aquifer is not changed substantially by the water-level fluctuations.

Apparent LNAPL thicknesses are shown in figure 9. LNAPL was detected floating on the water table in about a 657,000-square-foot area bounded approximately by 1st Street NW. on the north, Collins Avenue on the east, and 3rd Avenue NW. on the west (fig. 3). The southern extent is unclear because of the limited number of wells within the railway yard, but the LNAPL does not extend as far south as wells CS1 and RH7. In addition to the main LNAPL body, historic evidence (Roberts, 2001) and current recovery efforts (Burlington Northern Santa Fe Railway, 1999a through 1999d; 2000a through 2000d) by the railway show several other hydrocarbon bodies exist, including beneath the east and west fueling areas, at well RH1 (the Roundhouse area), and at well PL4, where in 1987 a diesel-fuel pipeline directly from the local refinery was found to be leaking.

The extent of the LNAPL (fig. 10) was based on kriging of apparent LNAPL thicknesses in wells. The kriging was done with a linear variogram model and zero nugget effect. Kriging is a geostatistical gridding method used to produce contour surface plots from irregularly spaced data, and nugget is an interpolation and smoothing factor. The apparent LNAPL thickness was greatest near well MW44 (6.88 feet). The areas of greatest thickness appear to follow two directional trends--from near wells MW2R and MW17 to the east-northeast toward well MW7R and to the north-northwest toward wells MW44, MW45, and PZ6 (fig. 10A). The kriged LNAPL thicknesses shown in figure 10A do not always agree with the apparent thicknesses shown in figure 9 because of the inherent limitations of kriging.

Top and bottom altitudes of the LNAPL body were correlated with geologic information to evaluate the extent of LNAPL in the sand and overlying units. LNAPL floating on the water table occurred in all three units because the altitude of the geologic contacts between the units is variable. The LNAPL was primarily in the silty sand unit in the area that includes wells FR4, MW5R, MW8, MW43, MW45, MW47, and PZ6 (fig. 10B) and exclusively in the sand unit in the area



Base from ThermoRetec Consulting Corporation
Cadd file 4438c11s, 2000

0 500 1,000 FEET

EXPLANATION

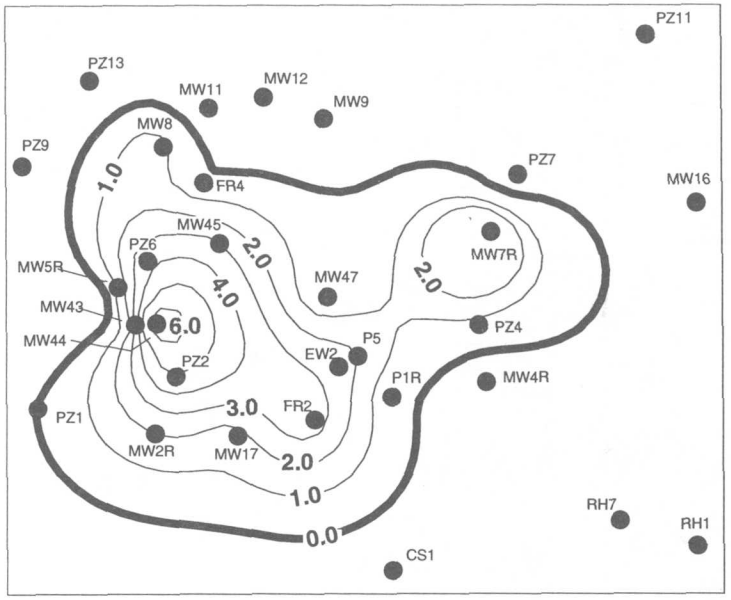
Extent of light nonaqueous phase liquid (LNAPL) floating on water table, November 14-16, 2000, based on kriged LNAPL thicknesses

A——A' Trace of section (See figure 5)

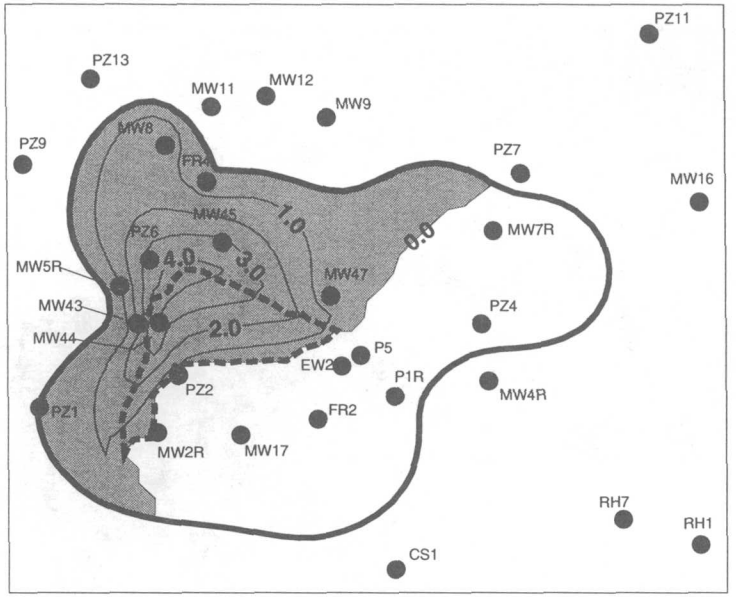
MW5R (0.56) ● Monitoring well and identifier. Number in parentheses is apparent LNAPL thickness, in feet (Kurt Geiser, ThermoRetec Consulting Corporation, written commun., 2001)

Figure 9. Apparent light nonaqueous phase liquid thickness in selected monitoring wells, Mandan, North Dakota.

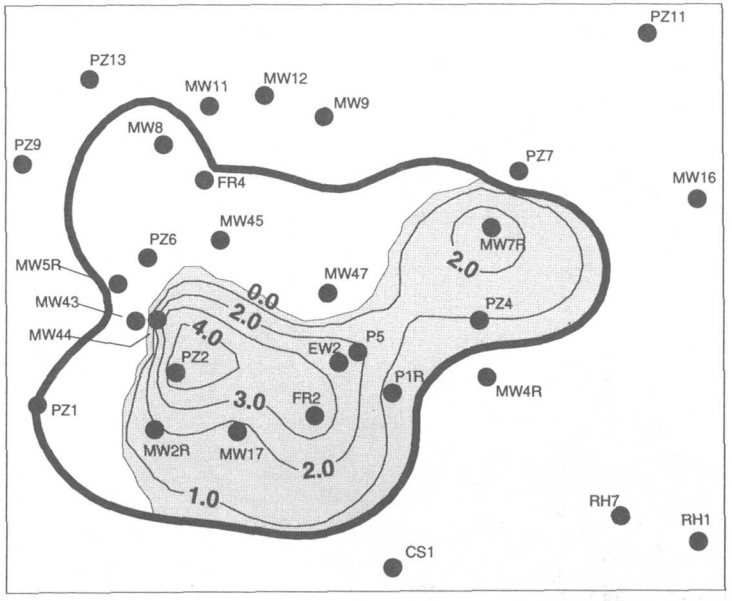
that includes wells EW2, FR2, MW7R, MW17, P1R, P5, and PZ4 (fig. 10C). The LNAPL was in both units in the relatively small area that includes wells MW2R, MW44, and PZ2 (fig. 10C). The areal extent exclusively in the silty sand unit was about 278,000 square feet in November 2000, and the areal extent exclusively in the sand unit was about 351,000 square feet. The LNAPL is in the silty sand unit where the unit extends deepest below land surface (fig. 6). The areal extent of the LNAPL in each unit changes with fluctuations in the water table. As the water table declines, for example, the extent of the LNAPL in the silty sand unit decreases and the extent in the sand unit increases, causing a smear zone.



(A) Extent and apparent thickness of LNAPL



(B) Extent and apparent thickness of LNAPL in silty sand unit



(C) Extent and apparent thickness of LNAPL in sand unit

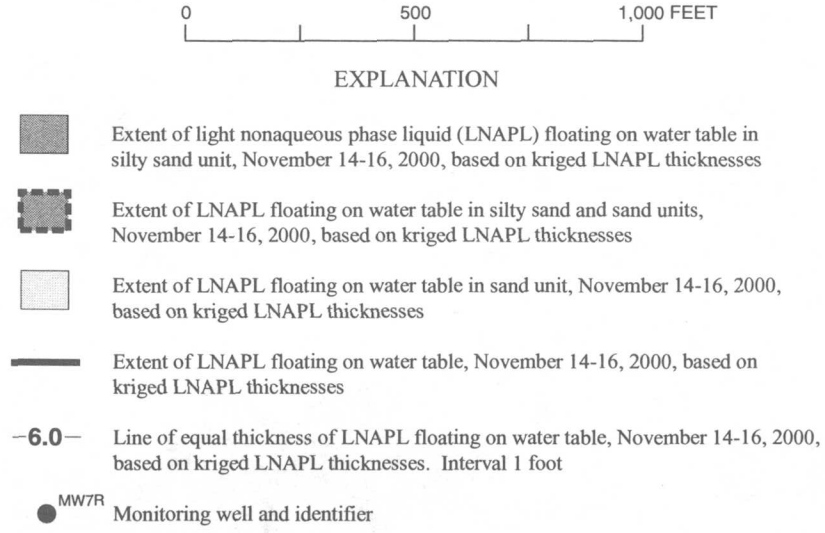


Figure 10. Extent and apparent thickness of (A) light nonaqueous phase liquid, (B) light nonaqueous phase liquid in silty sand unit, and (C) light nonaqueous phase liquid in sand unit, Mandan, North Dakota. (Note: The kriged thicknesses shown in this figure do not always agree with the apparent thicknesses shown in figure 9 because of the inherent limitations of kriging.)

LNAPL also was apparently present in the silty clay unit near well MW45 during November 2000. However, any LNAPL in this unit probably was located primarily in relatively thin sand lenses within the unit because silt and clay do not readily imbibe LNAPL fluids, particularly when saturated with water. The process by which LNAPL imbibition into the silty clay unit could occur is complex. A rising water table and the mounding of LNAPL near a source could have created a local zone of high pressure near the edge of the silty clay unit. This high pressure then could have forced the LNAPL into the sand lenses in the unit. The LNAPL also could have entered the silty clay unit if the porosity and permeability had been increased because of cracking or fracturing of the material. Fracturing could have occurred from anthropogenic activity at land surface or from alteration of the clay structure by the LNAPL. Soil cores would need to be collected and analyzed to evaluate the extent of fracturing and its effect on porosity and soil wettability.

The spatial extent of the LNAPL probably has been affected both by geology and transient ground-water-flow conditions. The LNAPL appears to be present mostly in the silty sand and sand units, which are the most permeable. Also, the LNAPL floats on the water table, which commonly is near the contact between the silty clay or silty sand unit and the sand unit. In areas where the silty clay unit extends below the water table, migration of the LNAPL probably has been inhibited or stopped. Because of changes in altitude of the water table, the effect of the silty clay unit could vary temporally. Furthermore, changing hydrologic conditions can change water-table gradients, which affect the directions of LNAPL migration. The heterogeneous geology and the temporally varying water-table gradient across the study area complicates interpretations regarding migration of the LNAPL based on available data.

GEOCHEMICAL CHARACTERIZATION OF HYDROCARBONS

Hydrocarbons in fossil fuels occur as a complex mixture, which includes acyclic alkanes, cycloalkanes, olefins, and aromatics (Altgelt and Boduszynski, 1994). Acyclic alkanes, also called paraffins, include normal and isoparaffins--that is, straight-chain and branched-chain hydrocarbons. Cycloalkanes, also called naphthenes, are classified by the number of rings. Cycloalkanes can have five-membered rings (cyclopentanes) or six-membered rings (cyclohexanes) and most have side chains. Olefins, also called alkenes, have at least one double bond; although scarce in crude oil, olefins may occur in large amounts in lighter distillates from cracked refinery streams. Aromatics contain at least one benzene ring; polycyclic aromatic hydrocarbons (PAHs) contain two or more fused benzene rings.

Gasoline and diesel fuel are two different refinery cuts, with gasoline a low boiling point distillation cut and diesel a mid-range cut. Hydrocarbons in gasoline are predominantly in the C_3 to C_{12} range. Hydrocarbons in diesel fuel are in the C_9 to C_{25} range. The fuels contain very distinct distributions of hydrocarbon components although some overlap in components occurs at the distillation endpoint for gasoline and beginning for diesel. Important volatile components that differentiate gasoline from diesel fuel are isooctane (2,2,4-trimethylpentane) and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), which are dominant in gasoline (Kaplan and others, 1997). Diesel fuel is characterized by a dominance of *n*-alkanes, seen in a chromatogram as a smooth, bell-shaped distribution pattern maximizing at about C_{14} to C_{17}. Within the given range of components in each of these two fuel classes, however, differences in relative amounts of specific components, such as alkylated PAHs, can occur. These differences are derived from the original crude-oil source from which the oils were produced and result in each oil having a unique chemical fingerprint.

Fuel additives are chemical components engineered to improve the performance of gasoline, diesel fuel, and other fuels. Performance benefits include octane (gasoline) and cetane (diesel) enhancement, emissions reduction, increased lubricity, storage stability, and the protection against deposits for fuel injectors, intake valves, and combustion chambers (Ethyl Corporation, 2001). Various petroleum products contain a variety of dyes, some federally mandated, to enable immediate distinction among fuel types such as gasoline (yellow), diesel (pink), and jet fuel (blue). Few dyes are pure, and sometimes mixtures of dyes are used (Youngless and others, 1985).

The most common approach to characterization and identification of a hydrocarbon spill in the environment is analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) (Mansuy and others, 1997). This technique allows separation, identification, and quantification of the individual components of the fuel mixture. Correlations then are made on the basis of the molecular distribution of the aliphatic and aromatic hydrocarbons or specific biomarkers on a chromatogram (Wang and others, 1994). This type of analysis, along with several sampling and analytical

methods, was used to characterize the LNAPL in the alluvial aquifer at Mandan. Samples were analyzed for volatile and semivolatile components, stable carbon isotopes, additives, and dyes.

Sampling Methods

LNAPL samples were collected for chemical analysis from selected monitoring wells (fig. 4) on November 14-16, 2000. The samples were collected using dedicated Teflon bailers and transferred to 1-liter glass containers by agitating the check-ball and allowing the liquid to flow from the bottom of the bailer into the glass container (modifications to this procedure at two sites are described in the next paragraph). The samples were placed in boxes and stored out of sunlight until being transferred to a locked refrigerator at the end of the day. Bailers were discarded after use. Samples were collected only from wells where LNAPL was readily collectible. Neither water in contact with the LNAPL nor sediment cores impacted (smeared) by the hydrocarbon product were targeted for sampling in this study. Sample PZ4 was received as an aqueous solution rather than free product and, therefore, was not included.

To ascertain whether sampling methodology affects reproducibility in the analysis of volatile components, samples were collected from wells WF11 and MW45 using several different methods. At well WF11, one sample was collected by releasing the check-ball with a glass pipet and allowing the liquid to flow from the bottom of the bailer. Another sample was collected by agitating the check-ball. The samples were labeled WF11 and WF11A, respectively. At well MW45, one sample was collected by pouring the liquid from the top of the bailer, a second sample was collected by releasing the check-ball with a glass pipet and allowing the liquid to flow from the bottom of the bailer, and a third sample was collected by agitating the check-ball and allowing the liquid to flow from the bailer to the glass container. These samples were labeled MW45P, MW45B, and MW45, respectively.

Aliquots of the LNAPL samples were transferred from the 1-liter glass containers to 40-milliliter bottles using 25-milliliter glass pipets. A new pipet was used for each sample. The LNAPL remaining after subsampling was archived and kept in locked, dark, refrigerated storage. The aliquot samples were double bagged, sealed with duct tape, and shipped to the laboratory using chain-of-custody protocol.

Samples of a current diesel fuel (RR40), a broader refinery-cut fuel similar to diesel fuel (HS#2), a crude-oil composite (COC), unleaded regular gasoline (ULR), and additives (Nalco 5375A, Stadis 450, Para Flow 511, DCI 6A, and Unisol Red B50) were received from the refinery in Mandan. Aliquots of each sample of reference fuels and additives also were transferred to 40-milliliter glass bottles using 25-milliliter glass pipets, double bagged, sealed with duct tape, and shipped to the laboratory using chain-of-custody protocol.

Finally, for comparison purposes, a sample of a diesel-fuel standard from a source completely unrelated to the Mandan reference-fuel samples was purchased from Restek Corporation, Bellefonte, Penn. Three solutions containing residues of the same fuel, weathered 25, 50, and 75 percent, also were purchased.

Analytical Techniques

Volatile Analysis

Purge-and-trap GC/MS was used to analyze the LNAPL and reference-fuel samples for volatile components. The analyses were done by the U.S. Geological Survey National Water Quality Laboratory, Denver, Colo., using modifications to Schedule 4054 (Connor and others, 1997). An aliquot of each sample was spiked into analyte-free reagent water at a dilution of 1:400,000 before analysis. The volatile analytes were similar to those listed in the U.S. Environmental Protection Agency Method 524 target compound list (U.S. Environmental Protection Agency, 1995), which includes solvents, disinfection byproducts, halogenated hydrocarbons, and alkylbenzenes, and also included the BTEX suite (benzene, toluene, ethylbenzene, and *meta*-, *para*-, and *ortho*-xylenes). In addition, qualitative and semiquantitative data were generated for nontarget analytes. Ratios of target compounds selected for fuel characterization were calculated using concentrations from the quantitative data. Semiquantitative ratios of nontarget compounds identified by library matches were calculated on the basis of estimated concentrations where a relative response factor of 1 to the internal standard, fluorobenzene, was assumed.

Semivolatile Analysis

Capillary GC/MS was used to analyze the LNAPL and reference-fuel samples for semivolatile components. A Hewlett Packard 6890 gas chromatograph interfaced to a 5973 Mass Selective Detector equipped with a Merlin microinlet was maintained at 35°C (degrees Celsius) for 2 minutes and programmed at 5°C per minute to 315°C, holding for 5 minutes. A DB-5MS 30-meter capillary column with a 0.25-millimeter inner diameter and a 0.25-micrometer bonded phase was used for the qualitative and quantitative analyses. Samples were analyzed as whole oils using 10 to 20 milligrams of sample diluted to 5.0 milliliters in hexane. For PAH quantitation, appropriate deuterated internal standards were added. Five-point calibration curves were constructed and were linear over the calibration range investigated. An analytical reference standard (NIST SRM-1491, aromatic hydrocarbons) was analyzed before, halfway through, and after the suite of samples; analytes in the standard in all cases were within the acceptable range of the stated values. All compounds of interest, especially those used in correlations, were identified by comparison with known reference standards. Members of homologous series were identified by extracted ion (EI) chromatograms of characteristic fragment ions. These series included *n*-alkanes [m/z 57 (mass-to-charge ratio)] and *n*-alkylated cyclohexanes (m/z 83; CHs). Ratios of selected components were calculated using either total ion chromatogram (TIC) peak heights (single analytes) or EI chromatogram peak areas (alkyl PAH isomer families). These ratios and other relevant parameters are defined later. Bar graphs for the three most prominent PAH families (naphthalenes, phenanthrenes, and dibenzothiophenes from C0 to C3) in the LNAPL and reference-fuel samples were constructed using quantitative data.

Stable Carbon Isotope Analysis

Isotope ratio mass spectrometry was used to analyze the LNAPL and reference-fuel samples for stable carbon isotopes ($\delta^{13}C$). The analyses were done by Zymax Forensics, San Luis Obispo, Calif. Analyses were done on whole oils, as bulk analyses. To assure accuracy, duplicate samples were analyzed for every 10 samples, and a National Bureau of Standards (NBS) oil sample also was analyzed.

Geochemical Parameters from Isotope and Gas Chromatographic/Mass Spectrometric Data

The following parameters were calculated from the isotope and GC/MS data:

(a) $\delta^{13}C$, the carbon isotopic composition of whole-oil residues--useful for oil-source correlations and as an indication of systemic biodegradation (Peters and Moldowan, 1993; Stout and Lundegard, 1998).

(b) Pr/Ph, pristane/phytane--a widely used source parameter (Peters and Moldowan, 1993) utilizing the two isoprenoids most common to fuel oils.

(c) *n*-C_{17}/Pr, *n*-C_{17} alkane/pristane--used to track biodegradation (Kaplan and others, 1997; Stout and Lundegard, 1998) because *n*-alkanes biodegrade faster than isoprenoids.

(d) *n*-Cmax--indicates the *n*-alkane or isoprenoid group at highest peak height in the EI chromatograms for m/z 57.

(e) C1D/C1P, methyl dibenzothiophenes (m/z 198)/methyl phenanthrenes (m/z 192)--a source-discriminant ratio (Kaplan and others, 1997). This ratio and that in (f) compare common fuel components that contribute to the chemical fingerprint.

(f) C2D/C2P, dimethyl dibenzothiophenes (m/z 198)/dimethyl phenanthrenes (m/z 206)--a source-discriminant ratio (Kaplan and others, 1997; Bence and others, 1996). This ratio and that in (e) compare common fuel components that contribute to the chemical fingerprint.

(g) C1N/C2N, methyl naphthalenes (m/z 142)/dimethyl naphthalenes (m/z 156)--a source and weathering ratio (Kaplan and others, 1997) that helps differentiate sources within fuel types, when the fuel is unweathered, and indicates weathering progression (C1 loss occurs before C2) in weathered fuels.

(h) 1,2,4-TMB/2MN, 1,2,4-trimethylbenzene/2-methylnaphthalene--a diesel-fuel component ratio. Both analytes are prominent, moderately refractory, aromatic compounds.

Liquid Chromatographic/Mass Spectrometric Analysis

Liquid chromatography/mass spectrometry (LC/MS) was used to analyze the LNAPL, reference-fuel, and additive samples by both positive and negative electrospray ionization. All solvents used were ultraviolet (UV) HPLC grade. Using flow-injection analysis, 5 microliters of sample diluted with methanol was injected into an isocratic stream of methanol at 0.2 milliliter per minute. This method transferred the sample directly into the ion source. Samples were injected in duplicate every minute, in random order.

Additives received from the refinery were diluted in methanol for analysis. Upon addition to the solvent, the Nalco, Stadis, and Para Flow additives formed a bead, indicating they were practically insoluble. Upon mixing, the bead dissolved, but flakes precipitated out of solution. The DCI additive dissolved into a cloudy solution. Because of the sensitivity of the instrumentation and additive concentration relative to the samples, the additives were diluted once at 1:1,000 and then again at 1:1,000 with methanol. The initial focus was on ionizing the additives effectively. Except for the Unisol Red B50 additive, dissolution into the methanol was poor. The additives also did not ionize well under either positive or negative electrospray ionization because most of the additives are composed solely of carbon- and hydrogen-based components (B. Devlin, Nalco/Exxon, oral commun., 2001), which do not respond to this ionization.

Samples were diluted for LC/MS analysis by adding 1 microliter of sample to 1,000 microliters of methanol. The samples were shaken well to mix and then refrigerated until analysis. Sample and standard solutions were analyzed unfiltered to eliminate bias from selective sorption onto filter media.

To investigate specific fuel types on the basis of dye additives used, the Unisol Red B50 sample provided by the refinery was analyzed by liquid chromatography/electrospray ionization/mass spectrometry (LC/ESI/MS). The sample was analyzed by negative ionization to optimize ionization conditions. Similar dyes were analyzed in case they had been used in the past. Reference standards of 10 similar solvent dyes were diluted to an appropriate concentration in methanol and analyzed to verify that ionization conditions were optimized to produce the deprotonated molecular ion without fragmentation or adduct formation. The Unisol Red B50 additive was diluted in methanol and hexane and analyzed for its UV spectrum using a CCD Array UV-Vis Spectrophotometer for comparison with literature values of the other dyes. Additive samples received from the refinery and LNAPL samples collected from the study area then were analyzed in quadruplicate. The polar or oxygenated species in the samples responded to this negative ionization method, but the aliphatic and aromatic components did not respond. The typical nonvolatility and thermal lability of dyes is not a limitation for this technique.

Analytical Results

Volatile Components

The LNAPL and reference-fuel samples were analyzed for volatile components to compare their respective compositions. TICs for the RR40, HS#2, and ULR reference-fuel samples are given in appendix B to enable visual comparison, and EI chromatograms for m/z 57, characteristic of normal alkanes, are given in appendix C. Concentrations or nondetect notations for all target volatile components searched for in the LNAPL and selected reference-fuel samples are given (in order of increasing boiling point) in appendix D. Concentrations of only the detected target volatile components are given in appendix E. Estimated concentrations (based on a relative response factor of 1 to the internal standard, fluorobenzene) of nontarget volatile components (semiquantitative) are given in appendix F. Ratios of concentrations of detected target components (in order of increasing boiling point) to the major volatile component, 1,2,4-trimethylbenzene (1,2,4-TMB), are given in approximate east-to-west order in table 4. Ratios of selected nontarget components to 1,2,4-TMB are given in table 5 for comparison. Ratios of selected nontarget components related to fuel characterization are given in table 6.

Semivolatile Components

The TIC from the semivolatile analysis of the RR40 reference-fuel sample is shown in figure 11 along with relevant chemical component EI chromatograms. TICs from the semivolatile analyses of the LNAPL samples, selected reference-fuel samples, and a Restek standard, RDF2-UN, are given in appendix G along with EI chromatograms characteristic of

Table 4. Ratios of concentrations of detected target components to 1,2,4-trimethylbenzene in light nonaqueous phase liquid and selected reference-fuel samples

[Based on analyses by U.S. Geological Survey; --, no data]

Sample identifier	Benzene	Toluene	Ethylbenzene	*m* & *p*-Xylene	*o*-Xylene	Styrene	Isopropylbenzene	*n*-Propylbenzene	1,3,5-Trimethylbenzene	2-Ethyltoluene	1,2,4-Trimethylbenzene	*sec*-Butylbenzene	*p*-Isopropyltoluene	1,2,3-Trimethylbenzene	*n*-Butylbenzene	1,2,3,5-Tetramethylbenzene	1,2,3,4-Tetramethylbenzene	Naphthalene
Light nonaqueous phase liquid samples																		
MW2R	0.005	--	0.09	0.11	0.01	--	0.02	0.11	0.14	0.08	1	0.04	0.04	0.42	0.15	0.51	0.34	0.59
MW17	0.009	0.002	0.12	0.27	0.03	--	0.03	0.14	0.25	0.13	1	0.05	0.04	0.49	0.17	0.50	0.35	0.70
PZ2	0.006	--	0.10	0.36	0.10	--	0.03	0.13	0.28	0.21	1	0.05	0.04	0.44	0.15	0.44	0.30	0.65
P5	0.008	--	0.12	0.37	0.09	--	0.03	0.13	0.31	0.18	1	0.06	0.05	0.33	0.18	0.58	0.40	0.72
P1R	0.005	--	0.09	0.35	0.08	--	0.02	0.10	0.28	0.15	1	0.04	0.03	0.37	0.14	0.50	0.33	0.66
EF1	0.004	--	0.08	0.10	0.02	--	0.04	0.13	0.23	0.23	1	0.08	0.06	0.32	0.22	0.81	0.48	0.92
PL4	0.007	0.003	0.08	0.14	0.03	--	0.02	0.08	0.23	0.15	1	0.03	0.02	0.32	0.12	0.46	0.26	0.69
RH1		--	0.06	0.08	--	--	0.02	0.09		0.02	1	0.06	0.06	0.54	0.16	0.76	0.59	0.82
WF11	0.006	--	0.04	0.09	--	--	0.03	0.11	0.32	0.21	1	0.06	0.05	0.14	0.19	0.73	0.42	0.92
WF11A	0.006	--	0.04	0.10	--	--	0.03	0.11	0.36	0.23	1	0.06	0.06	0.16	0.21	0.79	0.51	0.96
EW2	0.009	0.005	0.12	0.45	0.19	--	0.03	0.11	0.25	0.17	1	0.04	0.03	0.40	0.13	0.41	0.28	0.64
FR2	0.006	0.004	0.10	0.42	0.14	--	0.03	0.11	0.28	0.16	1	0.04	0.04	0.44	0.15	0.46	0.31	0.54
PZ6	0.003	0.002	0.07	0.30	0.15	--	0.02	0.11	0.30	0.21	1	0.05	0.04	0.43	0.16	0.47	0.31	0.66
MW44	0.003	0.004	0.09	0.36	0.18	--	0.03	0.14	0.31	0.21	1	0.05	0.05	0.46	0.18	0.47	0.35	0.67
MW43	0.002	--	0.08	0.29	0.06	--	0.03	0.13	0.27	0.19	1	0.04	0.04	0.37	0.15	0.40	0.26	0.60
MW45	0.008	--	0.11	0.38	--	--	0.03	0.14	0.29	0.04	1	0.05	0.05	0.45	0.18	0.48	0.35	0.71
MW45P	0.008	--	0.10	0.35	--	--	0.03	0.13	0.27	0.03	1	0.05	0.04	0.41	0.17	0.43	0.29	0.64
MW45B	0.007	--	0.10	0.34	--	--	0.03	0.12	0.25	0.03	1	0.04	0.04	0.40	0.13	0.38	0.27	0.60
FR4	--	--	--	0.03	--	--			0.26	0.25	1	0.05	0.09	0.60		1.53	1.12	0.31
MW8	0.036	0.004	0.13	0.16	0.06	--	0.02	0.11	0.19	0.22	1	0.03	0.03	0.28	0.11	0.40	0.26	0.52
MW7R	0.002	0.002	0.07	0.12	0.02	--	0.03	0.12	0.28	0.19	1	0.06	0.05	0.37	0.18	0.51	0.34	0.72
Reference-fuel samples																		
RR40	0.024	0.239	0.16	0.61	0.29	--	0.03	0.13	0.24	0.17	1	0.04	0.04	0.39	0.13	0.54	0.61	1.47
HS#2	0.019	0.232	0.17	0.57	0.28	--	0.05	0.16	0.26	0.18	1	0.07	0.06	0.45	0.17	0.39	0.61	0.71
ULR	1.030	3.874	0.68	2.53	0.94	0.04	0.06	0.17	0.28	0.20	1	0.02	0.01	0.23	0.05	0.14	0.06	0.16

Table 5. Ratios of selected nontarget components to 1,2,4-trimethylbenzene in light nonaqueous phase liquid and selected reference-fuel samples

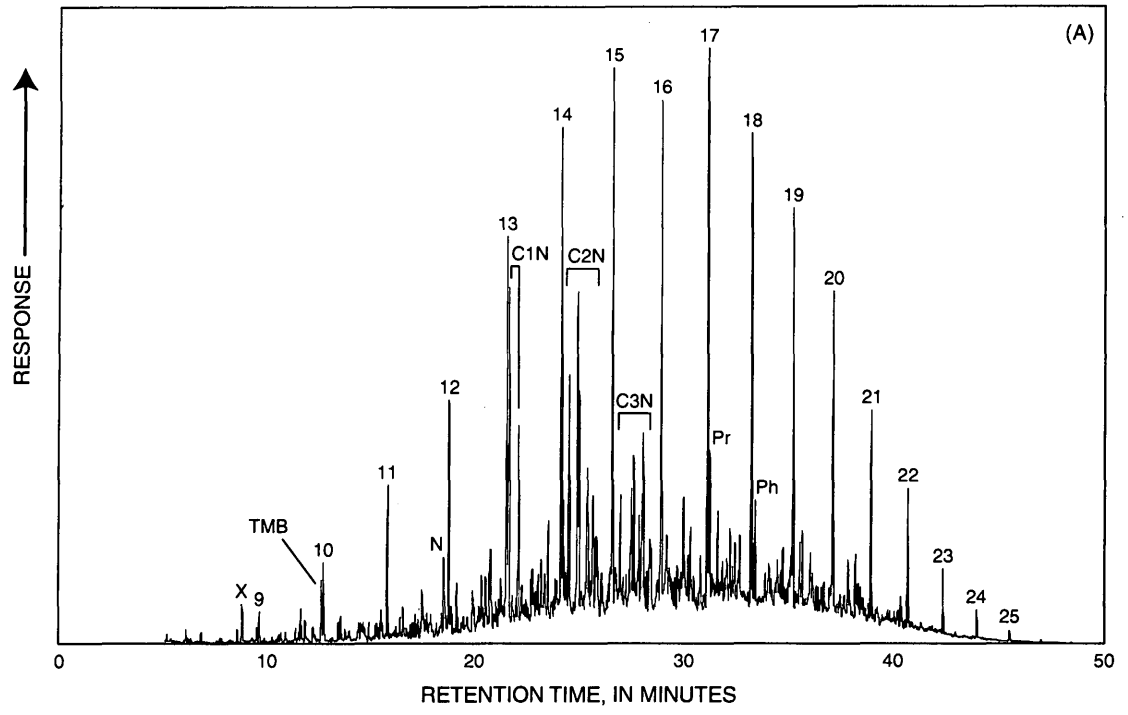
[Based on analyses by U.S. Geological Survey; nc, not calculable]

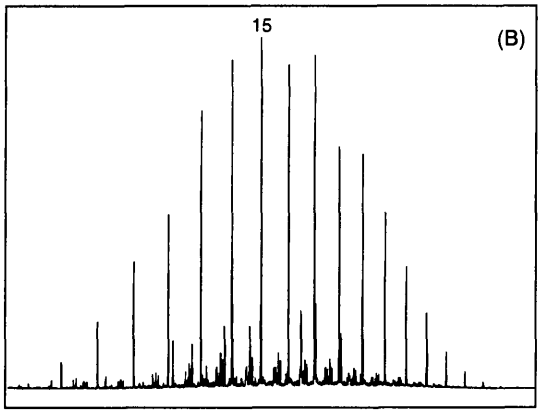
Sample identifier	2-Methylheptane	*n*-Undecane	1,2,3,4-Tetrahydro-naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	3-Methyloctane	Methylcyclohexane	1,1,3-Trimethylcyclohexane
Light nonaqueous phase liquid samples								
MW2R	0.06	0.87	0.07	0.22	0.17	0.10	0.08	0.05
MW17	0.08	nc	0.07	0.24	0.17	0.12	0.12	0.06
PZ2	0.03	0.94	0.08	0.24	0.18	0.05	0.06	0.03
P5	0.10	2.30	0.07	0.32	0.16	0.15	0.16	0.07
P1R	0.03	1.66	0.08	0.26	0.14	0.04	0.05	0.03
EF1	0.04	2.51	0.11	0.44	0.27	0.13	0.10	0.08
PL4	0.02	1.41	0.05	0.26	0.14	0.03	0.05	nc
RH1	0.04	nc	0.11	0.45	0.39	0.11	0.06	0.06
WF11	0.08	2.60	0.09	0.53	0.24	0.12	0.11	0.07
WF11A	0	2.80	0.11	0.49	0.24	0.13	0.14	0.08
EW2	0.04	1.45	0.07	0.23	0.13	0.04	0.06	0.03
FR2	0.09	nc	0.05	0.22	0.14	0.11	0.14	0.06
PZ6	0.03	2.62	0.07	0.28	0.20	0.12	0.08	0.05
MW44	0.06	2.00	0.07	0.42	0.18	0.11	0.07	0.06
MW43	0.05	1.66	0.07	0.20	0.15	0.10	0.06	0.04
MW45	0.04	0.95	0.07	0.26	0.19	0.13	0.10	0.06
MW45P	0.07	0.85	0.06	0.22	0.17	0.12	0.10	0.08
MW45B	0.02	0.78	0.07	0.21	0.14	0.03	0.05	0.02
FR4	nc	5.44	0.20	0.73	0.80	0.11	nc	nc
MW8	0.02	1.06	0.04	0.13	0.10	0.07	0.10	0.02
MW7R	0.03	2.11	0.07	0.24	0.19	0.12	0.09	0.06
Reference-fuel samples								
RR40	0.06	2.72	0.14	1.33	0.84	0.13	0.14	0.12
HS#2	0.09	4.15	0.12	0.51	0.28	0.25	0.24	0.26
ULR	0.05	0.25	0.004	0.01	0	0.04	0.08	nc

Table 6. Ratios of selected nontarget components related to fuel characterization in light nonaqueous phase liquid and selected reference-fuel samples

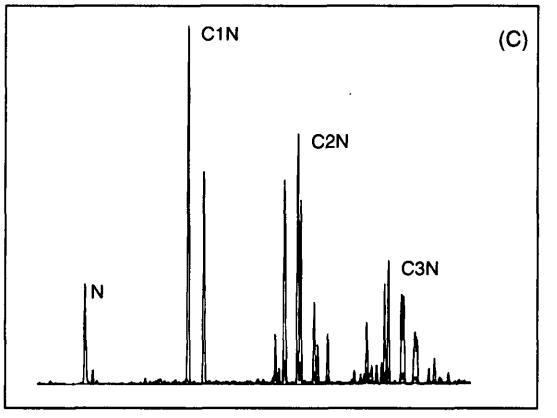
[Based on analyses by U.S. Geological Survey; MC_7, 2-methylheptane; C_{11}, *n*-undecane; THN, 1,2,3,4-tetrahydronaphthalene; 2MN, 2-methylnaphthalene; MC_8, 3-methyloctane; MCH, methylcyclohexane; TMCH, 1,1,3-trimethylcyclohexane; --, no data; E, east; SE, southeast; W, west]

Sample identifier	Location or place from which sample was obtained	MC_7/C_{11}	C_{11}/THN	THN/2MN	MC_7/THN	MC_7/MC_8	C_{11}/MC_8	C_{11}/MCH	THN/MCH	2MN/MCH	MC_8/MCH	MC_7/TMCH	C_{11}/TMCH	THN/TMCH	2MN/TMCH	MC_8/TMCH
Light nonaqueous phase liquid samples																
MW2R	Railway yard	0.07	13	0.3	0.9	0.6	9	11	0.9	2.8	1.3	1.1	17	1.3	4.3	1.9
MW17	Railway yard	--	--	0.3	1.1	0.7	--	0	0.6	2.1	1.1	1.4	0	1.2	4.1	2.1
PZ2	Railway yard	0.03	12	0.3	0.4	0.6	18	17	1.4	4.3	0.9	1.3	37	3.0	9.4	2.1
P5	Railway yard	0.04	32	0.2	1.3	0.7	15	15	0.5	2.0	0.9	1.3	31	1.0	4.3	2.0
P1R	Railway yard	0.02	22	0.3	0.4	0.9	45	37	1.7	5.9	0.8	1.3	66	3.1	10.6	1.5
EF1	Railway yard-E	0.01	22	0.3	0.3	0.3	19	24	1.1	4.2	1.2	0.5	32	1.4	5.6	1.7
PL4	Railway yard-SE	0.02	29	0.2	0.5	0.9	51	28	1.0	5.2	0.6	--	--	--	--	--
RH1	Railway yard-SE	--	--	0.3	0.4	0.4	--	0	1.8	7.1	1.8	0.7	0	1.9	7.5	1.9
WF11	Railway yard-W	0.03	29	0.2	0.8	0.6	22	24	0.8	4.8	1.1	1.1	38	1.3	7.8	1.8
WF11A	Railway yard-W	--	26	0.2	--	--	21	21	0.8	3.6	1.0	0	37	1.4	6.5	1.8
EW2	Railway yard	0.03	20	0.3	0.5	0.9	35	22	1.1	3.5	0.6	1.5	57	2.8	8.8	1.6
FR2	Railway yard	--	--	0.2	1.6	0.8		0	0.4	1.6	0.8	1.4	0	0.9	3.4	1.8
PZ6	North of Main Street	0.01	36	0.3	0.4	0.2	21	34	0.9	3.7	1.6	0.5	48	1.3	5.1	2.3
MW44	North of Main Street	0.03	27	0.2	0.8	0.5	18	29	1.1	6.1	1.6	1.1	36	1.4	7.6	2.0
MW43	North of Main Street	0.03	25	0.3	0.8	0.5	16	26	1.0	3.2	1.6	1.2	38	1.5	4.7	2.4
MW45	North of Main Street	0.04	14	0.3	0.6	0.3	7	9	0.7	2.5	1.3	0.7	15	1.1	4.1	2.1
MW45P	North of Main Street	0.08	13	0.3	1.1	0.6	7	8	0.6	2.2	1.1	0.9	11	0.8	2.9	1.5
MW45B	North of Main Street	0.03	11	0.3	0.3	0.7	23	17	1.5	4.7	0.7	1.2	39	3.5	10.9	1.7
FR4	North of Main Street	--	27	0.3	--	--	50	--	--	--	--	--	--	--	--	--
MW8	North of Main Street	0.02	27	0.3	0.6	0.4	16	11	0.4	1.3	0.7	1.1	47	1.8	5.6	3.0
MW7R	North of Main Street	0.01	28	0.3	0.4	0.2	17	25	0.9	2.8	1.4	0.5	33	1.2	3.8	1.9
Reference-fuel samples																
RR40	Refinery (current diesel fuel)	0.02	20	0.1	0.4	0.4	20	20	1.0	9.8	1.0	0.5	23	1.2	11.2	1.1
HS#2	Refinery (broader refinery-cut fuel)	0.02	33	0.2	0.7	0.3	16	18	0.5	2.2	1.1	0.3	16	0.5	2.0	1.0
ULR	Refinery (unleaded regular gasoline)	0.19	71	0.7	13.8	1.4	7	3	0	0.1	0.4	--	--	--	--	--

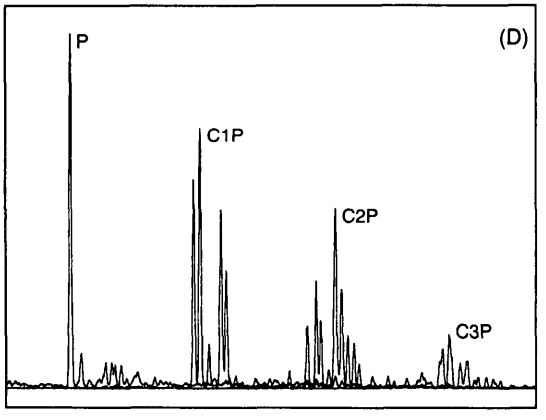




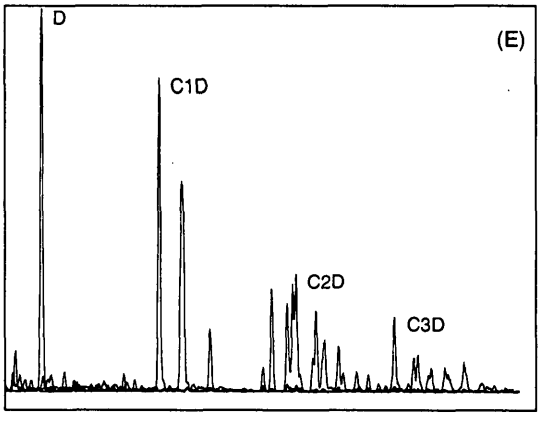
n-ALKANES AND ISOPRENOIDS: m/z 57



NAPHTHALENES (N): m/z 128, 142, 156, 170



PHENANTHRENES (P): m/z 178, 192, 206, 220



DIBENZOTHIOPHENES (D): m/z 184, 198, 212, 226

Figure 11. Chemical components in RR40 reference-fuel sample: (A) Total ion chromatogram (numbers indicate *n*-alkane homologs; TMB, 1,2,4-trimethylbenzene; Pr, pristane; Ph, phytane); (B) extracted ion chromatograms for m/z 57 (Cmax shown); (C), (D), and (E) extracted ion chromatograms for polycyclic aromatic hydrocarbon families with C1 to C3 alkylation.

cyclohexanes for m/z 83. EI chromatograms for alkanes for m/z 57 are shown in figure 12. Concentrations of PAHs in the LNAPL and reference-fuel samples and in the unweathered Restek standard, RDF2-UN, are given in appendix H, and bar graphs of PAH families are given in appendix I. Geochemical parameters from the semivolatile components are given in table 7.

Stable Carbon Isotopes

The LNAPL and reference-fuel samples were analyzed as whole oils for $\delta^{13}C$. The $\delta^{13}C$ ratio data are given in appendix J, and averaged, rounded values are given in table 7.

Dyes

Response by a compound to either positive or negative ionization is very compound dependent. The Unisol Red B50 additive, which contains a 2-naphthalenol phenyl azo alkyl derivative solvent dye, produced a strong negative ion at m/z 339, implying a molecular weight of 340, as shown in figure 13A. The positive ion spectrum (fig. 13B) was much more complex than the negative spectrum and was dominated by hydrocarbons and sample artifacts. Under the same ionization conditions, samples containing the Unisol Red B50 additive would be expected to produce ions characteristic of the compound. Therefore, the LNAPL and reference-fuel samples were analyzed for dye components. The concentration in each sample was based on the negative deprotonated molecular ion response of the Unisol Red B50 dye. Results of the analyses are given in table 8.

Initial full-scan analysis of the LNAPL samples in the positive mode produced peaks at nearly every mass because the hydrocarbons present ionized to produce a protonated molecular ion, a sodium adduct of the molecular ion, or both. The positive mode was, therefore, not applicable for specific compound analysis. The negative full-scan mass spectra from each sample are given in appendix K. The spectra are given numerically in table 9, with the most intense ions normalized to 100-percent intensity.

Degradation Analysis

The composition of a hydrocarbon oil product released into the environment begins to change almost immediately because of numerous biochemical and physical weathering processes (Kaplan and others, 1997). Physical weathering can include evaporation, water washing, or oxidation, and biochemical processes primarily involve microbial biodegradation (Hunt, 1996). Weathering, in general, removes the smaller, more volatile or more water soluble components. Microbial degradation removes components in a stepwise progression of chemical classes that is well documented in literature (for example, Kaplan and others, 1997). Straight-chain (*n*-) alkanes, the dominant series of compounds in diesel fuel, are preferentially degraded first. Branched-chain alkanes, such as the ubiquitous isoprenoid family, and cyclic alkanes, such as the *n*-alkylated cyclohexane homologous series, are more refractory but next in the degradation succession. PAHs are removed sequentially in the order of increasing numbers of aromatic rings and alkyl substituents. For example, the two-ringed naphthalenes degrade faster than the three-ringed phenanthrenes or dibenzothiophenes, and all of these PAHs with their alkylated derivatives degrade in the order C0>C1>C2>C3.

When a hydrocarbon body is analyzed, a profile of the components being degraded gives information on the state of weathering. In contrast, the components not yet degraded, whose profiles thus still hold the chemical fingerprint of the original hydrocarbon source, can be used for source correlations. Ratios using selected alkane and alkyl naphthalene, phenanthrene, and dibenzothiophene parameters commonly are used for these purposes (Kaplan and others, 1997; Bence and others, 1996).

The LNAPL samples from the various sites in this study appear, based on GC/MS analysis, to be closely related petroleum entities that are, however, at varying stages of degradation, probably related to their residence time in the aquifer. As discussed earlier, chronic spillage of diesel fuel into the subsurface is thought to have occurred from 1953 until 1991. Other contributions, if any, to the contaminant body are of unknown dates. The LNAPL in the samples is at a relatively early stage of degradation, impacting primarily the *n*-alkanes. The EI chromatograms for the alkanes (m/z 57; fig. 12) show the varying stages of degradation in approximate order from freshest product to most-degraded (oldest) product. The

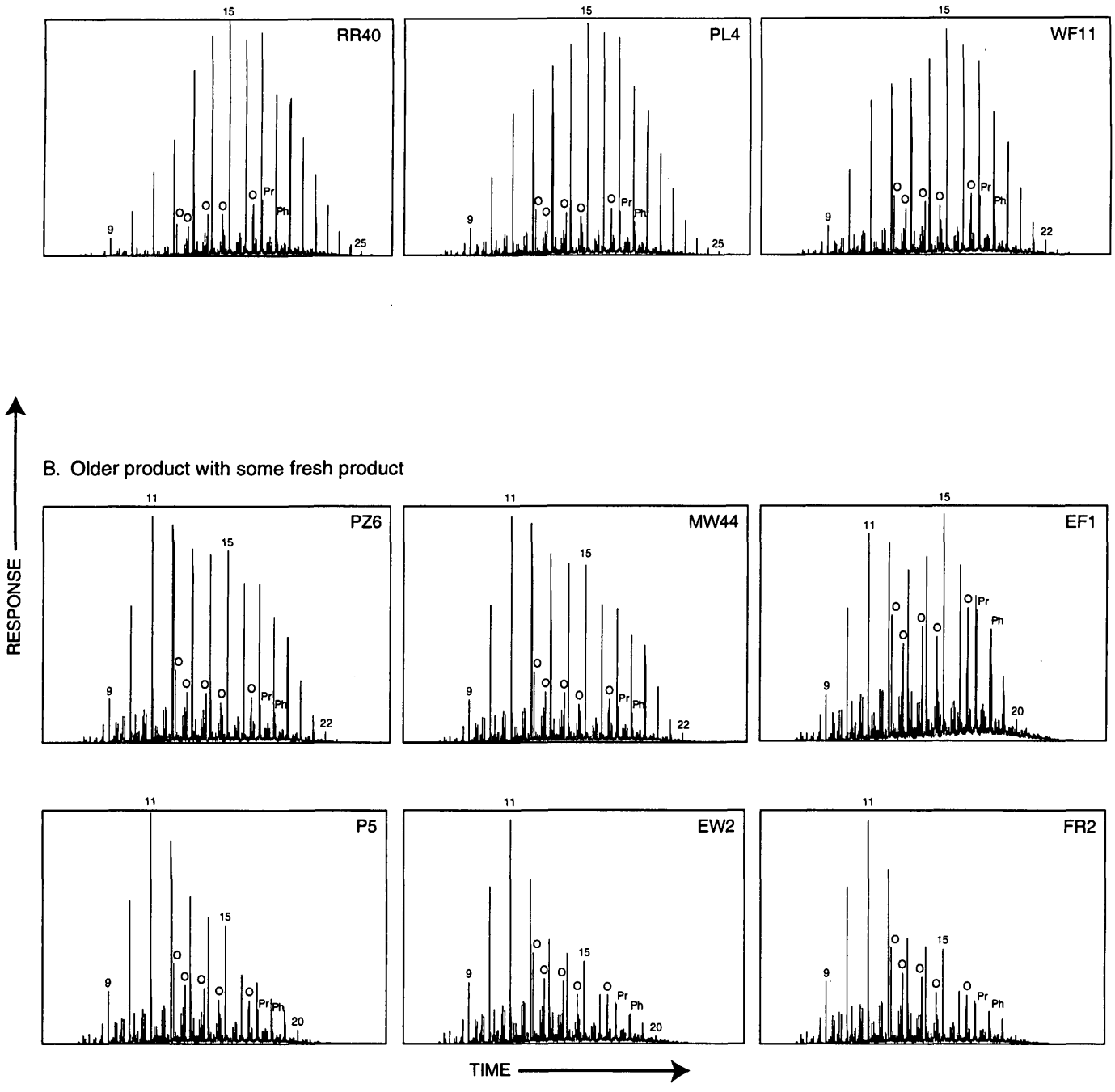


Figure 12. Extracted ion chromatograms for m/z 57, alkanes and isoprenoids, in approximate sample degradation order. [Carbon numbers of selected *n*-alkane homologs shown; Pr, Ph, and o are pristane, phytane, and other (C_{13} to C_{16} and C_{18}) isoprenoids.]

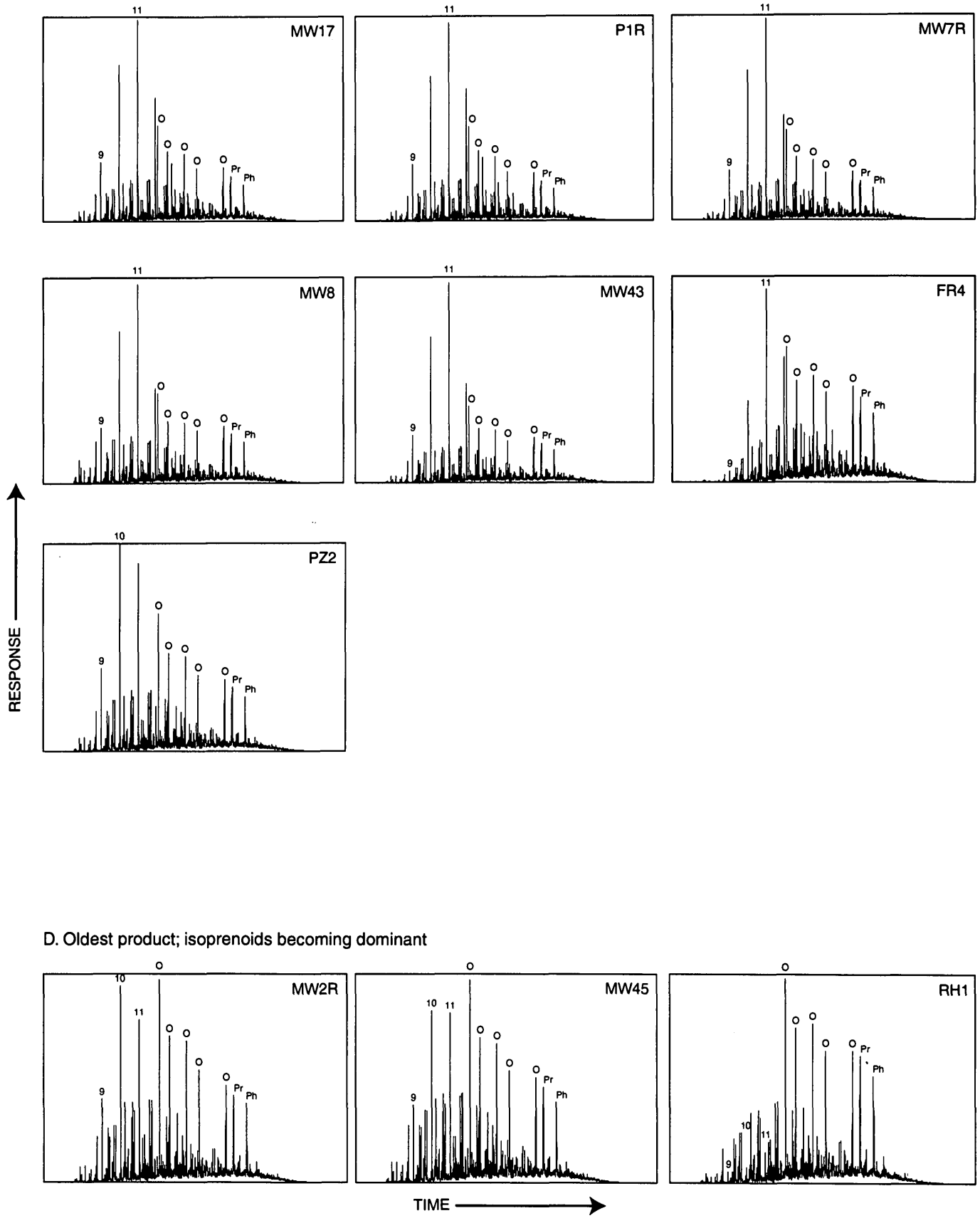


Figure 12. Extracted ion chromatograms for m/z 57, alkanes and isoprenoids, in approximate sample degradation order--continued. [Carbon numbers of selected *n*-alkane homologs shown; Pr, Ph, and o are pristane, phytane, and other (C_{13} to C_{16} and C_{18}) isoprenoids.]

Table 7. Geochemical parameters for light nonaqueous phase liquid samples, reference-fuel samples, and Restek standards

[$\delta^{13}C$ ratio data from Zymax Forensics, San Luis Obispo, California; remaining values based on analyses by U.S. Geological Survey; $\delta^{13}C$, stable carbon isotopes; ‰, per mil; Pr, pristane; Ph, phytane; *n*-C_{17}, normal alkane, C_{17}; *n*-Cmax, *n*-alkane (#) or isoprenoid (ipr) suite maximum; C1D, methyl dibenzothiophenes; C1P, methyl phenanthrenes; C2D, dimethyl dibenzothiophenes; C2P, dimethyl phenanthrenes; C1N, methyl naphthalenes; C2N, dimethyl naphthalenes; 1,2,4-TMB, 1,2,4-trimethylbenzene (dominant C3-benzene); 2MN, 2-methylnaphthalene; ipr, suite of C_{13}, C_{14}, C_{15}, C_{16}, C_{18}, C_{19} (pristane), and C_{20} (phytane) isoprenoids; >, greater than; nc, not calculable, --, no data]

Sample identifier	Location or place from which sample was obtained	$\delta^{13}C$ (‰)	Pr/Ph	*n*-C_{17}/Pr	*n*-Cmax	C1D/C1P	C2D/C2P	C1N/C2N	1,2,4-TMB/2MN
			Light nonaqueous phase liquid samples						
MW2R	Railway yard	-28.6	1.2	0	10, ipr	0.80	0.90	0.68	0.70
MW17	Railway yard	-28.7	1.3	0	11>ipr	0.79	0.86	0.73	0.70
PZ2	Railway yard	-28.6	1.2	0	10>ipr	0.75	0.83	0.73	0.73
P5	Railway yard	-28.8	1.2	1.5	11>15	0.81	0.90	0.73	0.61
P1R	Railway yard	-29.1	1.2	0.17	11>ipr>15	0.88	0.97	0.72	0.69
EF1	Railway yard-east	-29.2	1.2	0.91	15>12	0.82	0.92	0.65	0.51
PL4	Railway yard-southeast	-29.6	1.3	4.5	15,17	0.90	0.98	0.73	0.63
RH1	Railway yard-southeast	-28.5	1.3	0	ipr>>11	0.80	0.90	0.57	0.53
WF11	Railway yard-west	-29.0	1.3	3.0	15	0.84	0.92	0.66	0.50
WF11A	Railway yard-west	-29.0	1.3	2.9	15	0.84	0.92	0.66	0.49
EW2	Railway yard	-28.7	1.3	0.83	11>>15	0.82	0.89	0.74	0.62
FR2	Railway yard	-28.7	1.3	0.83	11>15	0.90	1.0	0.73	0.79
PZ6	North of Main Street	-28.6	1.2	3.6	11>15	0.74	0.81	0.73	0.69
MW44	North of Main Street	-28.7	1.2	3.3	11>15	0.75	0.81	0.73	0.65
MW43	North of Main Street	-28.4	1.2	0	11>ipr	0.75	0.82	0.73	0.76
MW45	North of Main Street	-28.4	1.3	0	ipr>10&11	0.75	0.81	0.74	0.70
MW45P	North of Main Street	-28.3	1.3	0	ipr>10&11	0.75	0.81	0.74	0.71
MW45B	North of Main Street	-28.3	1.2	0	ipr>10&11	0.75	0.83	0.74	0.71
FR4	North of Main Street	-28.3	1.2	0.21	11>ipr>15	0.74	0.83	0.38	0.27
MW8	North of Main Street	-28.3	1.2	0	11>ipr	0.75	0.80	0.67	0.98
MW7R	North of Main Street	-28.8	1.2	0	11>ipr	0.74	0.80	0.74	0.59
			Reference-fuel samples						
RR40	Refinery	-29.5	1.5	3.7	15,17	0.63	0.68	0.60	0.18
HS#2	Refinery	-29.4	1.4	4.1	13>11,17	0.63	0.68	0.64	0.47
ULR	Refinery	-29.5	nc	nc	8>>>11	0	0	3.2	8.6
COC	Refinery	-29.7	--	--	--	--	--	--	--
			Restek standards						
Diesel #2 (unweathered)	Restek Corporation	--	2.5	0.97	15	0.12	0.19	0.56	0.46
Diesel #2 (25-percent weathered)	Restek Corporation	--	2.5	0.96	15	0.12	0.19	0.46	0.03
Diesel #2 (50-percent weathered)	Restek Corporation	--	2.4	0.96	16	0.12	0.19	0.06	0
Diesel #2 (75-percent weathered)	Restek Corporation	--	1.9	0.91	18	0.12	0.19	0	0

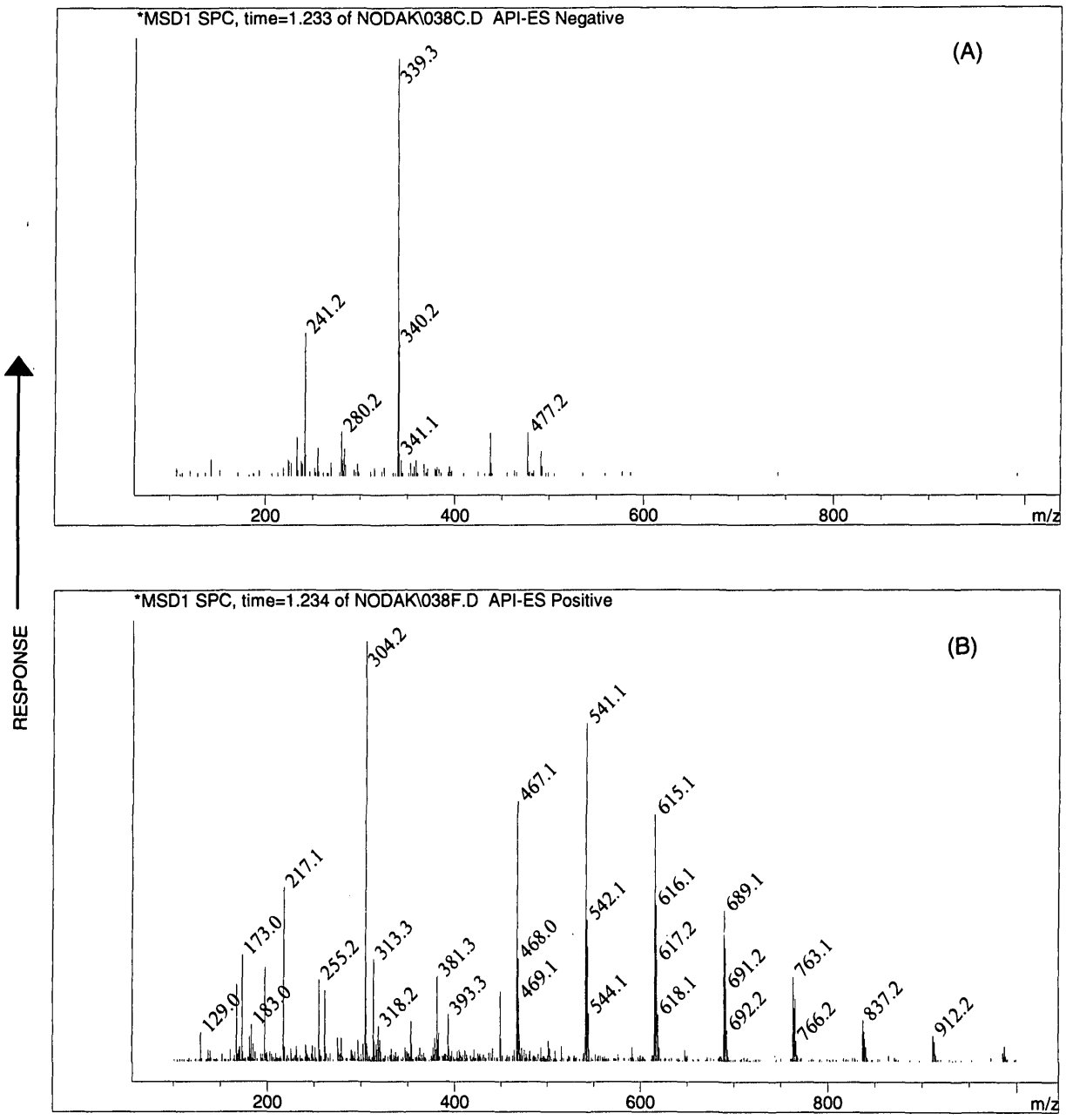


Figure 13. Electrospray ionization mass spectra of Unisol Red B50 additive in (A) negative and (B) positive modes. (m/z, mass-to-charge ratio.)

spatial distribution of the relative degradation is shown in figure 14. The *n*-alkane distributions range from (a) the full diesel suite with C_9 to C_{25} *n*-alkanes in a bell-shaped distribution with a Cmax at about C_{15} to (b) an intermediate state of depletion of long-carbon-chain (high boiling point; high molecular weight; right end of chromatogram) members and a residual narrow distribution of short-carbon-chain (low boiling point; low molecular weight; left end of chromatogram) members with a C_{10} or C_{11} maximum to (c) the complete loss of *n*-alkanes, leaving isoprenoids as the dominant aliphatic components. This alteration pattern of the depletion of longer-chain *n*-alkanes and the accompanying relative increase of shorter-chain *n*-alkanes matches the pattern reported for a diesel-fuel spill at a large western United States petroleum-operating facility (Stout and Lundegard, 1998). A similar pattern also has been observed within the oil body in a recent re-examination of the oil accumulation at the well-studied Bemidji crude-oil spill site (F. Hostettler, U.S. Geological Survey, unpub. data) where anaerobic biodegradation is known to occur (Bekins and others, in press). Overall, the degradation

Table 8. Concentrations of Unisol Red B50 dye in light nonaqueous phase liquid samples, selected reference-fuel samples, and additive samples

[Data from U.S. Geological Survey; relative standard deviation for eight replicates was 33 percent; samples were diluted in duplicate and each analyzed in duplicate; µg/L, micrograms per liter; ND, not detected]

Sample identifier	Average (µg/L)
Light nonaqueous phase liquid samples	
MW2R	52
MW17	16
PZ2	24
P5	36
P1R	16
EF1	33
PL4	1
RH1	44
WF11	28
WF11A	16
EW2	29
FR2	20
PZ6	14
MW44	15
MW43	20
MW45	33
MW45P	39
MW45B	30
FR4	45
MW8	23
MW7R	37
Reference-fuel samples	
RR40	53
HS#2	20
ULR	ND
Additive samples	
Nalco 5375A	ND
Stadis 450	ND
Para Flow 511	ND
DCI 6A	ND

process at Mandan is quite slow as shown by the dominantly fresh product from well PL4 near the pipeline spill. The product from that well probably was deposited as long ago as 1987 when pipeline leakage was observed and stopped (Roberts, 2001). Thus, the product probably has been in the subsurface for at least 14 years but is still relatively undegraded.

At many sites, alkane patterns that have several maxima are evident. Older, partly degraded fuel has a C_{10} or C_{11} maximum, whereas fresher fuel input has the C_{15} maximum, and a site where more than one maximum exists likely has experienced multiple episodic inputs of the same or closely related diesel fuels. The dominant maxima at each site are listed in table 7 along with the value for n-C_{17}/Pr, which relates to the age of the diesel fuel (age here refers to the length of time the diesel fuel has been in the subsurface environment). Values of about 3 to 4 indicate fresh diesel fuel is present, and

Table 9. Relative intensities of masses from negative electrospray ionization mass spectra for light nonaqueous phase liquid and selected reference-fuel samples

[Average of four analyses, normalized to 100-percent intensity; percent relative standard deviation is from eight replicate analyses of sample EW2; --, no data]

Sample identifier	Mass									
	107	121	166	180	194	195	208	209	222	236
Light nonaqueous phase liquid samples										
MW2R	--	--	13	63	100	18	55	17	28	--
MW17	--	--	13	65	100	16	70	13	25	--
PZ2	--	--	14	68	100	14	61	12	25	--
P5	--	--	13	60	100	14	69	13	24	10
P1R	--	--	17	67	100	13	68	13	28	--
EF1	--	--	--	39	96	15	100	15	57	29
PL4	--	--	13	58	100	15	77	13	34	12
RH1	--	--	--	46	100	19	99	20	50	16
WF11	--	--	--	50	100	13	92	13	48	15
WF11A	--	--	--	49	100	17	94	15	49	20
EW2	--	--	14	70	100	17	63	12	21	--
EW2	--	--	17	68	100	16	62	11	24	8
FR2	--	--	11	60	100	16	72	15	28	11
PZ6	--	--	14	67	100	13	73	11	28	10
MW44	--	--	14	65	100	18	52	28	26	--
MW43	--	--	13	62	100	13	62	12	25	--
MW45	--	--	15	65	100	15	65	12	25	--
MW45P	--	--	14	71	100	16	70	12	24	--
MW45B	--	--	15	67	100	15	72	11	27	--
FR4	--	--	--	--	38	--	93	17	100	45
MW8	--	--	12	66	100	18	65	16	27	19
MW7R	--	--	13	62	100	15	67	12	27	--
Reference-fuel samples										
RR40	--	--	--	52	100	15	79	16	30	11
HS#2	--	--	--	59	100	15	84	16	27	--
ULR	100	80	--	--	--	--	--	--	--	--
Percent relative standard deviation	--	--	18	7	0	6	4	6	18	--

values near zero indicate no fresh diesel fuel is present and the product that is present is at least 20 years old (Christensen and Larsen, 1993). Given the degradation beyond loss of n-C_{17} shown in the chromatograms, much of the LNAPL in the samples could be considerably older than 20 years. Wells EW2, FR2, MW44, P5, and PZ6, in particular, near the center of the LNAPL (fig. 14) show some recent input of diesel fuel in addition to the older, more degraded product. The remainder of the wells in the main body contain LNAPL that is made up only of older product.

When n-alkanes are severely or completely degraded, the distribution pattern of the more refractory CHs can be used to verify the presence of diesel fuel (Kaplan and others, 1997). The distribution of the CHs for the LNAPL and reference-fuel samples is given in appendix G in EI chromatograms for m/z 83. These chromatograms show the product at all sites contains CHs from C_7 to C_{22}, the same range as in the RR40 reference-fuel sample from the refinery. With advancing biodegradation within the samples, a lower-range maximum begins to appear, as with the n-alkanes, but the degradation has not caused the high-end CHs to be lost. This ubiquitous presence and the prominence of the diesel-fuel range CHs is further evidence the LNAPL samples primarily are degraded diesel fuel.

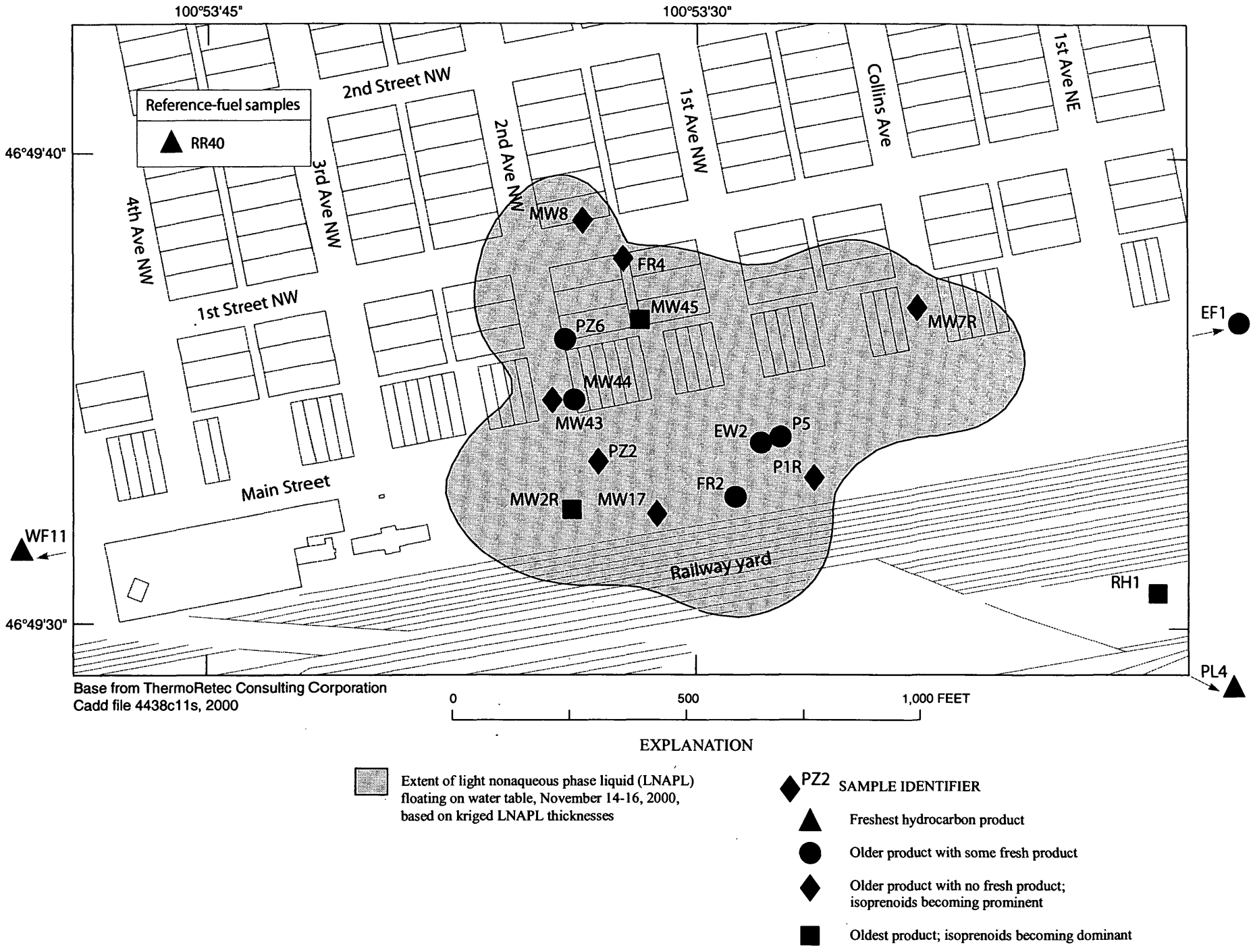


Figure 14. Relative degradation from *n*-alkane profiles.

Characterization Based on Correlations

To ascertain if the LNAPL at all sites is related, comparisons were made on the basis of stable carbon isotopes, several parameter ratios, PAHs and alkylated derivatives, and several analyses.

Stable Carbon Isotopes

The $\delta^{13}C$ values for the LNAPL and reference-fuel samples are given in table 7. The spatial distribution of the isotopes is shown in figure 15. If the railway used diesel fuel only from local sources when fueling at Mandan during 1953-91, the $\delta^{13}C$ values for the current and older diesel fuels were expected to be similar. The values in table 7 have a narrow range (-29.7 to -28.3‰, from lighter to heavier) but are not identical. A correlation does exist, however, with the approximate age of the diesel fuel in the subsurface. The reference-fuel samples and sample PL4 from the pipeline spill were the lightest. Samples from the east and west fueling areas (separate accumulations from the main LNAPL body and presumably containing more recently spilled diesel fuel) and sample P1R (from the main LNAPL body) were the next lightest. Samples from the remaining wells in the main LNAPL body and from well RH1 (another small disconnected accumulation in the Roundhouse area) were at the heavier end of the range. Stout and Lundegard (1998) have shown that systematic biodegradation severely impacting the *n*-alkanes results in a steady enrichment of the residue in ^{13}C, thus giving somewhat heavier $\delta^{13}C$ values. This relation was observed in the LNAPL samples. Therefore, the stable carbon isotope data are consistent with a common source for the hydrocarbons in the main LNAPL body.

Parameter Ratios

The values for the source parameters (Pr/Ph, C1D/C1P, C2D/C2P, and C1N/C2N) used in this study also are given in table 7. The Pr/Ph ratio was constant throughout the LNAPL samples but was slightly different for the RR40 and HS#2 reference-fuel samples. The ratios were very different from those for the unrelated Restek diesel-fuel standards. This result indicates the chemical fingerprint of the current diesel fuel is quite close but nonetheless slightly different from that of the older diesel fuel in the LNAPL body.

The ratios of refractory alkylated PAHs, namely C1D/C1P and C2D/C2P, confirm this result although they show some small areal differences within the main LNAPL body. The spatial distribution of the source-parameter values is shown in figure 16. The parameter values for the RR40 and HS#2 samples agree but were somewhat lower than the parameter values for samples from the main LNAPL body. Sample PL4 from the pipeline spill has been shown to contain the freshest spilled product, but the parameter values for that sample were at the opposite end of the range from those for the current diesel fuel. The parameter values for samples from the fueling areas and most of the railway yard were intermediate between those for the reference-fuel samples and sample PL4. The parameter values for samples from wells north of Main Street and from well PZ2 have a narrow range and were lower than those for samples from the other downtown wells but still were intermediate between the values for the current diesel fuel and those for sample PL4. Note again that a very significant difference exists between the parameter values for the LNAPL and reference-fuel samples and those for the Restek diesel-fuel standards analyzed for comparison (table 7).

The C1N/C2N ratio can have source and/or weathering implications, the latter depending on the stage of degradation of the product. The values for most of the LNAPL samples have a narrow range, 0.72 to 0.74, indicating the samples were very similar and the degradation progression has not reached the alkylated naphthalenes. Note that the values for the physically weathered Restek diesel-fuel standards rapidly decrease from 0.56 to 0, indicating that physical weathering has a substantial effect on this parameter. The LNAPL samples with values only slightly lower than 0.72 probably either have slight chemical-source-related differences or have undergone very mild weathering. The sample from well FR4 near the north edge of the main LNAPL body had a substantially lower value of 0.38, most likely indicating physical weathering in addition to biodegradation. Further evidence for this weathering is the TIC (appendix G) for that sample, which shows a loss of low-end components. The location of well FR4 near the north edge of the main body where the accumulation is relatively thin (figs. 9 and 10) increases the likelihood that physical weathering is causing this difference. The values of C1N/C2N for the RR40 and HS#2 samples differ slightly from each other, perhaps because of those samples being different refinery cuts, and again, were close but not identical to those for the LNAPL samples. All of this source correlation is consistent with an interpretation that the Mandan diesel products are closely related with minor chemical-fingerprint differences that likely reflect small changes in fuel composition over 50 years.

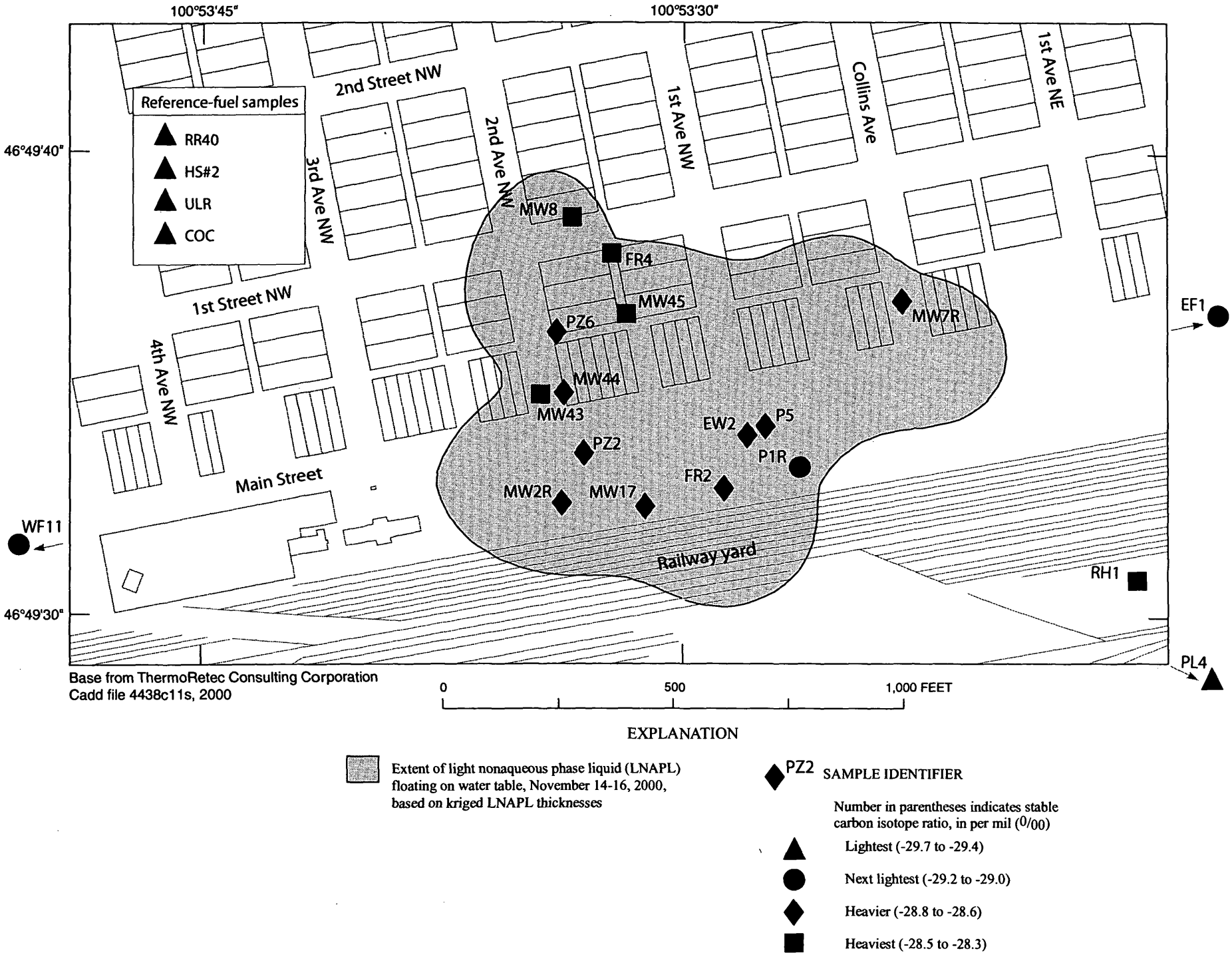


Figure 15. Stable carbon isotope distribution.

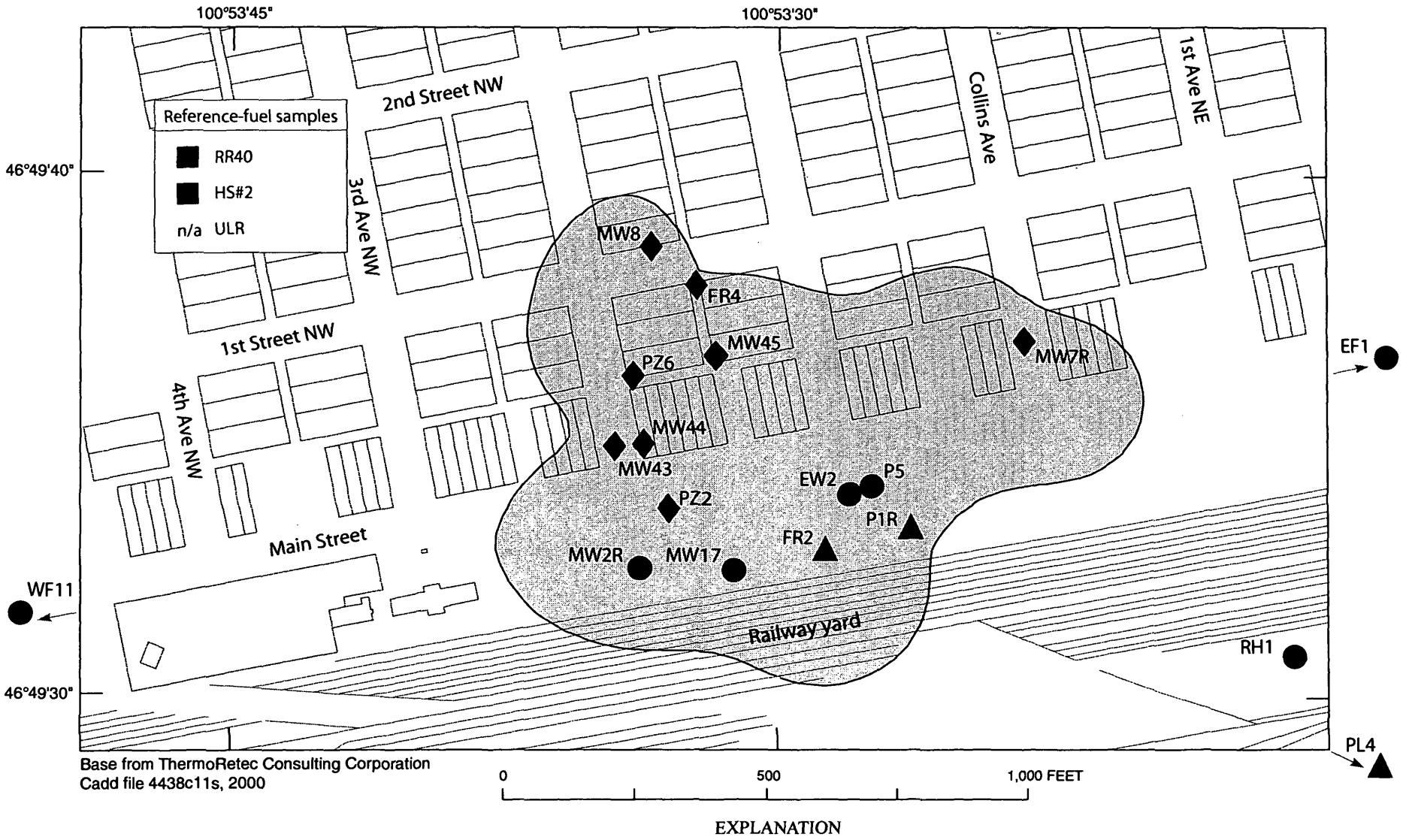


Figure 16. Source-parameter value distribution.

1,2,4-TMB (the dominant member of a suite of C3-benzenes) is a low-end component of diesel fuel. 1,2,4-TMB is present at substantially higher levels in lower-cut refinery fuels such as gasoline and kerosene. The 1,2,4-TMB/2MN ratio gives a relative value for the concentration of 1,2,4-TMB in comparison to 2-methylnaphthalene, a more refractory component of these fuels.

Diesel fuel, as used in railroad engines, commonly is amended with various additives to enhance performance or improve viscosity to prevent jelling in the winter. Some of these additives were enumerated previously, but another additive used in the past is EC5375A; this additive, as used at this railway location, contained mainly 1,2,4-TMB at 1 to 5 percent (Nalco/Exxon Energy Chemicals, 1997). Diesel fuel also commonly is mixed, just before loading, with lower-cut refinery products, especially kerosene, which also can be a source of enhanced 1,2,4-TMB. Use of any of these additives in the Mandan environment probably has varied seasonally and temporally, thus causing some variation in the chemical makeup of the diesel products and impacting the 1,2,4-TMB/2MN ratio. 1,2,4-TMB was present at varying levels in the LNAPL samples, and the range for the ratio is broader than the ranges for the source ratios discussed earlier that are not impacted by variable adulteration. However, distinct trends do occur in the data (table 7, fig. 17).

The value for 1,2,4-TMB/2MN was low for the RR40 sample, which should be free of additives. The value also was low for sample FR4, which probably was affected by weathering as previously discussed. The value was significantly higher for most other samples, including those from the fueling areas and from well PL4. Medium-low values occurred in samples from the east and west fueling areas, and medium values occurred in most samples from the main LNAPL body (fig. 17). Sample MW8 had a somewhat higher value, and the ULR reference-fuel sample, as expected, had a substantially higher value. The ubiquity of 1,2,4-TMB throughout the sample set, especially the relatively uniform value of the ratio in the main LNAPL body, supports its being an intrinsic part of similarly amended diesel-fuel input rather than being contributed by a separate contaminant source. The slightly higher value for sample MW8 suggests a possible trace of gasoline input.

Polycyclic Aromatic Hydrocarbons and Alkylated Derivatives

Bar graphs as graphic representations of PAH families [C0 (parent), C1, C2, and C3 for naphthalene, phenanthrene, and dibenzothiophene] commonly are used (Kaplan and others, 1997) to compare oil samples. Bar graphs for the LNAPL samples, the RR40 and HS#2 reference-fuel samples, and the Restek diesel-fuel standard, RDF2-UN, are given in appendix I. The patterns for the LNAPL samples and the RR40 and HS#2 samples are noticeably consistent, but the pattern for the Restek standard is noticeably different, especially for the phenanthrene and dibenzothiophene concentrations. Sample FR4, again, shows a pattern of slight loss of low-end components (naphthalenes), consistent with physical weathering, but the overall pattern fits with those of the other LNAPL samples. This result is additional strong evidence for a very similar or common source for the LNAPL samples and the current diesel fuel.

Volatile Analysis

Volatile analysis focuses on the compounds in the low range of the boiling-point spectrum. The presence of volatile components related to gasoline would be indicated by this analysis. General volatile content of the reference-fuel samples was typical of their respective types (appendix B). Generally, the RR40 and HS#2 reference-fuel samples had far fewer volatile components than the ULR reference-fuel sample.

In mass chromatograms for m/z 57, characteristic of alkanes (Philp, 1985), the RR40 sample shows peaks from *n*-C_8 through *n*-C_{14} in a bell-shaped curve maximizing at *n*-C_{10} and *n*-C_{11} (appendix C). The chromatogram for the HS#2 sample was similar. In contrast, the chromatogram for the ULR sample shows alkane peaks including *n*-C_5 through *n*-C_{13} with a primary maximum at *n*-C_6 and a lower maximum at *n*-C_{11}. None of the LNAPL samples contained a C_6 maximum, and only three samples--MW8, MW45, and MW45P--contained any traces of C_6. Most LNAPL samples maximized at *n*-C_{10}. Because the range of alkanes is limited within volatile analysis, results given in the semivolatile data, which show a more complete range, are more comprehensive.

Hydrocarbons were the only compounds detected in the target analysis which searches for a wide variety of selected compounds (appendix D). Except for styrene, which was detected in the ULR sample, the components detected in the RR40, HS#2, and ULR samples were the same; however, the components were detected in very different relative amounts,

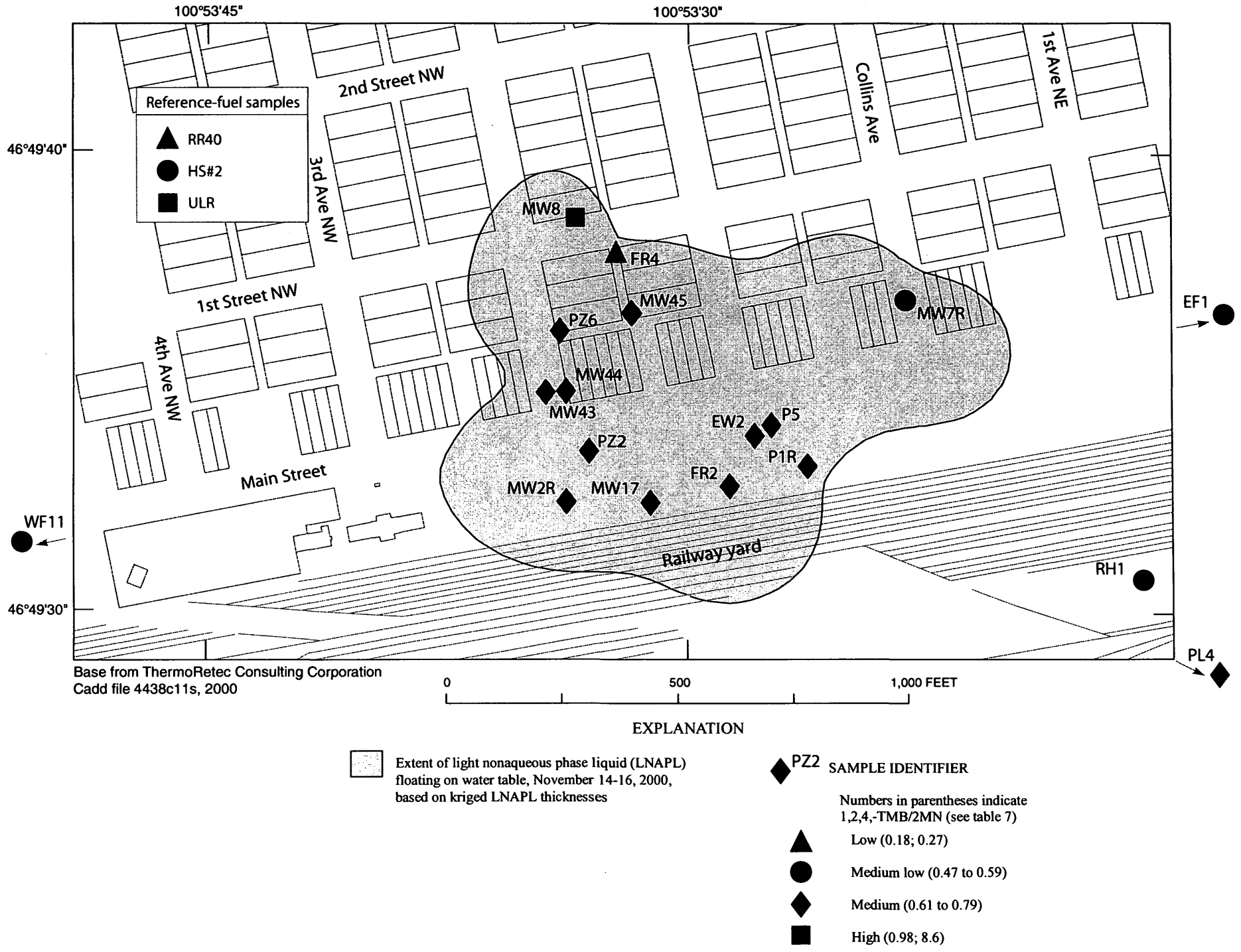


Figure 17. Additive indicator distribution.

with low boiling point components dominant in the ULR sample and higher boiling point components in the RR40 and HS#2 samples. Solvents such as diethylether, acetone, methylene chloride, methyl-t-butyl ether (MTBE), ethyl-t-butyl ether (ETBE), and t-amyl-methyl ether (TAME) were not detected in any LNAPL samples. Halogenated hydrocarbons such as perchloroethylene (tetrachloroethylene) and 1,1,2-trichloro-1,2,2-trifluoroethane associated with drycleaning (Occupational Safety and Health Administration, 2001) also were not detected.

The different sample-handling methods described previously for samples WF11 and WF11A and MW45, MW45B, and MW45P would have the greatest effect on the most volatile components such as benzene and toluene. However, the ratio of benzene to the most dominant component in the mixture, 1,2,4-TMB, was consistent in these two groups of samples (table 4). Therefore, differences in volatile component concentrations due to differences in sample-handling methods were minimal.

Ratios of the concentrations of the detected target components to the dominant component, 1,2,4-TMB, are given in table 4. The ratios for the ULR sample relative to those for the RR40 and HS#2 samples reflect the characteristics of gasoline in contrast to diesel fuel; the gasoline has greater amounts of the more volatile components (left side of table) and lesser amounts of the higher boiling point components (right side of table). The ratios of benzene to 1,2,4-TMB for the RR40 and HS#2 samples were 0.024 and 0.019, respectively, indicating that benzene was a minor component compared to 1,2,4-TMB. In the ULR sample, however, the ratio was greater than 1, indicating the concentration of benzene was approximately equal to that of 1,2,4-TMB. The ratios for all but one of the LNAPL samples were even lower than those for the RR40 and HS#2 samples, reflecting some loss of benzene through either water washing, volatilization, or biodegradation (Kaplan and others, 1996). However, sample MW8 had a slightly elevated ratio compared to the RR40 and HS#2 samples and the remaining LNAPL samples, again suggesting a possible trace of gasoline components in this sample.

As shown by the ULR sample (table 4), BTEX components are dominant in gasoline. Generally, the ratios of the BTEX components for the RR40 and HS#2 samples were quite different from the ratios for the ULR sample (table 4). The ratios for the ULR sample were much higher than those for the RR40 and HS#2 samples. Values for the LNAPL samples were even lower than those for the reference-fuel samples. Again, these losses may be due to water washing, volatilization, or degradation (Kaplan and others, 1996). None of the BTEX components in the LNAPL samples were present at levels even close to those in the ULR sample.

Styrene, a unique component of the ULR sample, was not detected in the LNAPL samples or the RR40 and HS#2 samples. However, styrene is one of the least stable components in gasoline mixtures. Therefore, its absence in the LNAPL samples is not confirmatory for lack of gasoline presence.

For the compounds with higher boiling points than 1,2,4-TMB, the ratios for the RR40 and HS#2 samples were greater than those for the ULR sample. Although some natural variability occurred in the data, the ratios for the LNAPL samples generally were similar to those for the RR40 and HS#2 samples.

Ratios of selected nontarget components to 1,2,4-TMB were greater for the RR40 and HS#2 samples than for the ULR samples (table 5), and the differences sometimes were appreciable. The ratios for undecane, n-C_{11}, a degradation-vulnerable alkane, varied in the LNAPL samples but were not as low as the ratio for the ULR sample. This trend was true for most of the LNAPL samples. For several components, sample MW8 had the lowest ratio except for the ULR sample. Several of the components were not detected in sample FR4. Although some natural variability of the data occurred, the ratios for the LNAPL samples resembled those for the RR40 and HS#2 samples, not those for the ULR sample.

Ratios of selected nontarget components are given in table 6 to enable a comparison between the LNAPL and reference-fuel samples. Due to differences between gasoline and diesel fuel, few nontarget components were present in both fuel types. The ratios for the RR40 and HS#2 samples were very different from those for the ULR sample. Generally, the ratios for the LNAPL samples were similar to those for the RR40 and HS#2 samples.

The isooctane/methylcyclohexane (IsoC8/MCH) ratio is considered by Kaplan and others (1996) to be a characteristic gasoline ratio relating to octane rating. Isooctane in gasoline is, therefore, ubiquitous and, although degradable, is less easily degraded than the n-alkanes. Isooctane was not identified in the reference-fuel samples or in the LNAPL samples except for sample MW8, which likely had a trace; identification was somewhat tentative due to coeluting interferences.

The benzene/methylcyclohexane (Bz/MCH) ratio, which is similar to the water-washing ratio given in Kaplan and others (1996), was very different for the ULR sample than for the LNAPL, RR40, and HS#2 samples. The 2-methylheptane to undecane ratio, which is the ratio of a lower (more volatile) alkane to a higher one, was very low for the RR40 and HS#2 samples and much greater for the ULR sample. Ratios for the LNAPL samples were less than half those for the ULR sample.

Generally, most ratios for the LNAPL samples were between those for the RR40 and HS#2 samples. The ratios for the ULR sample were distinctly different from those for the LNAPL samples. Many of the volatile components were not detected in sample FR4, which, as indicated earlier, appears to be more weathered than the other LNAPL samples. Volatile components related to gasoline, including 1,2,4-TMB, n-C_6, benzene, and isooctane, were uniquely detected or found at slightly elevated levels in sample MW8.

Dye Analysis

The UV maximum of the Unisol Red B50 sample was compared to literature values for similar dyes (Green, 1990). The maximum, 518 nanometers (data not shown), was most similar to the maximums for Sudan Red B and Sudan IV. Between methanol and hexane, the solvent used essentially caused no change in the UV maximum of the Unisol Red B50 sample. Under the ionization conditions used for LC/MS analysis, Sudan Red B and Sudan IV ionized well. Therefore, the same ionization conditions were assumed to be appropriate for the unknown component in the Unisol Red B50 sample.

All samples were analyzed by LC/MS for dye components. The red component in Unisol Red B50 was present in every sample except for the ULR reference-fuel and other additive samples (table 8). The RR40 reference-fuel sample had the highest concentration, at 53 micrograms per liter, and was followed by samples MW2R, FR4, and RH1. The lowest concentration, 1 microgram per liter, was in sample PL4. Although the concentrations were too random to discern a pattern, probably because of the chemical sensitivity of the dye, the presence of the dye is further evidence diesel fuel is present at all sites.

Alkyl disazonaphthol dyes, including Unisol Red B50, are toxic irritants and possible mutagens. These dyes and their degradation products (aromatic amines) have been shown to possess mutagenic and carcinogenic properties (Gregory, 1986). These dyes are not light-fast and may degrade upon prolonged exposure to light. The Unisol Red B50 dye is not water soluble and, therefore, is not expected to dissolve into the nearby ground water.

Electrospray Analysis

When analyzed by LC/ESI/MS, the RR40 and HS#2 reference-fuel samples produced a pattern of alkyl moieties (table 9; appendix K) with peaks differing by 14 mass units. The compounds shown in these LC/ESI/MS spectra were most likely a series of homologous alkylated carbazoles; an authentic standard of carbazole (molecular weight 167) analyzed under similar conditions gave a peak corresponding to the lowest member of the series. These nitrogen-containing compounds are present in various petroleum products at very trace levels (Tissot and Welte, 1984). Due to the higher boiling point of carbazoles, they are not present in gasoline, and, thus, are not seen in the ULR reference-fuel sample chromatograms. Distributions of these compounds were very similar in the RR40, HS#2, and LNAPL samples, with minor differences in samples EF1 and FR4 only in the distribution of homologs from 0 to 4 carbons. Differences in sample FR4 probably are due to weathering as previously discussed.

The additive samples produced little response to LC/ESI/MS analysis. The ULR sample was distinctly different from all other samples; the major masses generated by the components in the ULR sample were not found in the remaining samples.

SUMMARY AND CONCLUSIONS

Free-phase hydrocarbons [light nonaqueous phase liquid (LNAPL)] are present floating on the water table in the alluvial aquifer at Mandan, North Dakota, over a subsurface area of about 657,000 square feet. The alluvium can be divided into three stratigraphic units--silty clay, silty sand, and sand--and is underlain by shales and sandstones. Although

the general water-table gradient may be from west-northwest to east-southeast, ground-water-flow directions can vary depending on the river stage and recharge events. Any movement of the LNAPL is influenced by the gradients created by changes in water-level altitudes. The thickness of the LNAPL body is about 6 feet.

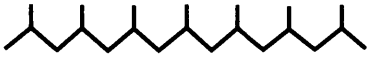
To characterize geochemical composition, LNAPL samples were analyzed by purge-and-trap gas chromatography/mass spectrometry (volatile components), capillary gas chromatography/mass spectrometry (semivolatile components), isotope ratio mass spectrometry (stable carbon isotopes), and liquid chromatography/mass spectrometry with electrospray ionization (additives and other organic components).

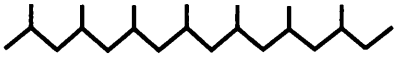
Characterization of the LNAPL samples by gas chromatography/mass spectrometry indicates the samples were all diesel product with a variable loss of *n*-alkanes from biodegradation. Bulk stable carbon isotope data suggest a biodegraded hydrocarbon fuel from a common source. Source-parameter ratios of the LNAPL components indicate an overall similarity among the samples, especially when compared with an unrelated diesel-fuel standard. However, slight differences exist in the chemical distribution within the samples, probably because of small variations in refinery-fuel composition over a long period of local diesel-fuel usage. Very similar polycyclic aromatic hydrocarbon distributions in the LNAPL samples gives more evidence for a common source. The distribution of alkylated carbazoles shows a commonality of diesel-fuel components in samples throughout the downtown area. The red dye marker for diesel fuel is present in all LNAPL samples. These results, therefore, indicate the LNAPL body consists of closely correlatable diesel fuel at various stages of degradation. None of the samples contained chlorinated solvents associated with industries such as drycleaning or automotive maintenance. Solvents such as acetone, dimethyl ether, and methylene chloride and the gasoline additives methyl-t-butyl ether (MTBE), ethyl-t-butyl ether (ETBE), and t-amyl-methyl ether (TAME) were not found. At one site near the north edge of the main LNAPL body, evidence exists for traces of possible gasoline components in addition to the diesel fuel. With this possible exception, no evidence of a different diesel or other hydrocarbon fuel contribution was identified. The geochemical analysis of the LNAPL and correlations with other fuel products and additives strongly suggest episodic releases of a single, local-source, diesel fuel into the aquifer over an extended period of time.

CHEMICAL GLOSSARY FOR SEMIVOLATILES

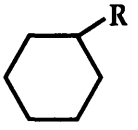
1. *n*-alkanes $CH_3(CH_2)_nCH_3$ n=4-23 for *n*-C_6-*n*C_{25}

   e.g. *n*-C_{15} = $CH_3(CH_2)_{13}(CH_3)$ or

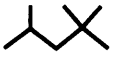
2. Isoprenoids  Pristane (C_{19})

    Phytane (C_{20})

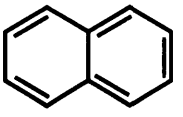
   Others: C_{13}, C_{14}, C_{15}, C_{16}, C_{18}

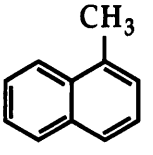
3. *n*-alkylated cyclohexanes 

   R = H, CH_3, C_2H_5 . . . $C_{16}H_{33}$

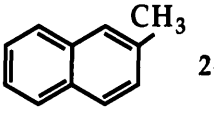
4. isooctane 

5. PAH

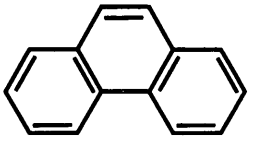
   naphthalene  with 0, 1, 2, 3 C_1 constituents:

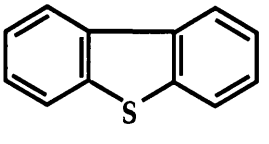
   e.g., C_1-naphthalenes: 

   1-methylnaphthalene

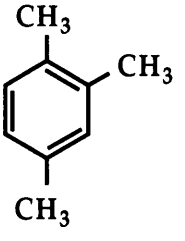
   

   2-methylnaphthalene

   phenanthrene  with 0, 1, 2, 3 C_1 constituents

   dibenzothiophene 

   with 0, 1, 2, 3 C_1 constituents

6. 1, 2, 4 - trimethylbenzene 

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APPENDIX A. Construction information for monitoring wells in study area

[Data from several contractors; --, no data]

Site identifier	Well identifier	Date well constructed	Depth drilled (feet)	Depth of well (feet)	Depth of top of open interval (feet)	Depth of bottom of open interval (feet)	Altitude of land surface (feet)
464929100532701	CS1	04-13-1990	29.5	29.5	9.1	29.5	1,647.7
464937100525768	DBT1	--	--	--	--	--	1,648
464937100525765	DBT2	08-04-1997	24.5	--	--	--	1,648.54
464940100523701	EF1	04-18-1990	29.5	29.5	9.1	29.5	1,645.4
464939100524101	EF4	10-23-1991	28	28	18	28	1,649.1
464940100523101	EF5	10-24-1991	28	26	16	26	1,645.4
464941100523701	EF6	10-25-1991	31	26	16	26	1,647.9
464940100523344	EF7	11-18-1991	28	27	17	27	1,644.1
464939100523901	EF8	11-18-1991	28	27	17	27	1,646.1
464938100523701	EF9	11-19-1991	33	33	18	33	1,650
464934100532709	EW1	05-07-1999	24.5	24	14	24	1,646.3
464934100532813	EW2	05-07-1999	24.5	24	14	24	1,647.2
464934100532759	EW3	06-03-1999	20	18	13.2	18	1,647
464933100533288	EW4	06-03-1999	18	18	12.9	18	1,647.7
464933100532742	FR1	--	--	--	--	--	1,646.5
464932100532885	FR2	12-03-1986	47	45	15	35	1,646.9
464933100532596	FR3	12-02-1986	45	41.5	15.5	41.5	1,646
464937100533214	FR4	12-05-1986	49	42	12	42	1,645.6
464933100533201	FR5	11-12-1991	43	41	16	36	1,648.1
464925100542401	FR6	08-04-1992	45	43	15	35	1,645.3
464928100530808	FR7	--	--	--	--	--	1,648.4
464930100531801	FR8	08-06-1992	40	35	10	25	1,645.6
464939100523701	FR9	08-07-1992	40	36	11	31	1,650.3
464931100533671	MW1R	10-28-1986	40	38.5	8.5	38.5	1,647.2
464932100533357	MW2R	10-29-1986	30	28	8	28	1,647.6
464933100532790	MW3R	--	--	--	--	--	--
464933100532378	MW4R	10-28-1986	30	28	8	28	1,647.9
464935100533501	MW5R	04-16-1990	29.5	29.4	9.0	29.4	1,646.6
464935100532801	MW6	09-06-1984	19.5	19	9	19	1,646.8
464936100532401	MW7R	04-17-1990	29.5	29.5	9.1	29.5	1,646.9
464938100533301	MW8	09-06-1984	19.5	18	8	18	1,645.7
464939100532901	MW9	09-06-1984	21	18.5	8.5	18.5	1,644.9
464941100533201	MW10	09-11-1984	21	18.6	8.6	18.6	1,645
464939100533199	MW11	--	--	--	--	--	1,645.6
464939100533037	MW12	--	--	--	--	--	1,645.3
464946100533101	MW13	04-17-1990	29.5	29.5	9.1	29.5	1,645.8
464941100533601	MW14	04-15-1990	30.1	30.1	9.7	30.1	1,646.3
464937100531801	MW16	04-15-1990	30	29.7	9.3	29.7	1,647
464932100533101	MW17	04-16-1990	31	29.4	9	29.4	1,647.4
464933100533301	MW18	11-14-1991	40	37	27	37	1,648
464932100533401	MW20	11-14-1991	40	34	24	34	1,648.77
464934100533890	MW40	10-25-2000	28	24.5	10	24.5	1,646.95
464935100533738	MW41	10-24-2000	28	24.5	10	24.5	1,646.62
464937100533414	MW42	10-24-2000	28	23.5	9	23.5	1,645.62
464934100533415	MW43	10-23-2000	28	26	11.5	26	1,647.18

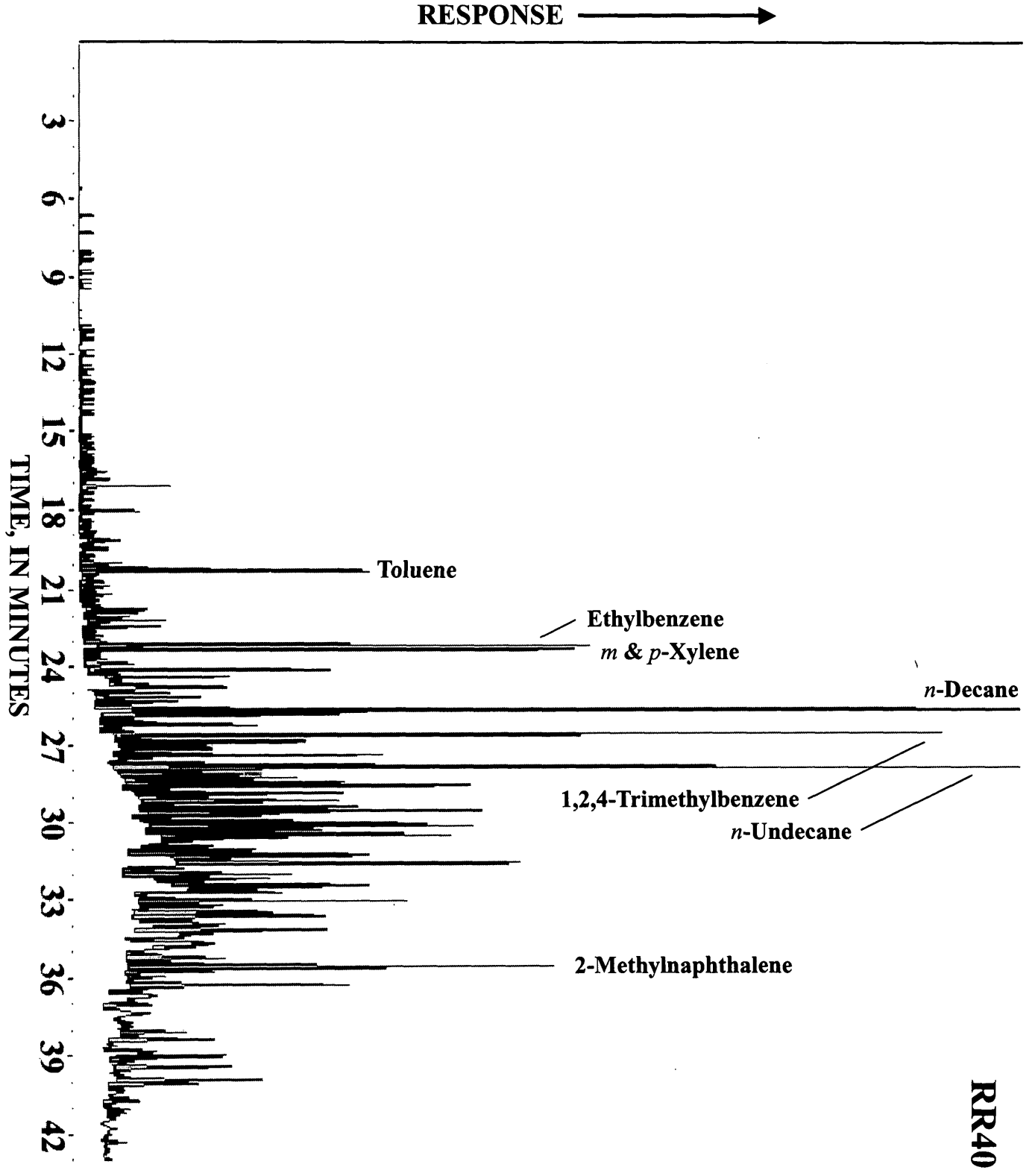
[Data from several contractors; --, no data]

Site identifier	Well identifier	Date well constructed	Depth drilled (feet)	Depth of well (feet)	Depth of top of open interval (feet)	Depth of bottom of open interval (feet)	Altitude of land surface (feet)
464934100533355	MW44	10-23-2000	28	24.5	10	24.5	1,646.94
464936100533165	MW45	10-21-2000	26	22	7.5	22	1,646.82
464937100532818	MW46	10-21-2000	26	24	9.5	24	1,647.06
464935100532847	MW47	10-20-2000	26	21.5	7	21.5	1,646.94
464933100533488	MW48	10-19-2000	26	25	10	25	1,647.66
464932100532659	P1R	10-28-1986	30	27	7	27	1,650.1
464933100532723	P2	10-28-1986	40	37	7	37	1,646.5
464933100532749	P3	10-29-1986	30	28	8	28	1,646.5
464933100532752	P4	11-10-1986	28	28	8	28	1,646.9
464934100532760	P5	10-29-1986	30	28	8	28	1,646.6
464930100530906	PL1	11-07-1991	30	26	16	26	1,649.2
464929100530601	PL2	11-11-1991	28	27	17	27	1,647.6
464929100531101	PL3	11-11-1991	28	27	17	27	1,649.2
464930100530901	PL4	11-11-1991	28	27	17	27	1,647.9
464929100530801	PL5	11-11-1991	28	27	17	27	1,648.4
464928100530801	PL6	11-19-1991	28	27	17	27	1,647.6
464926100530701	PL7	11-21-1991	28	25	15	25	1,644.7
464931100530901	PL8	11-21-1991	28	26	15.5	26	1,646.3
464933100533701	PZ1	12-16-1998	24	24	14	24	1,648.1
464933100533295	PZ2	12-16-1998	24	24	14	24	1,647.7
--	PZ3	--	--	--	--	--	1,647.2
464934100532401	PZ4	12-15-1998	24	24	14	24	1,647.3
--	PZ5	--	--	--	--	--	1,646.8
464936100533401	PZ6	12-16-1998	24	24	14	24	1,646.3
464937100532301	PZ7	12-16-1998	24	24	14	24	1,646.2
464938100532001	PZ8	12-16-1998	24	24	14	24	1,646.4
464938100533801	PZ9	12-16-1998	24	24	14	24	1,645.8
464939100532891	PZ10	12-17-1998	23	23	13	23	1,645.8
464940100532501	PZ11	12-16-1998	24	24	14	24	1,645.3
464940100531901	PZ12	12-17-1998	24	24	14	24	1,644.4
464939100533601	PZ13	12-17-1998	24	24	14	24	1,645.5
464941100533001	PZ14	12-17-1998	24	24	14	24	1,644.5
464930100531753	RH1	04-13-1990	31	29.5	9.7	29.5	1,645.2
464931100531670	RH2	04-14-1990	29.5	29.1	8.7	29.1	1,648.1
464930100531601	RH3	04-13-1990	31	29.4	9.1	29.4	1,645
464931100531701	RH4	04-18-1990	29.5	29.5	9.1	29.5	1,648
464933100531401	RH5	11-05-1991	26	24	12	24	1,645.9
464932100532101	RH6	11-06-1991	26	25	10	25	1,646.7
464930100532001	RH7	11-06-1991	26	25	15	25	1,644.8
464927100531701	RH8	11-06-1991	26	25	15	25	1,646.7
464929100531801	RH9	11-19-1991	31	30	15	25	1,645.1
464934100531901	RH10	11-19-1991	31	30	15	--	1,647
464931100531401	RH11	11-20-1991	27	26	16	26	1,645
464930100534601	W1	04-14-1990	29.5	29.2	8.8	29.2	1,648.6
464924100542401	WF1	04-12-1990	32.5	32.3	9.8	32.3	1,653.8

[Data from several contractors; --, no data]

Site identifier	Well identifier	Date well constructed	Depth drilled (feet)	Depth of well (feet)	Depth of top of open interval (feet)	Depth of bottom of open interval (feet)	Altitude of land surface (feet)
464924100542198	WF2	04-12-1990	34.5	34	8.5	34	1,652.6
464926100542301	WF3	04-16-1990	29.5	29.5	9.1	29.5	1,649.8
464927100542301	WF4	10-25-1991	28	28	16	26	1,650
464926100542601	WF5	10-25-1991	27	26.5	16.5	26.5	1,648.5
464925100541801	WF6	10-30-1991	29	29	17	27	1,651.3
464923100542101	WF7	10-30-1991	30	27	17	27	1,651.7
464924100543001	WF8	10-31-1991	35	32.5	17.5	32.5	1,656.3
464923100542701	WF9	10-31-1991	32	29	17	29	1,653.8
464924100542201	WF10	11-20-1991	31	30	15	30	1,652.5
464925100542301	WF11	11-20-1991	28	27.5	15	27.5	1,649.7
464924100542701	WF12	11-20-1991	33	32	17	32	1,653.2
464925100542001	WF13	11-20-1991	30	30	15	30	1,651.9

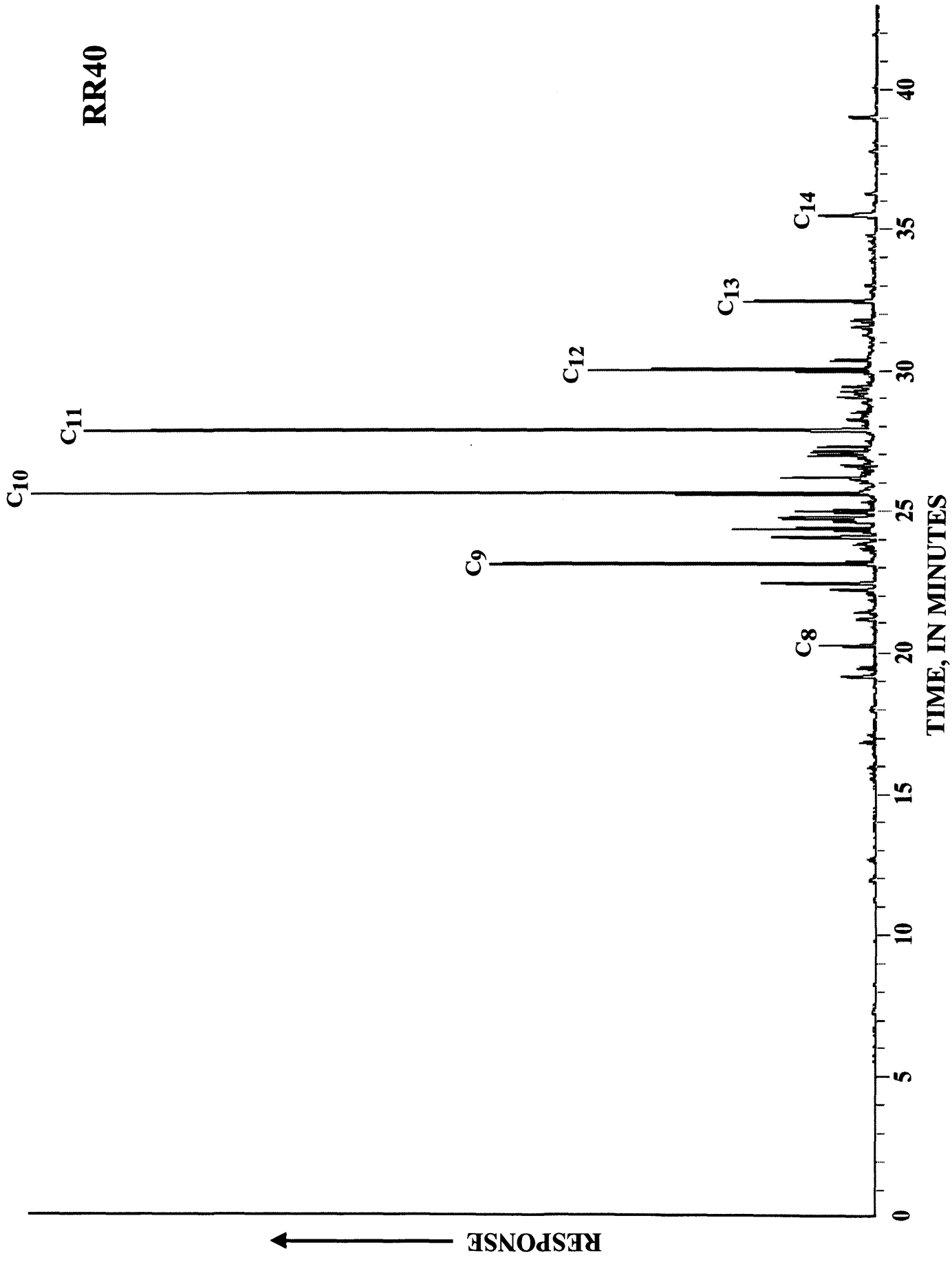
APPENDIX B. Total ion chromatograms from volatile analysis for RR40, HS#2, and ULR reference-fuel samples

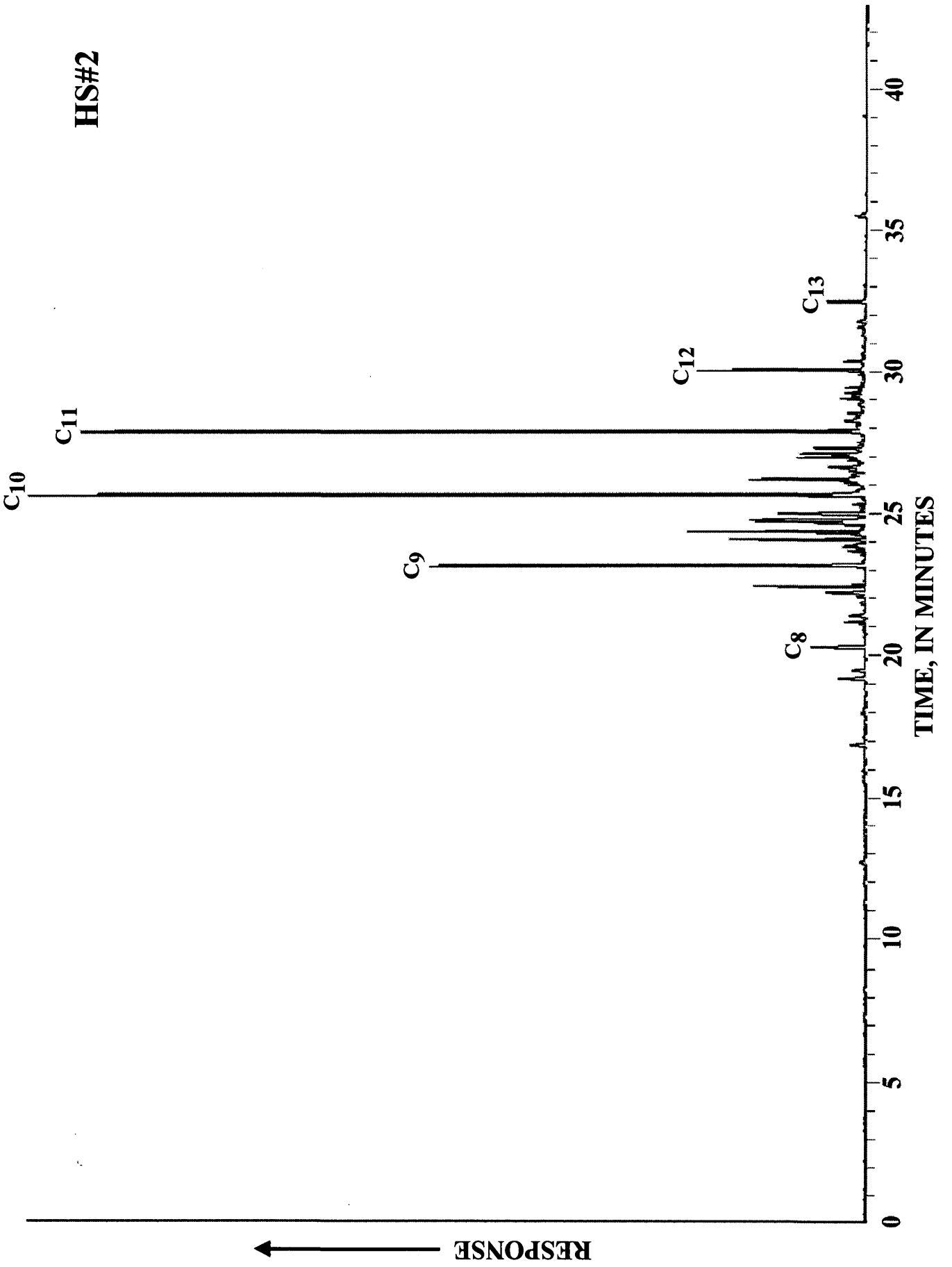

RESPONSE
TIME, IN MINUTES
3
6
9
12
15
18
21
24
27
30
33
36
39
42
Toluene
Ethylbenzene
m & p-Xylene
n-Decane
1,2,4-Trimethylbenzene
n-Undecane
2-Methylnaphthalene
RR40

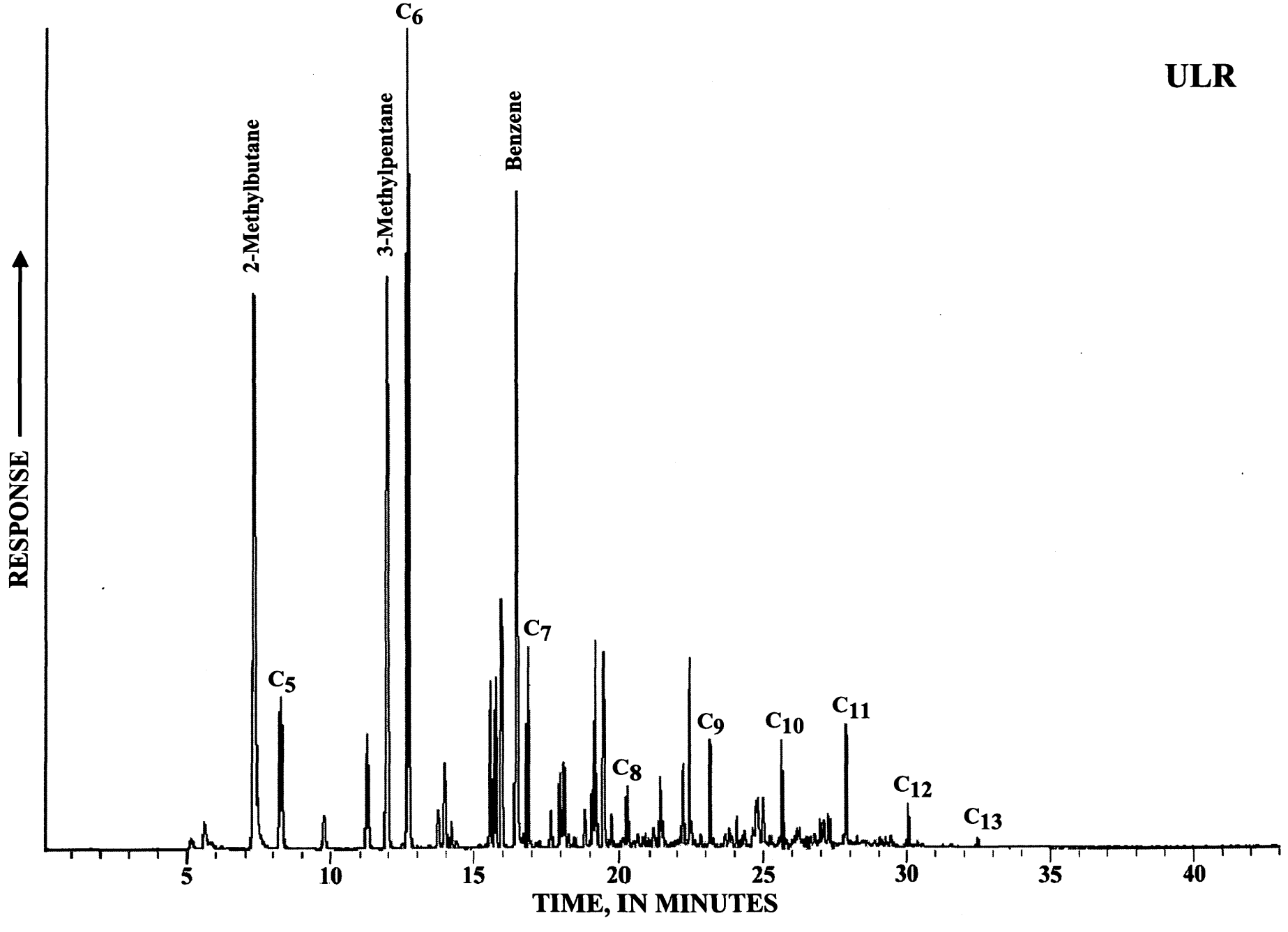
HS#2
RESPONSE
TIME, IN MINUTES
3
6
9
12
15
18
21
24
27
30
33
36
39
42
Toluene
Ethylbenzene
m & p-Xylene
n-Decane
n-Undecane
2-Methylnaphthalene

ULR
RESPONSE
TIME, IN MINUTES
3
6
9
12
15
18
21
24
27
30
33
36
39
42
n-Pentane
n-Hexane
Benzene
Toluene
Ethylbenzene
m & p-Xylene
1,2,4-Trimethylbenzene

APPENDIX C. Extracted ion chromatograms for m/z 57, characteristic of normal alkanes, from volatile analysis for RR40, HS#2, and ULR reference-fuel samples


RR40
C8
C9
C10
C11
C12
C13
C14
0
5
10
15
20
25
30
35
40
TIME, IN MINUTES
RESPONSE


HS#2
C10
C11
C9
C8
C12
C13
0
5
10
15
20
25
30
35
40
TIME, IN MINUTES
RESPONSE


ULR
RESPONSE
2-Methylbutane
3-Methylpentane
Benzene
C6
C5
C7
C8
C9
C10
C11
C12
C13
5
10
15
20
25
30
35
40
TIME, IN MINUTES

APPENDIX D. Concentrations, in micrograms per liter, of target volatile components

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	Location or place from which sample was obtained	Dichloro-difluoro-methane	Chloro-methane	Vinyl-chloride	Bromo-methane	Chloro-ethane	Vinyl-bromide	Trichloro-fluoro-methane	Diethyl-ether	1,1-Dichloro-ethene	1,1,2-Trichloro-1,2,2-trifluoroethane	Acetone	Iodo-methane
Light nonaqueous phase liquid samples													
MW2R	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW17	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
PZ2	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
P5	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
P1R	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
EF1	Railway yard-east	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
PL4	Railway yard-southeast	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
RH1	Railroad yard-southeast	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
WF11	Railway yard-west	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
WF11A	Railway yard-west	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
EW2	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
FR2	Railway yard	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
PZ6	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW44	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW43	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW45	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW45P	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW45B	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
FR4	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW8	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
MW7R	North of Main Street	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
Reference-fuel samples													
RR40	Refinery (current diesel fuel)	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
HS#2	Refinery (broader refinery-cut fuel)	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000
ULR	Refinery (unleaded regular gasoline)	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<80,000	<40,000	<40,000	<2e+06	<160,000

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	Carbon disulfide	3-Chloro-1-propene	Methylene chloride	Acrylonitrile	*trans*-1,2-dichloro-ethene	Methyl-t-butyl ether (MTBE)	1,1-Dichloro-ethane	Di-iso-propylether	Ethyl-t-butyl ether (ETBE)	2,2-Dichloro-propane	*cis*-1,2-Dichloro-ethene	2-Butanone	Methyl-acrylate
Light nonaqueous phase liquid samples													
MW2R	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW17	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
PZ2	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
P5	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
P1R	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
EF1	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
PL4	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
RH1	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
WF11	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
WF11A	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
EW2	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
FR2	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
PZ6	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW44	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW43	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW45	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW45P	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW45B	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
FR4	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW8	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
MW7R	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
Reference-fuel samples													
RR40	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
HS#2	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06
ULR	<160,000	<80,000	<80,000	<1e+06	<40,000	<80,000	<40,000	<80,000	<40,000	<80,000	<40,000	<1.2e+06	<1.2e+06

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	Bromo-chloromethane	Methyl-acrylonitrile	Tetrahydrofuran	Chloroform	1,1,1-Trichloro-ethane	Carbon tetrachloride	1,1-Dichloro-propene	Benzene	1,2-Dichloro-ethane	t-Amyl-methyl ether (TAME)	Trichloro-ethene	1,2-Dichloro-propane
Light nonaqueous phase liquid samples												
MW2R	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E33,060	<80,000	<80,000	<40,000	<40,000
MW17	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	55,430	<80,000	<80,000	<40,000	<40,000
PZ2	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	43,240	<80,000	<80,000	<40,000	<40,000
P5	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	40,830	<80,000	<80,000	<40,000	<40,000
P1R	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	840,000	E34,160	<80,000	<80,000	<40,000	<40,000
EF1	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E13,790	<80,000	<80,000	<40,000	<40,000
PL4	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	40,020	<80,000	<80,000	<40,000	<40,000
RH1	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	<40,000	<80,000	<80,000	<40,000	<40,000
WF11	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E24,450	<80,000	<80,000	<40,000	<40,000
WF11A	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	20,230	<80,000	<80,000	<40,000	<40,000
EW2	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	56,030	<80,000	<80,000	<40,000	<40,000
FR2	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	45,370	<80,000	<80,000	<40,000	<40,000
PZ6	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E15,720	<80,000	<80,000	<40,000	<40,000
MW44	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E13,940	<80,000	<80,000	<40,000	<40,000
MW43	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E15,200	<80,000	<80,000	<40,000	<40,000
MW45	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	55,260	<80,000	<80,000	<40,000	<40,000
MW45P	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	56,090	<80,000	<80,000	<40,000	<40,000
MW45B	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	51,710	<80,000	<80,000	<40,000	<40,000
FR4	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	<40,000	<80,000	<80,000	<40,000	<40,000
MW8	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	252,000	<80,000	<80,000	<40,000	<40,000
MW7R	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	E13,460	<80,000	<80,000	<40,000	<40,000
Reference-fuel samples												
RR40	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	44,480	<80,000	<80,000	<40,000	<40,000
HS#2	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	74,420	<80,000	<80,000	<40,000	<40,000
ULR	<40,000	<40,0000	<3.6e+06	<40,000	<40,000	<80,000	<40,000	17,390,000	<80,000	<80,000	<40,000	<40,000

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	Dibromo-methane	Methyl-methacrylate	Bromodichloro-methane	*cis*-1,3-Dichloro-propene	4-Methyl-2-pentanone	Toluene	*trans*-1,3-Dichloro propene	Ethyl methacrylate	1,1,2-Trichloro-ethane	Tetrachloro-ethene	1,3-Dichloro-propane	2-Hexanone
Light nonaqueous phase liquid samples												
MW2R	440,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW17	<40,000	<280,000	<40,000	<80,000	<40,0000	E14,960	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
PZ2	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
P5	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
P1R	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
EF1	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
PL4	<40,000	<280,000	<40,000	<80,000	<40,0000	E17,560	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
RH1	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
WF11	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
WF11A	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
EW2	<40,000	<280,000	<40,000	<80,000	<40,0000	E30,600	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
FR2	<40,000	<280,000	<40,000	<80,000	<40,0000	E28,490	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
PZ6	<40,000	<280,000	<40,000	<80,000	<40,0000	E11,510	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW44	<40,000	<280,000	<40,000	<80,000	<40,0000	E22,850	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW43	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW45	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW45P	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW45B	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
FR4	<40,000	<280,000	<40,000	<80,000	<40,0000	<40,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW8	<40,000	<280,000	<40,000	<80,000	<40,0000	E26,680	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
MW7R	<40,000	<280,000	<40,000	<80,000	<40,0000	E12,410	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
Reference-fuel samples												
RR40	<40,000	<280,000	<40,000	<80,000	<40,0000	450,800	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
HS#2	<40,000	<280,000	<40,000	<80,000	<40,0000	902,500	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000
ULR	<40,000	<280,000	<40,000	<80,000	<40,0000	65,430,000	<80,000	<240,000	<80,000	<40,000	<80,000	<800,000

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	Dibromochloro-methane	1,2-Dibromo-ethane	Chloro-benzene	1,1,1,2-Tetra-chloroethane	Ethylbenzene	m & p-Xylene	o-Xylene	Styrene	Bromoform	Isopropyl-benzene	Bromobenzene	1,1,2,2-Tetra-chloroethane
Light nonaqueous phase liquid samples												
MW2R	<80,000	<40,000	<40,000	<40,000	542,200	712,400	42,180	<40,000	<80,000	151,100	<40,000	<80,000
MW17	<80,000	<40,000	<40,000	<40,000	773,300	1,690,000	206,000	<40,000	<80,000	204,500	<40,000	<80,000
PZ2	<80,000	<40,000	<40,000	<40,000	705,100	2,517,000	664,600	<40,000	<80,000	199,500	<40,000	<80,000
P5	<80,000	<40,000	<40,000	<40,000	628,800	1,957,000	456,000	<40,000	<80,000	172,000	<40,000	<80,000
P1R	<80,000	<40,000	<40,000	<40,000	624,400	2,336,000	559,400	<40,000	<80,000	157,800	<40,000	<80,000
EF1	<80,000	<40,000	<40,000	<40,000	305,400	359,300	56,920	<40,000	<80,000	132,800	<40,000	<80,000
PL4	<80,000	<40,000	<40,000	<40,000	461,500	768,800	153,000	<40,000	<80,000	96,390	<40,000	<80,000
RH1	<80,000	<40,000	<40,000	<40,000	252,400	324,100	<40,000	<40,000	<80,000	103,200	<40,000	<80,000
WF11	<80,000	<40,000	<40,000	<40,000	165,800	383,600	<40,000	<40,000	<80,000	113,300	<40,000	<80,000
WF11A	<80,000	<40,000	<40,000	<40,000	159,300	369,100	<40,000	<40,000	<80,000	109,000	<40,000	<80,000
EW2	<80,000	<40,000	<40,000	<40,000	744,000	2,887,000	1,232,000	<40,000	<80,000	173,400	<40,000	<80,000
FR2	<80,000	<40,000	<40,000	<40,000	704,500	3,028,000	1,008,000	<40,000	<80,000	181,200	<40,000	<80,000
PZ6	<80,000	<40,000	<40,000	<40,000	396,600	1,676,000	848,000	<40,000	<80,000	136,000	<40,000	<80,000
MW44	<80,000	<40,000	<40,000	<40,000	508,700	1,932,000	961,800	<40,000	<80,000	165,700	<40,000	<80,000
MW43	<80,000	<40,000	<40,000	<40,000	597,800	2,271,000	449,600	<40,000	<80,000	200,400	<40,000	<80,000
MW45	<80,000	<40,000	<40,000	<40,000	758,900	2,631,000	<40,000	<40,000	<80,000	224,800	<40,000	<80,000
MW45P	<80,000	<40,000	<40,000	<40,000	755,800	2,634,000	<40,000	<40,000	<80,000	223,800	<40,000	<80,000
MW45B	<80,000	<40,000	<40,000	<40,000	696,100	2,451,000	<40,000	<40,000	<80,000	194,600	<40,000	<80,000
FR4	<80,000	<40,000	<40,000	<40,000	<40,000	E50,780	<40,000	<40,000	<80,000	<40,000	<40,000	<80,000
MW8	<80,000	<40,000	<40,000	<40,000	908,400	1,128,000	394,900	<40,000	<80,000	163,900	<40,000	<80,000
MW7R	<80,000	<40,000	<40,000	<40,000	395,300	683,600	143,200	<40,000	<80,000	167,200	<40,000	<80,000
Reference-fuel samples												
RR40	<80,000	<40,000	<40,000	<40,000	305,900	1,147,000	551,600	<40,000	<80,000	62,590	<40,000	<80,000
HS#2	<80,000	<40,000	<40,000	<40,000	673,700	2,220,000	1,072,000	<40,000	<80,000	198,600	<40,000	<80,000
ULR	<80,000	<40,000	<40,000	<40,000	11,540,000	42,770,000	15,800,000	601,400	<80,000	1,047,000	<40,000	<80,000

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	1,2,3-Trichloropropane	*trans*-1,4-Dichloro-2-butene	n-Propylbenzene	2-Chlorotoluene	4-Chlorotoluene	1,3,5-Trimethylbenzene	2-Ethyltoluene	tert-Butylbenzene	1,2,4-Trimethylbenzene	*sec*-Butylbenzene	1,3-Dichlorobenzene	p-Isopropyltoluene
Light nonaqueous phase liquid samples												
MW2R	<80,000	<800,000	683,100	<40,000	<40,000	856,000	522,600	<80,000	6,253,000	270,500	<40,000	250,400
MW17	<80,000	<800,000	904,500	<40,000	<40,000	1,581,000	832,300	<80,000	6,292,000	327,900	<40,000	281,100
PZ2	<80,000	<800,000	941,800	<40,000	<40,000	1,957,000	1,449,000	<80,000	6,984,000	320,800	<40,000	274,700
P5	<80,000	<800,000	715,400	<40,000	<40,000	1,636,000	962,700	<80,000	5,318,000	302,200	<40,000	258,400
P1R	<80,000	<800,000	648,400	<40,000	<40,000	1,853,000	998,900	<80,000	6,622,000	261,600	<40,000	230,900
EF1	<80,000	<800,000	468,300	<40,000	<40,000	852,200	859,500	<80,000	3,736,000	280,700	<40,000	236,100
PL4	<80,000	<800,000	463,700	<40,000	<40,000	1,304,000	852,600	<80,000	5,610,000	155,100	<40,000	136,400
RH1	<80,000	<800,000	370,100	<40,000	<40,000	<40,000	65,420	<80,000	4,212,000	254,100	<40,000	259,900
WF11	<80,000	<800,000	429,000	<40,000	<40,000	1,319,000	842,300	<80,000	4,060,000	233,100	<40,000	210,400
WF11A	<80,000	<800,000	400,000	<40,000	<40,000	1,270,000	809,800	<80,000	3,556,000	225,000	<40,000	202,100
EW2	<80,000	<800,000	714,100	<40,000	<40,000	1,635,000	1,078,000	<80,000	6,421,000	249,900	<40,000	214,400
FR2	<80,000	<800,000	773,300	<40,000	<40,000	2,014,000	1,154,000	<80,000	7,195,000	320,200	<40,000	267,300
PZ6	<80,000	<800,000	602,700	<40,000	<40,000	1,708,000	1,181,000	<80,000	5,639,000	267,000	<40,000	241,900
MW44	<80,000	<800,000	762,000	<40,000	<40,000	1,664,000	1,141,000	<80,000	5,402,000	296,400	<40,000	250,600
MW43	<80,000	<800,000	1,002,000	<40,000	<40,000	2,089,000	1,500,000	<80,000	7,809,000	344,400	<40,000	291,600
MW45	<80,000	<800,000	1,006,000	<40,000	<40,000	2,024,000	266,000	<80,000	6,990,000	382,000	<40,000	319,100
MW45P	<80,000	<800,000	999,300	<40,000	<40,000	2,000,000	253,600	<80,000	7,421,000	381,000	<40,000	314,900
MW45B	<80,000	<800,000	851,900	<40,000	<40,000	1,820,000	235,100	<80,000	7,200,000	299,800	<40,000	254,600
FR4	<80,000	<800,000	<40,000	<40,000	<40,000	386,200	376,800	<80,000	1,479,000	78,840	<40,000	131,500
MW8	<80,000	<800,000	767,800	<40,000	<40,000	1,343,000	1,504,000	<80,000	6,924,000	218,600	<40,000	199,300
MW7R	<80,000	<800,000	692,000	<40,000	<40,000	1,644,000	1,096,000	<80,000	5,777,000	330,100	<40,000	283,100
Reference-fuel samples												
RR40	<80,000	<800,000	243,000	<40,000	<40,000	458,600	318,800	<80,000	1,886,000	83,280	<40,000	74,010
HS#2	<80,000	<800,000	637,000	<40,000	<40,000	1,001,000	699,100	<80,000	3,884,000	277,200	<40,000	244,700
ULR	<80,000	<800,000	2,914,000	<40,000	<40,000	4,719,000	3,442,000	<80,000	16,890,000	347,600	<40,000	174,100

[Elevated detection limits are due to 1:400,000 dilution of sample before purge-and-trap gas chromatographic/mass spectrometric analysis; <, less than; E, estimated because of level below lowest calibrated amount]

Sample identifier	1,4-Dichloro-benzene	1,2,3-Trimethyl-benzene	1,2-Dichloro-benzene	n-Butyl-benzene	Hexachloro-ethane	1,2-Dibromo-2-chloropropane	1,2,3,5-Tetra-methyl-benzene	1,2,3,4-Tetra-methyl-benzene	1,2,4-Trichloro-benzene	Hexachloro-butadiene	Naph-thalene	1,2,3-Trichloro-benzene
Light nonaqueous phase liquid samples												
MW2R	<40,000	2,610,000	<40,000	930,000	<160,000	<160,000	3,198,000	2,157,000	<80,000	<80,000	3,672,000	<80,000
MW17	<40,000	3,073,000	<40,000	1,069,000	<160,000	<160,000	3,120,000	2,184,000	<80,000	<80,000	4,388,000	<80,000
PZ2	<40,000	3,051,000	<40,000	1,071,000	<160,000	<160,000	3,103,000	2,111,000	<80,000	<80,000	4,506,000	<80,000
P5	<40,000	1,764,000	<40,000	982,300	<160,000	<160,000	3,073,000	2,125,000	<80,000	<80,000	3,808,000	<80,000
P1R	<40,000	2,441,000	<40,000	934,700	<160,000	<160,000	3,287,000	2,169,000	<80,000	<80,000	4,342,000	<80,000
EF1	<40,000	1,198,000	<40,000	811,200	<160,000	<160,000	3,043,000	1,804,000	<80,000	<80,000	3,453,000	<80,000
PL4	<40,000	1,771,000	<40,000	645,300	<160,000	<160,000	2,553,000	1,480,000	<80,000	<80,000	3,872,000	<80,000
RH1	<40,000	2,293,000	<40,000	691,100	<160,000	<160,000	3,213,000	2,500,000	<80,000	<80,000	3,442,000	<80,000
WF11	<40,000	576,100	<40,000	786,900	<160,000	<160,000	2,984,000	1,721,000	<80,000	<80,000	3,715,000	<80,000
WF11A	<40,000	561,300	<40,000	755,700	<160,000	<160,000	2,808,000	1,798,000	<80,000	<80,000	3,406,000	<80,000
EW2	<40,000	2,574,000	<40,000	805,900	<160,000	<160,000	2,609,000	1,808,000	<80,000	<80,000	4,100,000	<80,000
FR2	<40,000	3,191,000	<40,000	1,072,000	<160,000	<160,000	3,287,000	2,198,000	<80,000	<80,000	3,899,000	<80,000
PZ6	<40,000	2,397,000	<40,000	921,500	<160,000	<160,000	2,646,000	1,749,000	<80,000	<80,000	3,735,000	<80,000
MW44	<40,000	2,458,000	<40,000	973,300	<160,000	<160,000	2,558,000	1,893,000	<80,000	<80,000	3,637,000	<80,000
MW43	<40,000	2,868,000	<40,000	1,206,000	<160,000	<160,000	3,097,000	2,024,000	<80,000	<80,000	4,685,000	<80,000
MW45	<40,000	3,143,000	<40,000	1,238,000	<160,000	<160,000	3,325,000	2,425,000	<80,000	<80,000	4,969,000	<80,000
MW45P	<40,000	3,051,000	<40,000	1,249,000	<160,000	<160,000	3,175,000	2,116,000	<80,000	<80,000	4,715,000	<80,000
MW45B	<40,000	2,884,000	<40,000	964,000	<160,000	<160,000	2,729,000	1,966,000	<80,000	<80,000	4,294,000	<80,000
FR4	<40,000	889,300	<40,000	<226,200	<160,000	<160,000	2,267,000	1,652,000	<80,000	<80,000	4,55,600	<80,000
MW8	<40,000	1,914,000	<40,000	757,200	<160,000	<160,000	2,790,000	1,818,000	<80,000	<80,000	3,574,000	<80,000
MW7R	<40,000	2,138,000	<40,000	1,065,000	<160,000	<160,000	2,956,000	1,954,000	<80,000	<80,000	4,142,000	<80,000
Reference-fuel samples												
RR40	<40,000	744,100	<40,000	251,900	<160,000	<160,000	1,010,000	1,156,000	<80,000	<80,000	2,771,000	<80,000
H#2	<40,000	1,742,000	<40,000	660,600	<160,000	<160,000	1,522,000	2,372,000	<80,000	<80,000	2,753,000	<80,000
ULR	<40,000	3,860,000	<40,000	812,,800	<160,000	<160,000	2,390,000	1,071,000	<80,000	<80,000	2,727,000	<80,000

APPENDIX E. Concentrations, in micrograms per liter, of detected target volatile components

[nd, not detected; BTEX, benzene, toluene, ethylbenzene, and xylene; --, no data]

Sample identifier	Location or place from which sample was obtained	Benzene	Toluene	Ethylbenzene	m & p-Xylene	o-Xylene	Styrene	Isopropyl-benzene	n-Propylbenzene	1,3,5-Trimethyl-benzene	2-Ethyltoluene
					Light nonaqueous phase liquid samples						
MW2R	Railway yard	33,060	nd	542,200	712,400	42,180	nd	151,100	683,100	856,000	522,600
MW17	Railway yard	55,430	14,960	773,300	1,690,000	206,000	nd	204,500	904,500	1,581,000	832,300
PZ2	Railway yard	43,240	nd	705,100	2,517,000	664,600	nd	199,500	941,800	1,957,000	1,449,000
P5	Railway yard	40,830	nd	628,800	1,957,000	456,000	nd	172,000	715,400	1,636,000	962,700
P1R	Railway yard	34,160	nd	624,400	2,336,000	559,400	nd	157,800	648,400	1,853,000	998,900
EF1	Railway yard-east	13,790	nd	305,400	359,300	56,920	nd	132,800	468,300	852,200	859,500
PL4	Railway yard-southeast	40,020	17,560	461,500	768,800	153,000	nd	96,390	463,700	1,304,000	852,600
RH1	Railway yard-southeast	nd	nd	252,400	324,100	nd	nd	103,200	370,100	nd	65,420
WF11	Railway yard-west	24,450	nd	165,800	383,600	nd	nd	113,300	429,000	1,319,000	842,300
WF11A	Railway yard-west	20,230	nd	159,300	369,100	nd	nd	109,000	400,000	1,270,000	809,800
EW2	Railway yard	56,030	30,600	744,000	2,887,000	1,232,000	nd	173,400	714,100	1,635,000	1,078,000
FR2	Railway yard	45,370	28,490	704,500	3,028,000	1,008,000	nd	181,200	773,300	2,014,000	1,154,000
PZ6	North of Main Street	15,720	11,510	396,600	1,676,000	848,000	nd	136,000	602,700	1,708,000	1,181,000
MW44	North of Main Street	13,940	22,850	508,700	1,932,000	961,800	nd	165,700	762,000	1,664,000	1,141,000
MW43	North of Main Street	15,200	nd	597,800	2,271,000	449,600	nd	200,400	1,002,000	2,089,000	1,500,000
MW45	North of Main Street	55,260	nd	758,900	2,631,000	nd	nd	224,800	1,006,000	2,024,000	266,000
MW45P	North of Main Street	56,090	nd	755,800	2,634,000	nd	nd	223,800	999,300	2,000,000	253,600
MW45B	North of Main Street	51,710	nd	696,100	2,451,000	nd	nd	194,600	851,900	1,820,000	235,100
FR4	North of Main Street	nd	nd	nd	50,780	nd	nd	nd	nd	386,200	376,800
MW8	North of Main Street	252,000	26,680	908,400	1,128,000	394,900	nd	163,900	767,800	1,343,000	1,504,000
MW7R	North of Main Street	13,460	12,410	395,300	683,600	143,200	nd	167,200	692,000	1,644,000	1,096,000
					Reference-fuel samples						
RR40	Refinery (current diesel fuel)	44,480	450,800	305,900	1,147,000	551,600	nd	62,590	243,000	458,600	318,800
HS#2	Refinery (broader refinery-cut fuel)	74,420	902,500	673,700	2,220,000	1,072,000	nd	198,600	637,000	1,001,000	699,100
ULR	Refinery (unleaded regular gasoline)	17,390,000	65,430,000	11,540,000	42,770,000	15,800,000	601,400	1,047,000	2,914,000	4,719,000	3,442,000

[nd, not detected; BTEX, benzene, toluene, ethylbenzene, and xylene; --, no data]

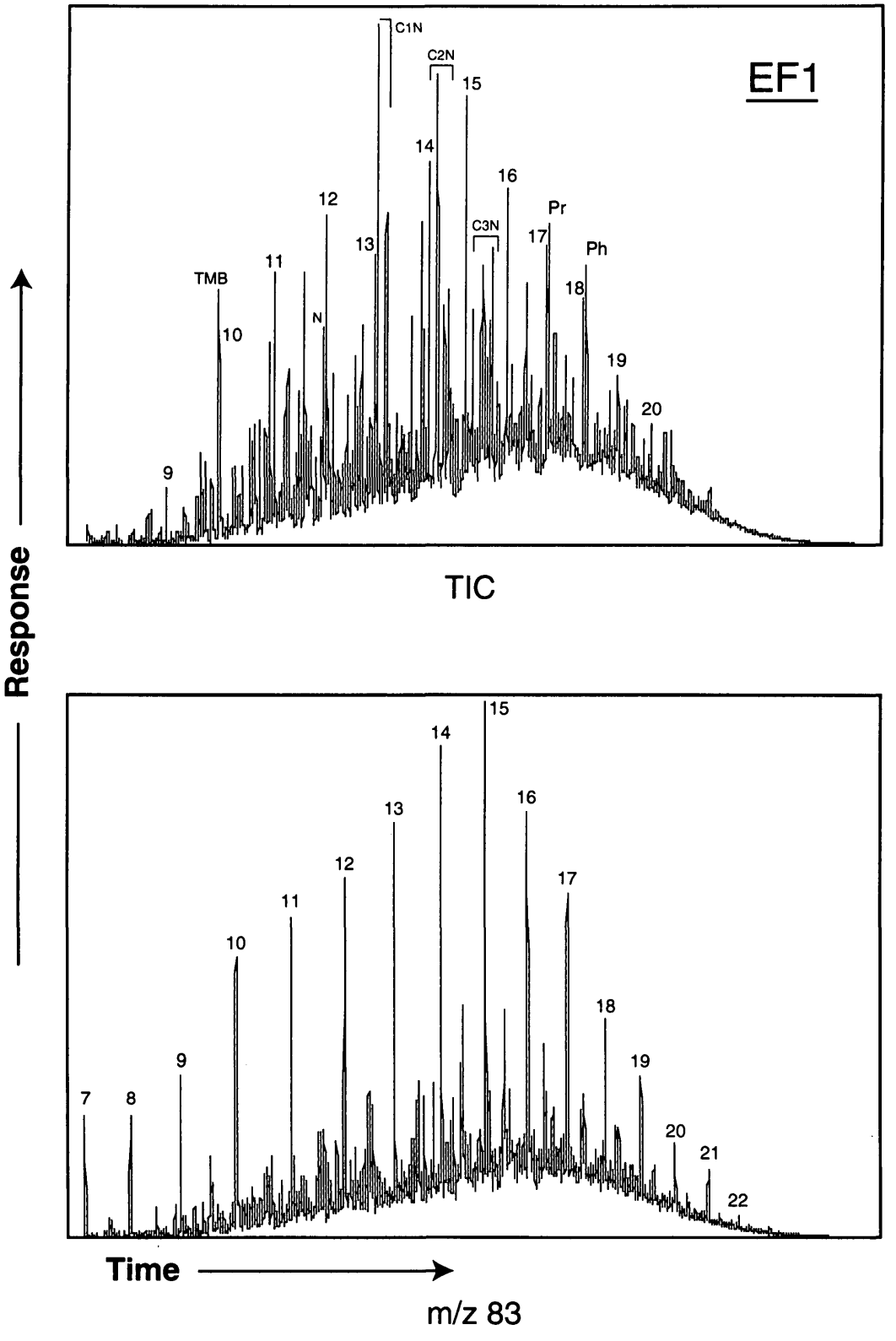
Sample identifier	Location or place from which sample was obtained	1,2,4-Trimethyl-benzene	sec-Butyl-benzene	p-Isopropyl-toluene	1,2,3-Trimethyl-benzene	n-Butylbenzene	1,2,3,5-Tetra-methylbenzene	1,2,3,4-Tetra-methylbenzene	Naphthalene	BTEX
					Light nonaqueous phase liquid samples					
MW2R	Railway yard	6,253,000	270,500	250,400	2,610,000	930,000	3,198,000	2,157,000	3,672,000	--
MW17	Railway yard	6,292,000	327,900	281,100	3,073,000	1,069,000	3,120,000	2,184,000	4,388,000	2,739,690
PZ2	Railway yard	6,984,000	320,800	274,700	3,051,000	1,071,000	3,103,000	2,111,000	4,506,000	--
P5	Railway yard	5,318,000	302,200	258,400	1,764,000	982,300	3,073,000	2,125,000	3,808,000	--
P1R	Railway yard	6,622,000	261,600	230,900	2,441,000	934,700	3,287,000	2,169,000	4,342,000	--
EF1	Railway yard-east	3,736,000	280,700	236,100	1,198,000	811,200	3,043,000	1,804,000	3,453,000	--
PL4	Railway yard-southeast	5,610,000	155,100	136,400	1,771,000	645,300	2,553,000	1,480,000	3,872,000	1,440,880
RH1	Railway yard-southeast	4,212,000	254,100	259,900	2293,000	691,100	3,213,000	2,500,000	3,442,000	--
WF11	Railway yard-west	4,060,000	233,100	210,400	576,100	786,900	2,984,000	1,721,000	3,715,000	--
WF11A	Railway yard-west	3,556,000	225,000	202,100	561,300	755,700	2,808,000	1,798,000	3,406,000	--
EW2	Railway yard	6,421,000	249,900	214,400	2,574,000	805,900	2,609,000	1,808,000	4,100,000	4,949,630
FR2	Railway yard	7,195,000	320,200	267,300	3,191,000	1,072,000	3,287,000	2,198,000	3,899,000	4,814,360
PZ6	North of Main Street	5,639,000	267,000	241,900	2,397,000	921,500	2,646,000	1,749,000	3,735,000	2,947,830
MW44	North of Main Street	5,402,000	296,400	250,600	2,458,000	973,300	2,558,000	1,893,000	3,637,000	3,439,290
MW43	North of Main Street	7,809,000	344,400	291,600	2,868,000	1,206,000	3,097,000	2,024,000	4,685,000	--
MW45	North of Main Street	6,990,000	382,000	319,100	3,143,000	1,238,000	3,325,000	2,425,000	4,969,000	--
MW45P	North of Main Street	7,421,000	381,000	314,900	3,051,000	1,249,000	3,175,000	2,116,000	4,715,000	--
MW45B	North of Main Street	7,200,000	299,800	254,600	2,884,000	964,000	2,729,000	1,966,000	4,294,000	--
FR4	North of Main Street	1,479,000	78,840	131,500	889,300	nd	2,267,000	1,652,000	455,600	--
MW8	North of Main Street	6,924,000	218,600	199,300	1,914,000	757,200	2,790,000	1,818,000	3,574,000	2,709,980
MW7R	North of Main Street	5,777,000	330,100	283,100	2,138,000	1,065,000	2,956,000	1,954,000	4,142,000	1,247,970
					Reference-fuel samples					
RR40	Refinery (current diesel fuel)	1,886,000	83,280	74,010	744,100	251,900	1,010,000	1,156,000	2,771,000	2,499,780
HS#2	Refinery (broader refinery-cut fuel)	3,884,000	277,200	244,700	1,742,000	660,600	1,522,000	2,372,000	2,753,000	4,942,620
ULR	Refinery (unleaded regular gasoline)	16,890,000	347,600	174,100	3,860,000	812,800	2,390,000	1,071,000	2,727,000	152,930,000

APPENDIX F. Estimated concentrations, in micrograms per liter, of nontarget volatile components

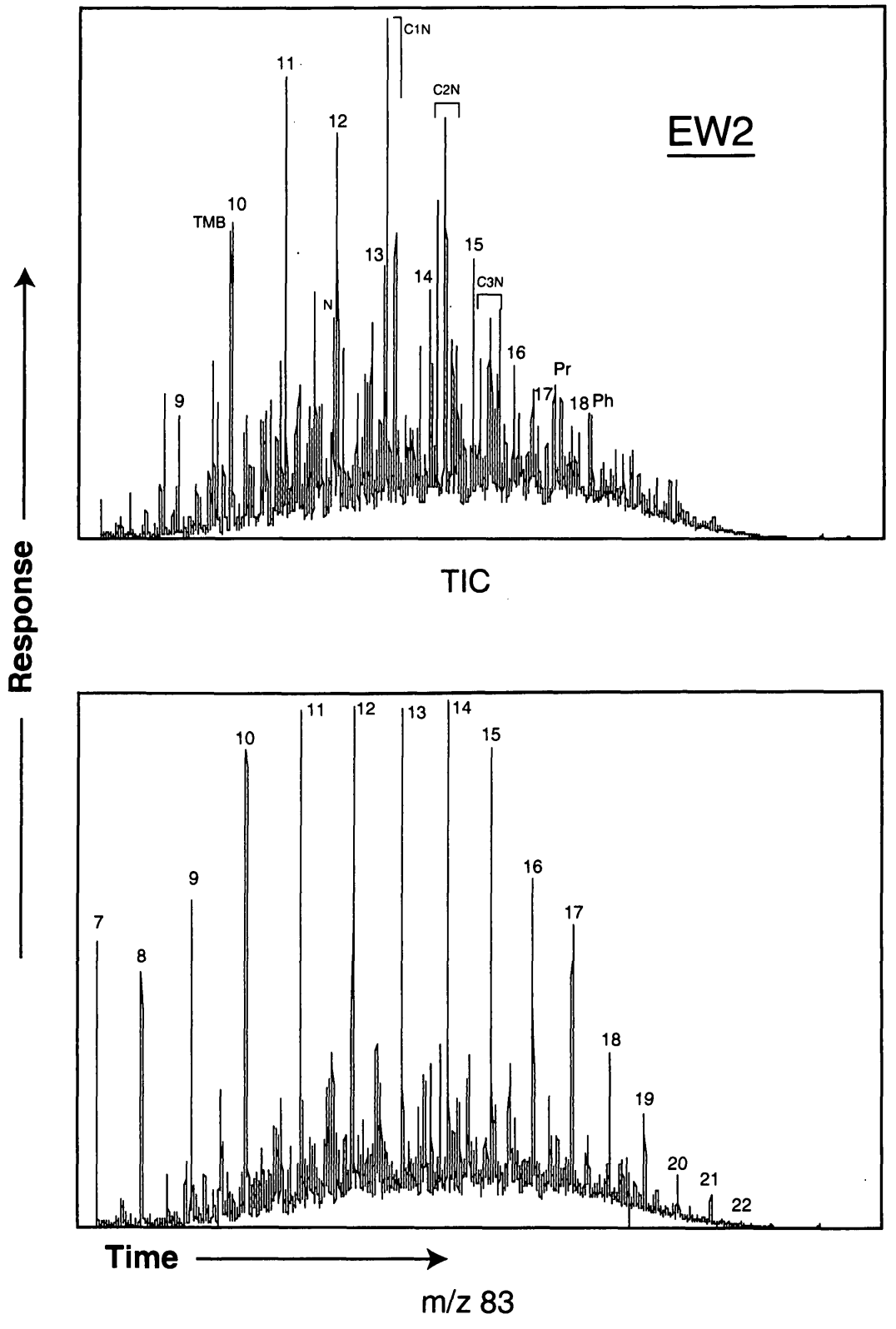
[--, no data]

Sample identifier	Location or place from which sample was obtained	2-Methylheptane	Undecane	1,2,3,4-Tetrahydro-naphthalene	2-Methyl-naphthalene	1-Methyl-naphthalene	3-Methyl-octane	Methylcyclohexane	1,1,3-Trimethyl-cyclohexane
				Light nonaqueous phase liquid samples					
MW2R	Railway yard	352,300	5,417,000	413,000	1,348,000	1,077,000	608,600	478,400	314,000
MW17	Railway yard	522,300	--	456,900	1,518,000	1,050,000	784,900	735,700	369,400
PZ2	Railway yard	228,500	6,538,000	529,500	1,667,000	1,241,000	366,600	386,500	178,100
P5	Railway yard	513,400	12,230,000	386,000	1,691,000	872,200	789,200	838,500	394,000
P1R	Railway yard	215,100	10,980,000	510,600	1,753,000	929,700	242,200	299,100	165,900
EF1	Railway yard-east	133,800	9,370,000	419,000	1,643,000	1,019,000	481,800	388,700	290,800
PL4	Railway yard-southeast	135,300	7,888,000	276,000	1,455,000	794,700	155,100	279,000	--
RH1	Railway yard-southeast	189,300	--	480,300	1,899,000	1,662,000	477,800	268,200	252,800
WF11	Railway yard-west	311,700	10,560,000	370,200	2,163,000	960,800	487,600	448,500	275,600
WF11A	Railway yard-west	--	9,955,000	387,100	1,740,000	852,000	472,800	482,200	267,500
EW2	Railway yard	246,000	9,327,000	468,900	1,454,000	844,000	265,900	417,100	165,000
FR2	Railway yard	632,300	--	394,400	1,589,000	976,200	812,600	985,800	462,100
PZ6	North of Main Street	167,400	14,770,000	406,000	1,594,000	1,141,000	701,600	434,800	310,100
MW44	North of Main Street	320,700	10,790,000	404,300	2,268,000	953,200	589,500	372,500	298,800
MW43	North of Main Street	411,000	12,940,000	507,600	1,592,000	1,194,000	814,300	499,000	337,900
MW45	North of Main Street	284,100	6,632,000	466,000	1,785,000	1,305,000	909,200	706,000	431,000
MW45P	North of Main Street	531,600	6,288,000	467,600	1,658,000	1,250,000	868,800	756,600	565,800
MW45B	North of Main Street	168,500	5,600,000	504,300	1,544,000	979,200	242,300	326,900	142,300
FR4	North of Main Street	--	8,049,000	296,000	1,080,000	1,181,000	159,700	--	--
MW8	North of Main Street	166,900	7,371,000	276,400	877,800	709,100	467,000	672,900	156,500
MW7R	North of Main Street	175,300	12,190,000	431,400	1,401,000	1,108,000	705,900	493,400	365,400
				Reference-fuel samples					
RR40	Refinery (current diesel fuel)	108,400	5,133,000	258,400	2,504,000	1,590,000	251,200	256,300	224,400
HS#2	Refinery (broader refinery-cut fuel)	340,000	16,130,000	481,500	1,984,000	1,104,000	983,000	918,800	1,001,000
ULR87	Refinery (unleaded regular gasoline)	829,700	4,287,000	60,140	90,250	40,460	608,900	1,355,000	--

APPENDIX G. Total ion chromatograms (top figures) and extracted ion chromatograms (bottom figures) for m/z 83 from semivolatile analysis



Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
TMB = 1,2,4-trimethylbenzene; N, C1N, C2N, C3N = naphthalene series;
Pr = pristane; Ph = phytane.



Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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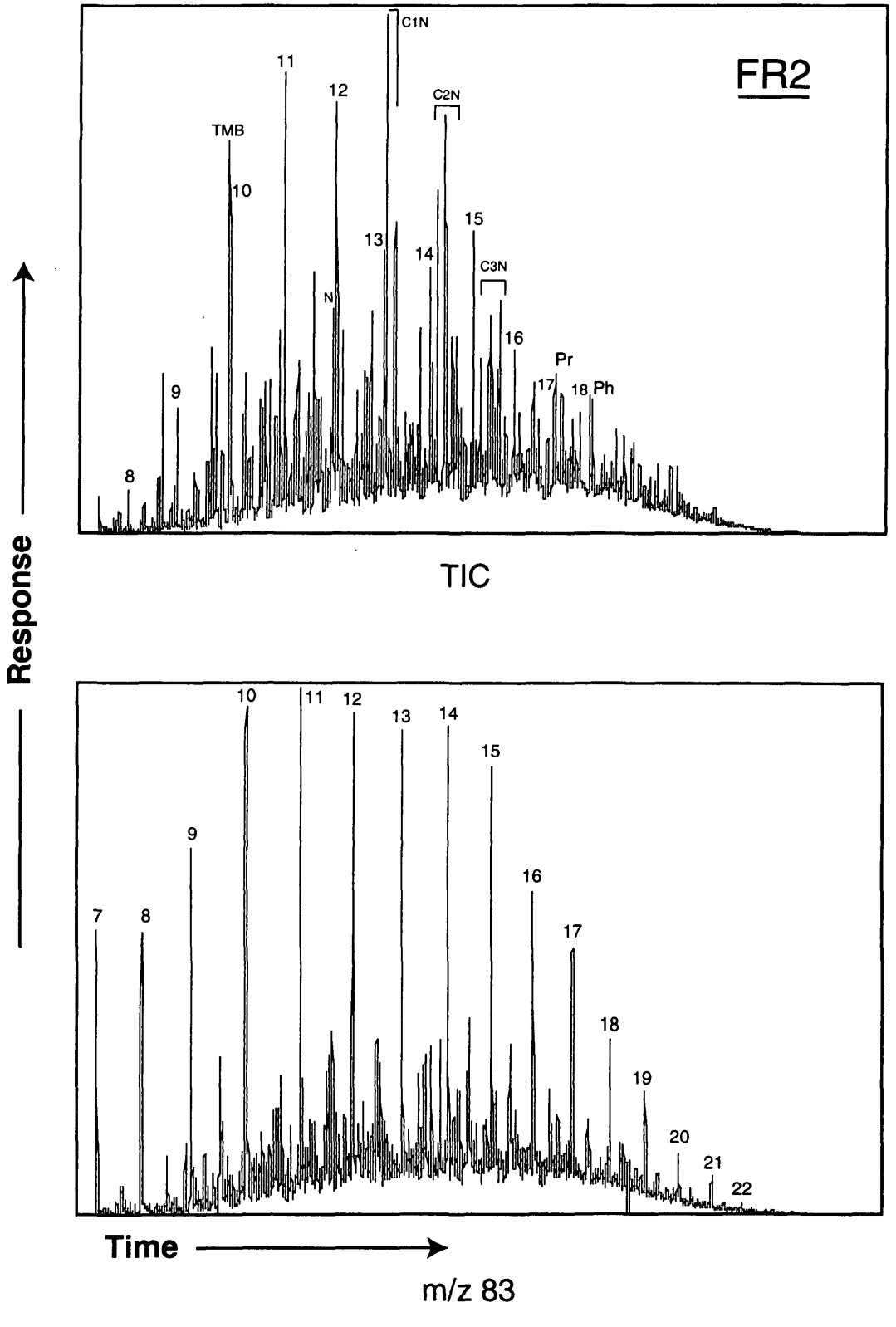
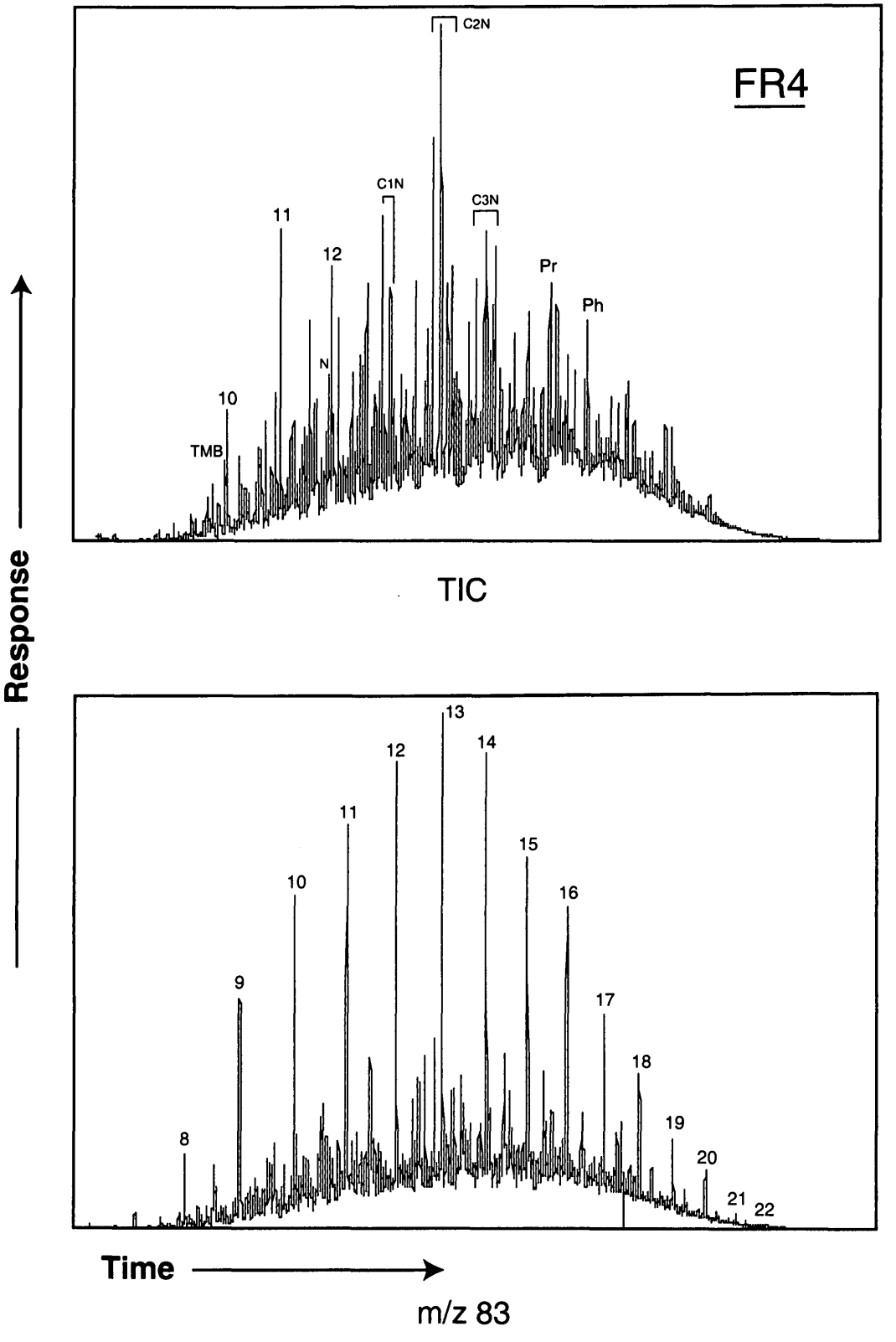


Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
TMB = 1,2,4-trimethylbenzene; N, C1N, C2N, C3N = naphthalene series;
Pr = pristane; Ph = phytane.



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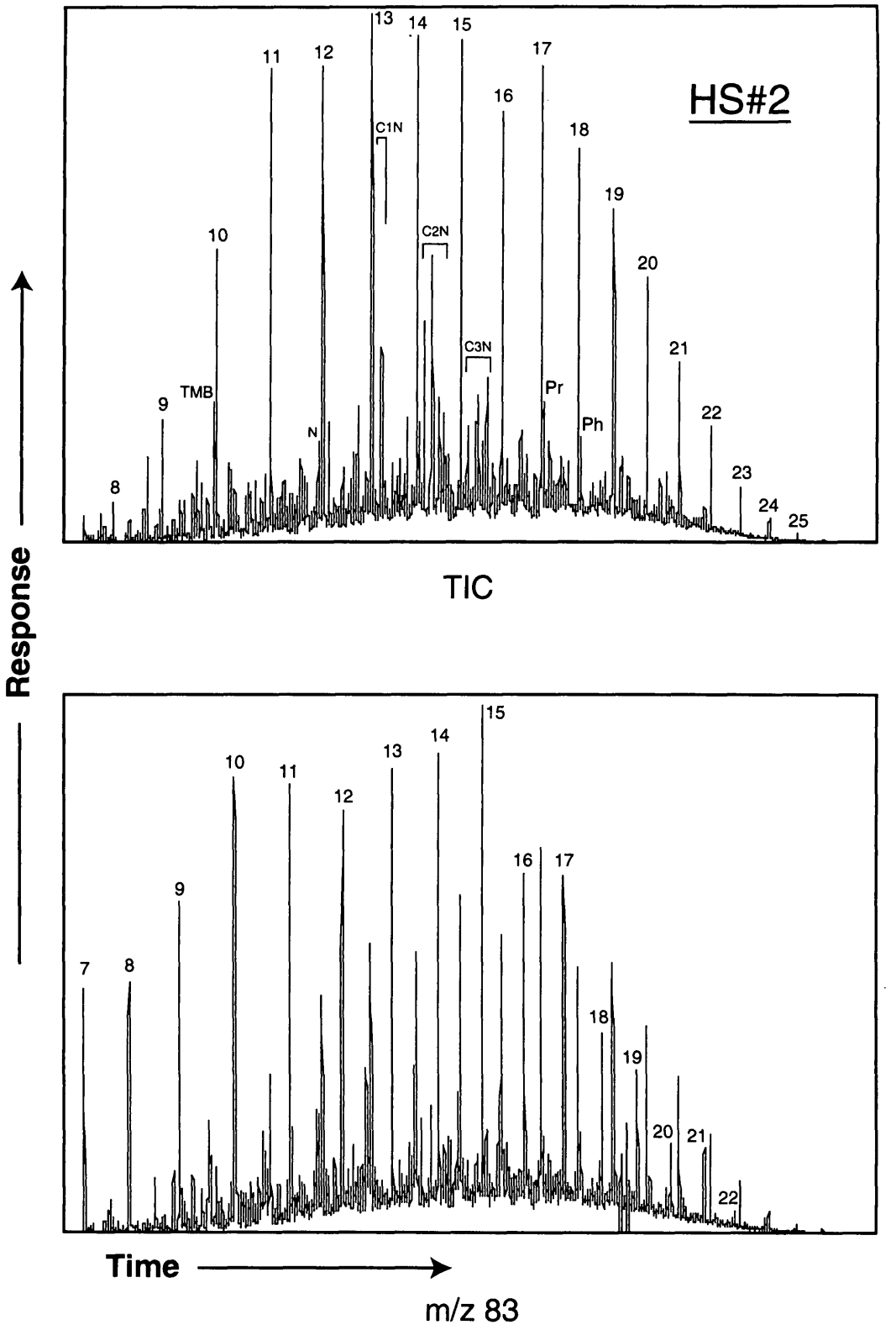

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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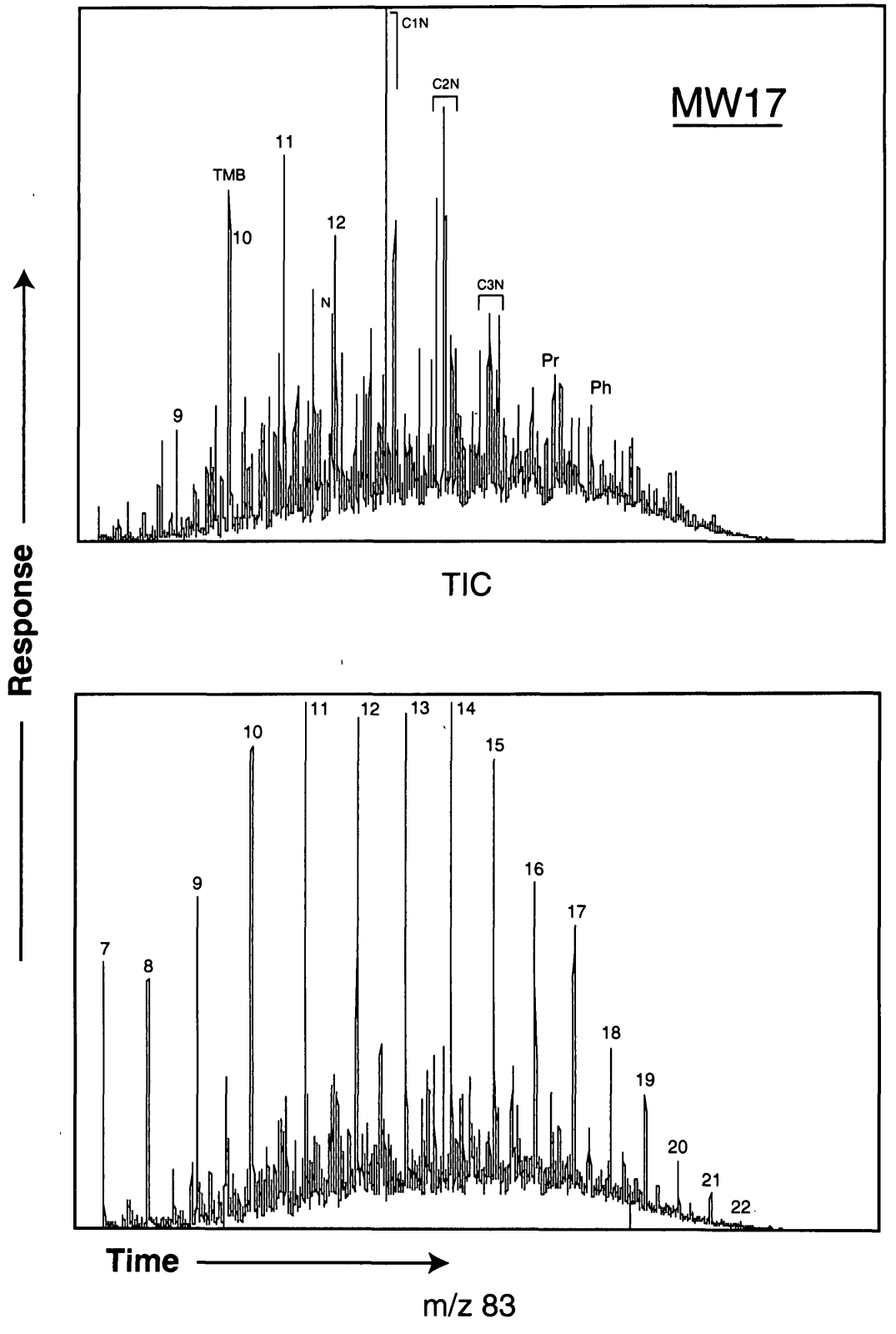

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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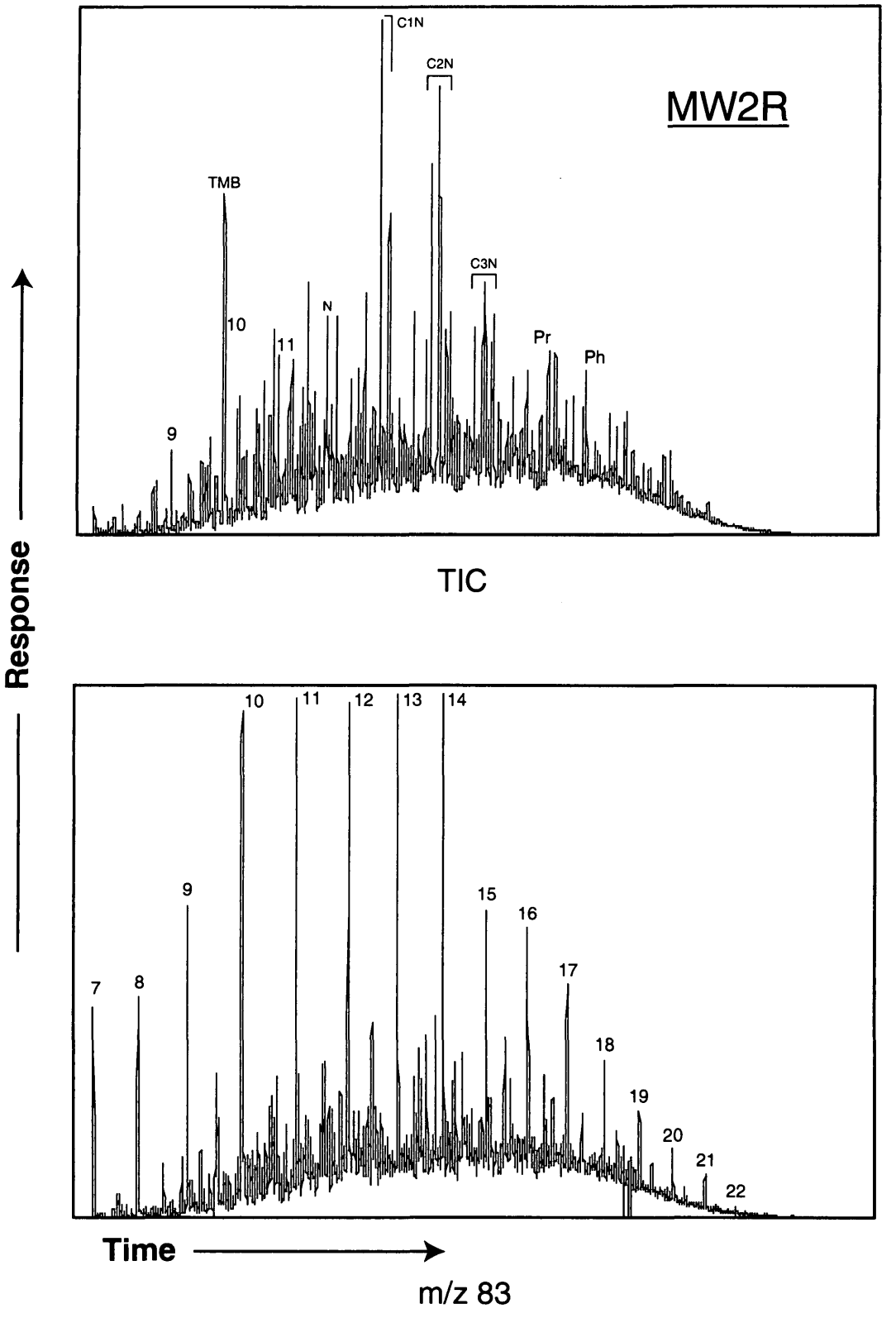
Pr = pristane; Ph = phytane.



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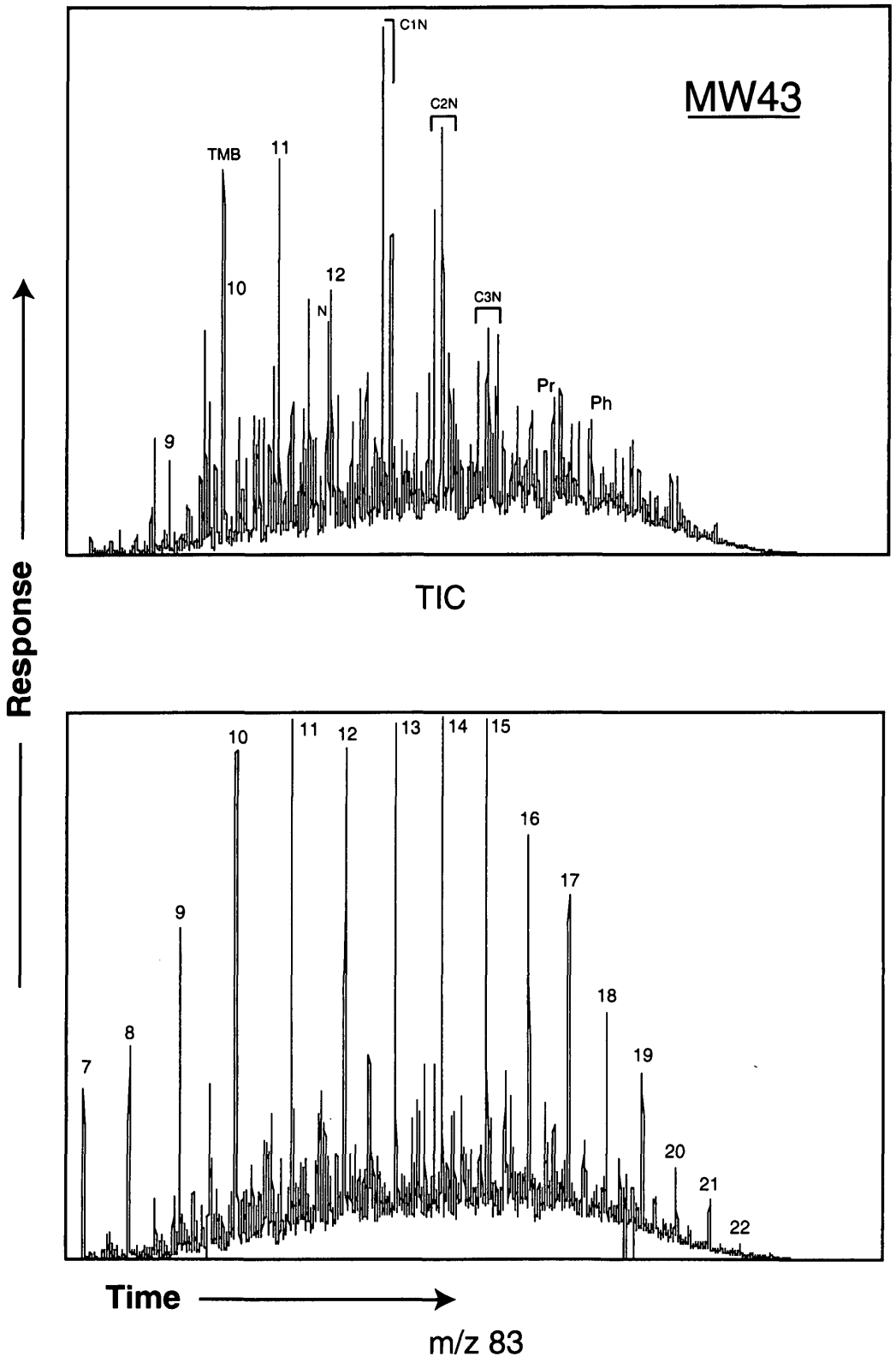

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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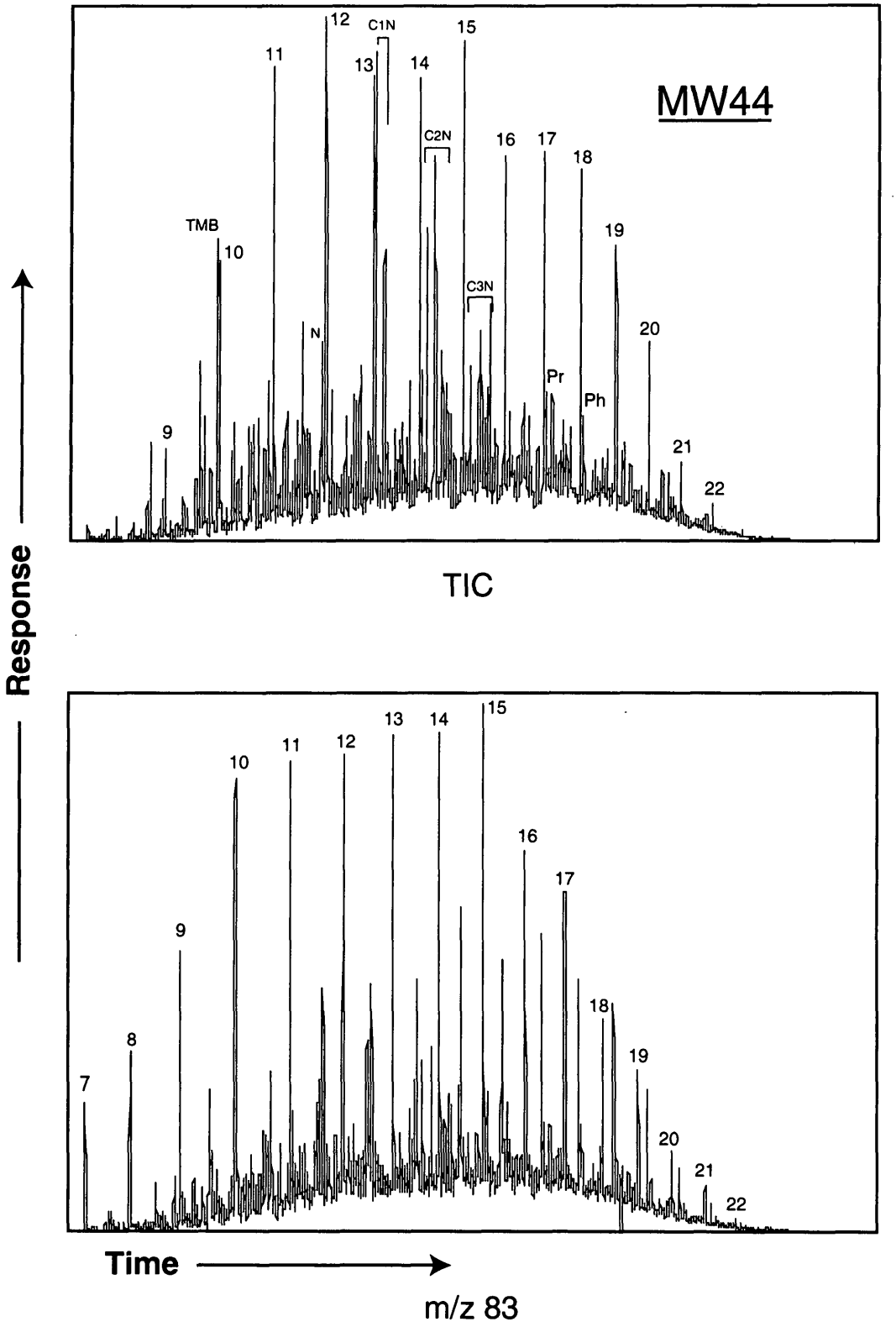

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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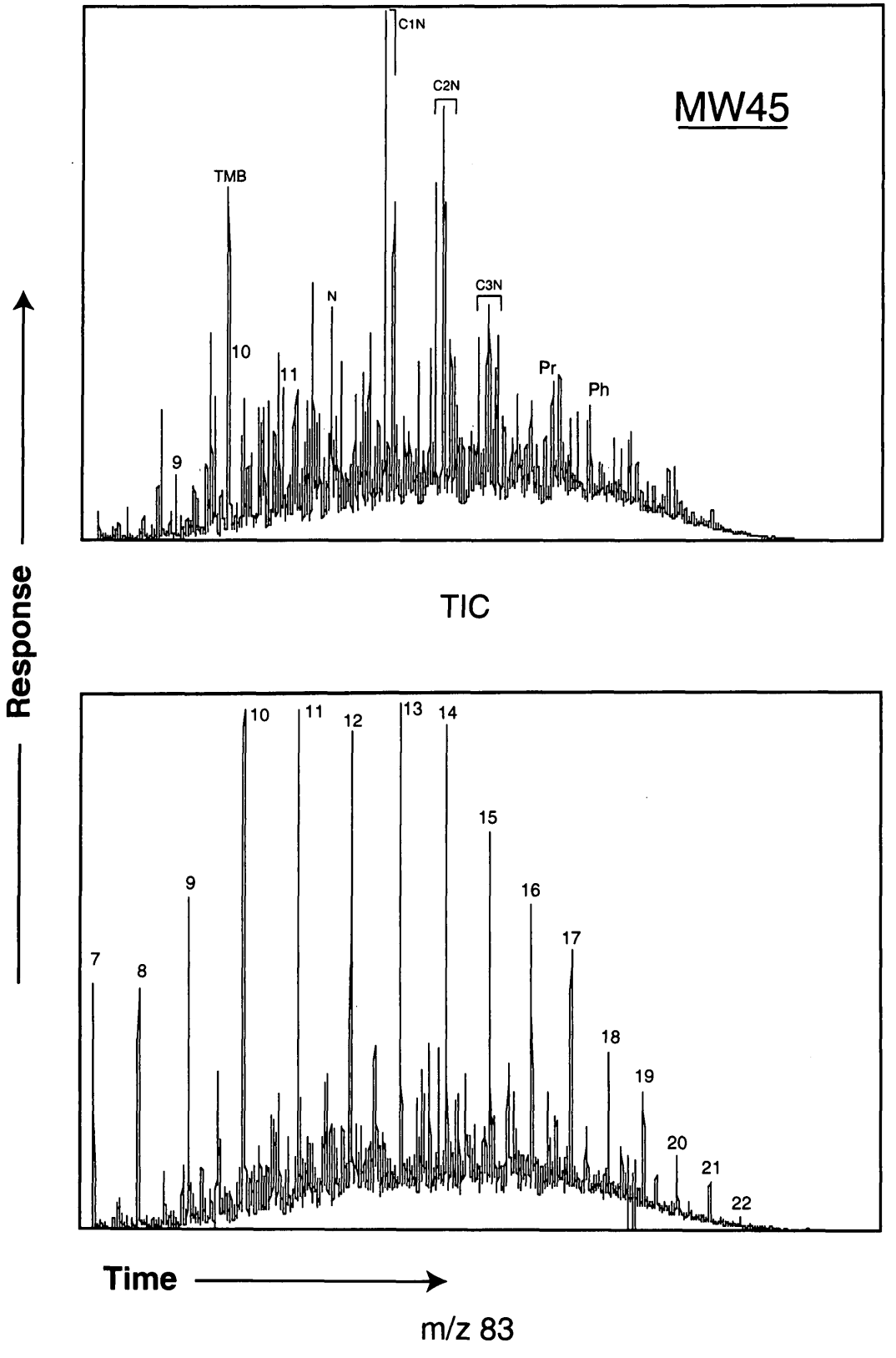

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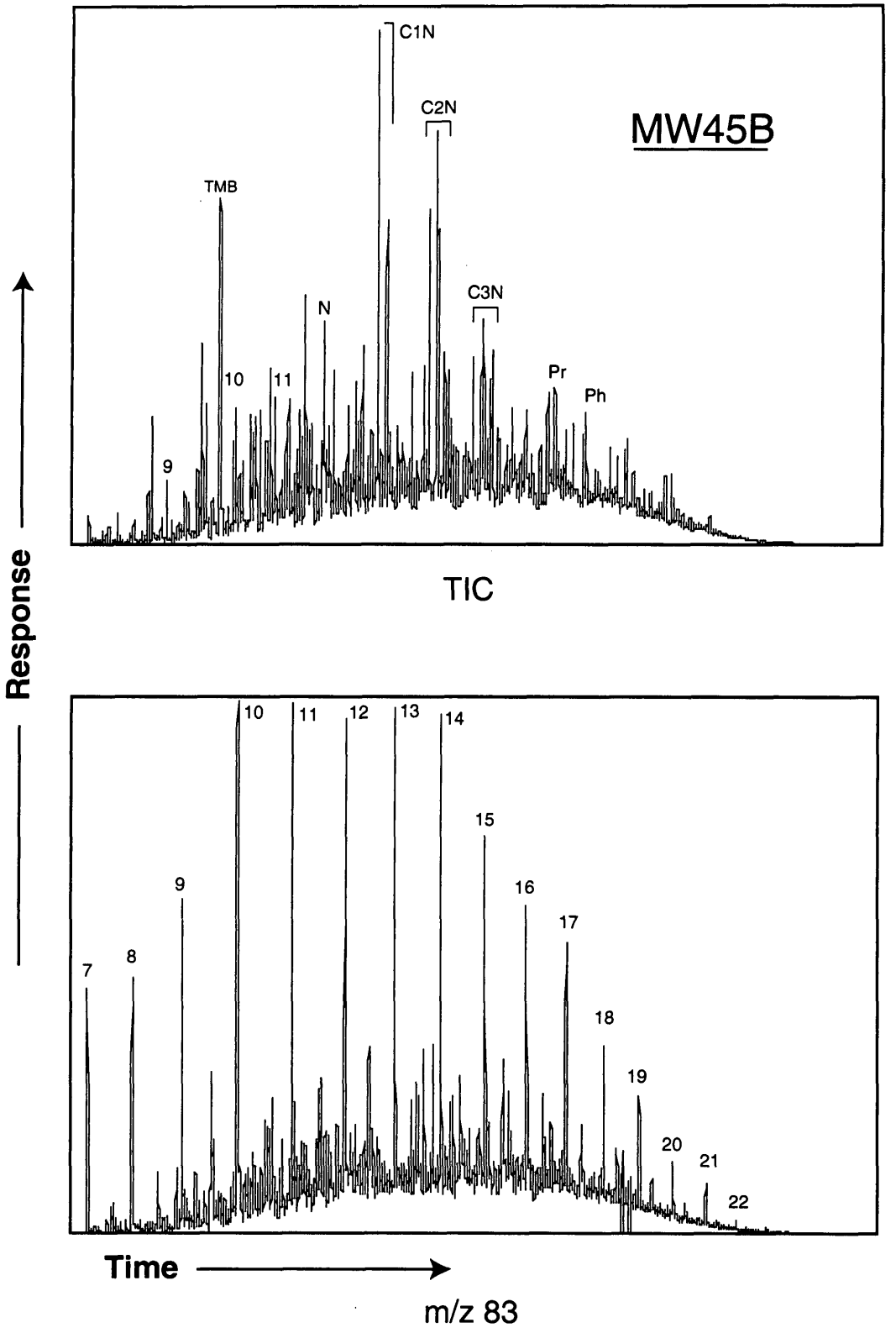

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
TMB = 1,2,4-trimethylbenzene; N, C1N, C2N, C3N = naphthalene series;
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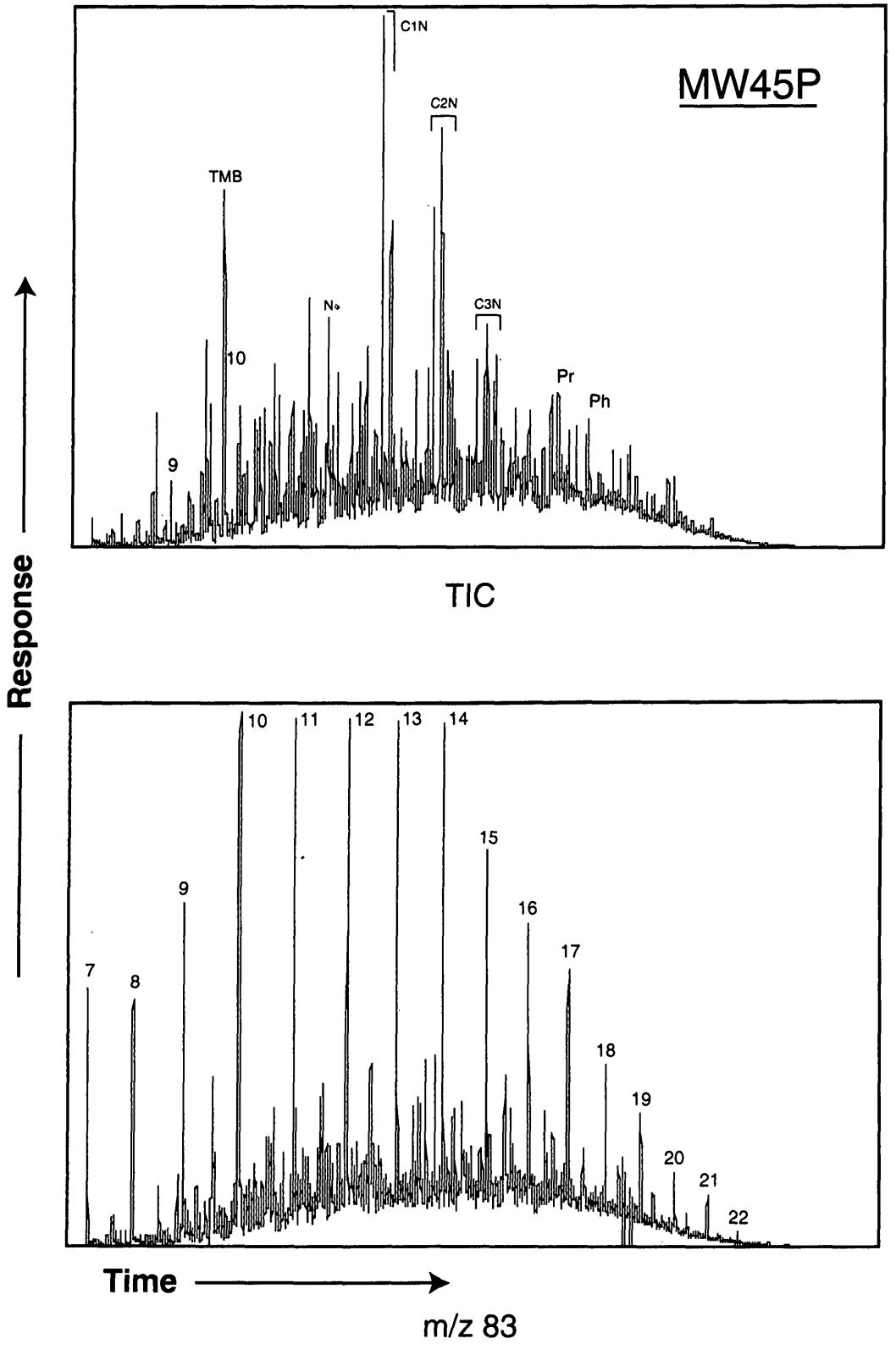

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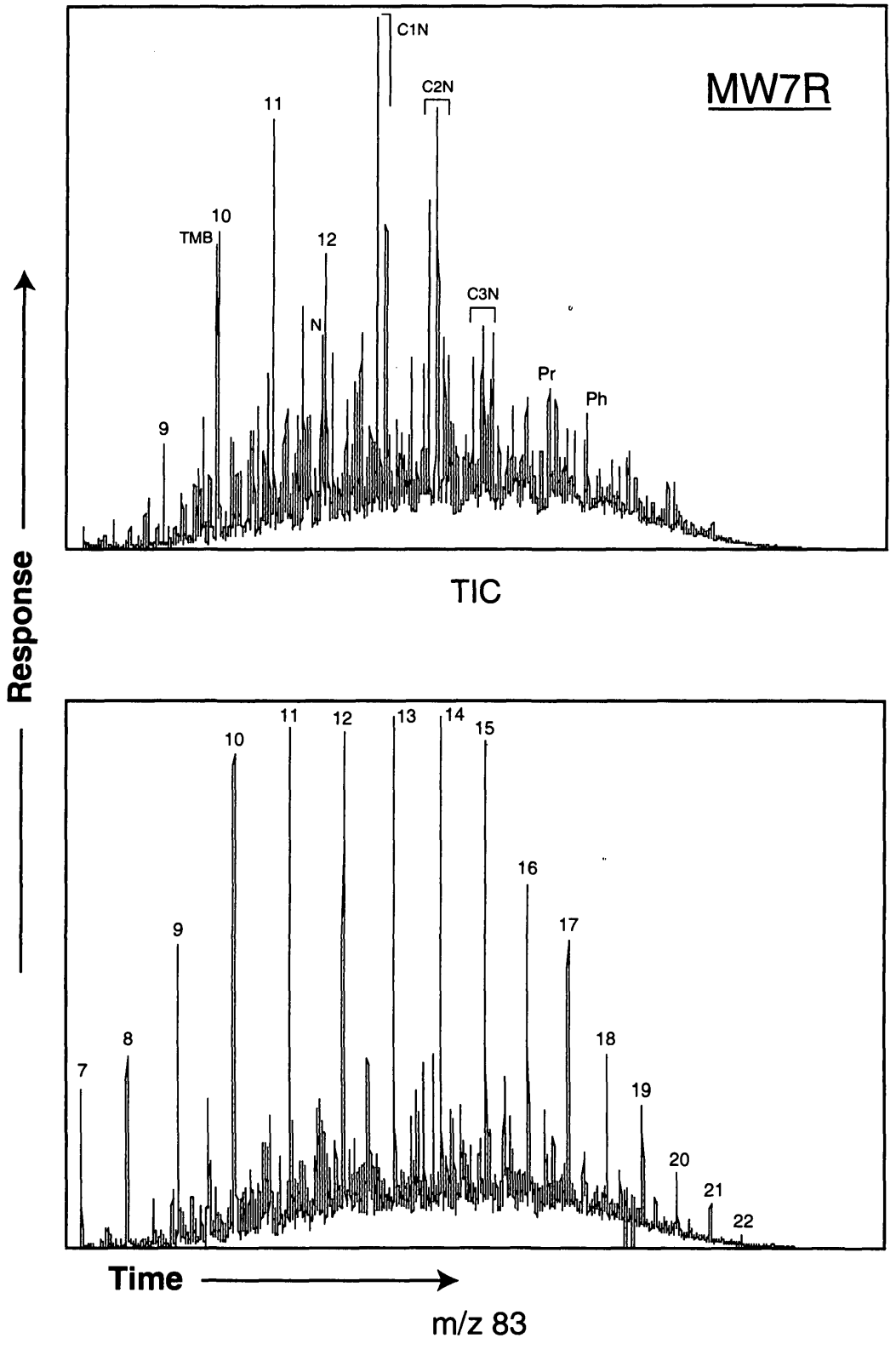

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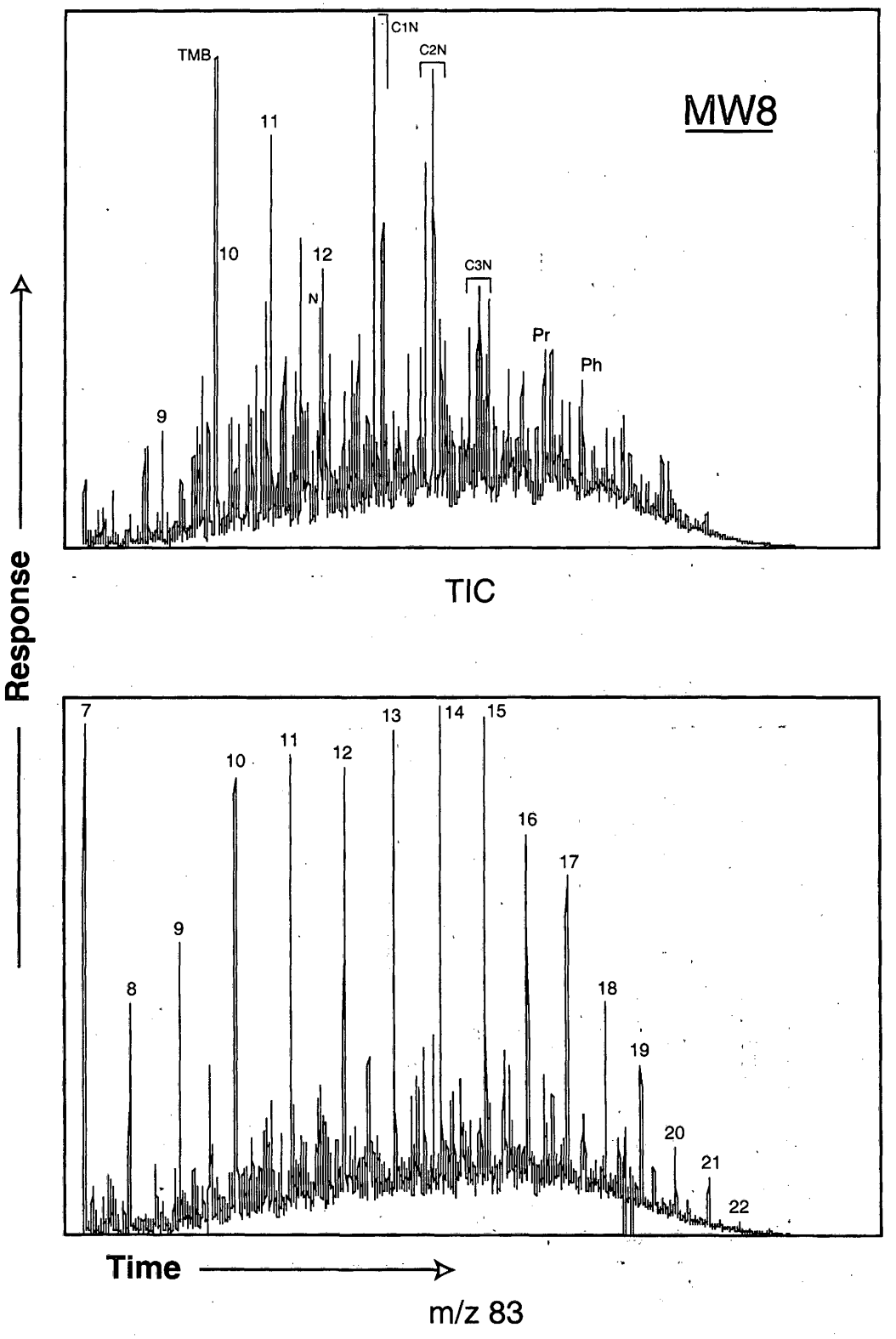

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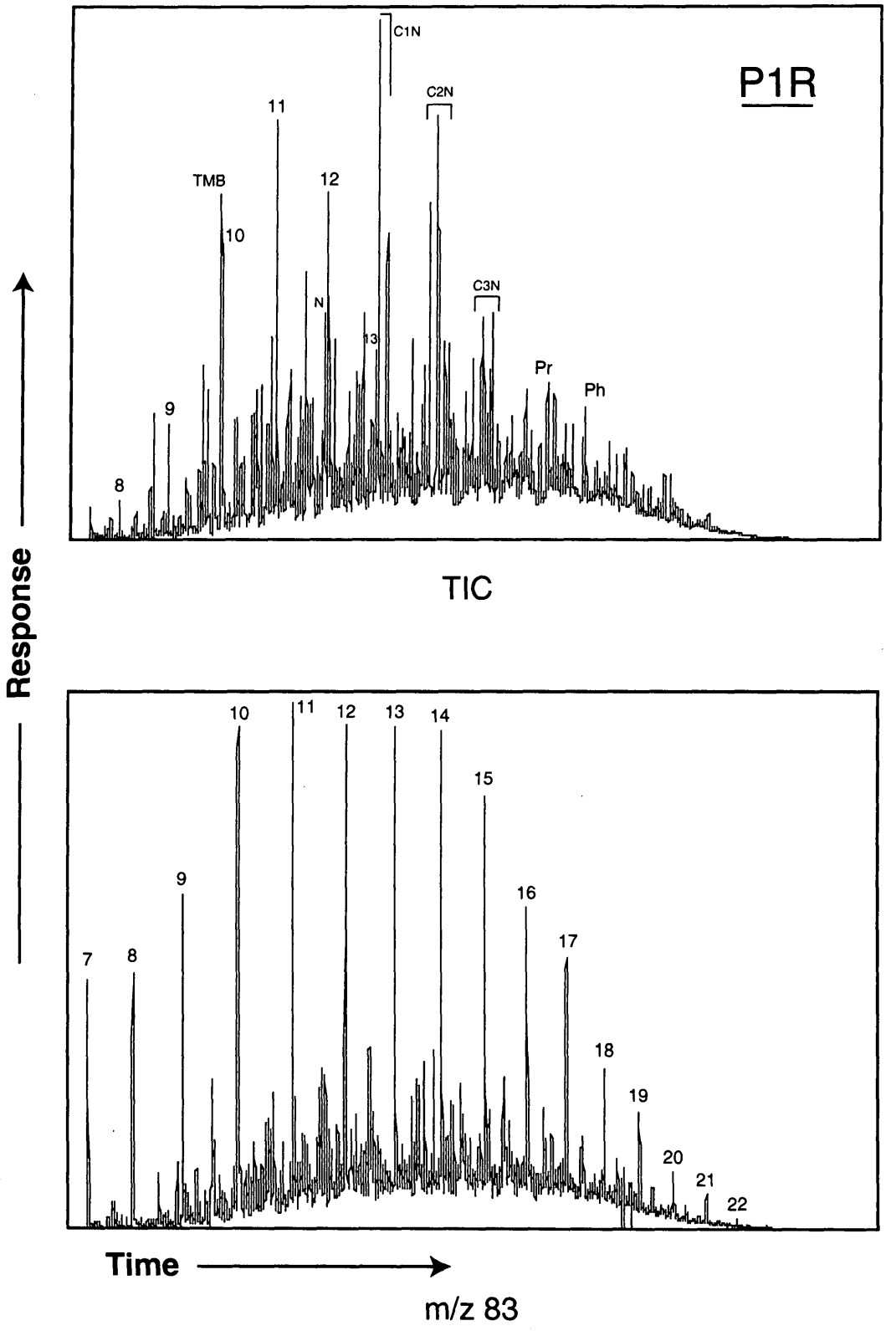

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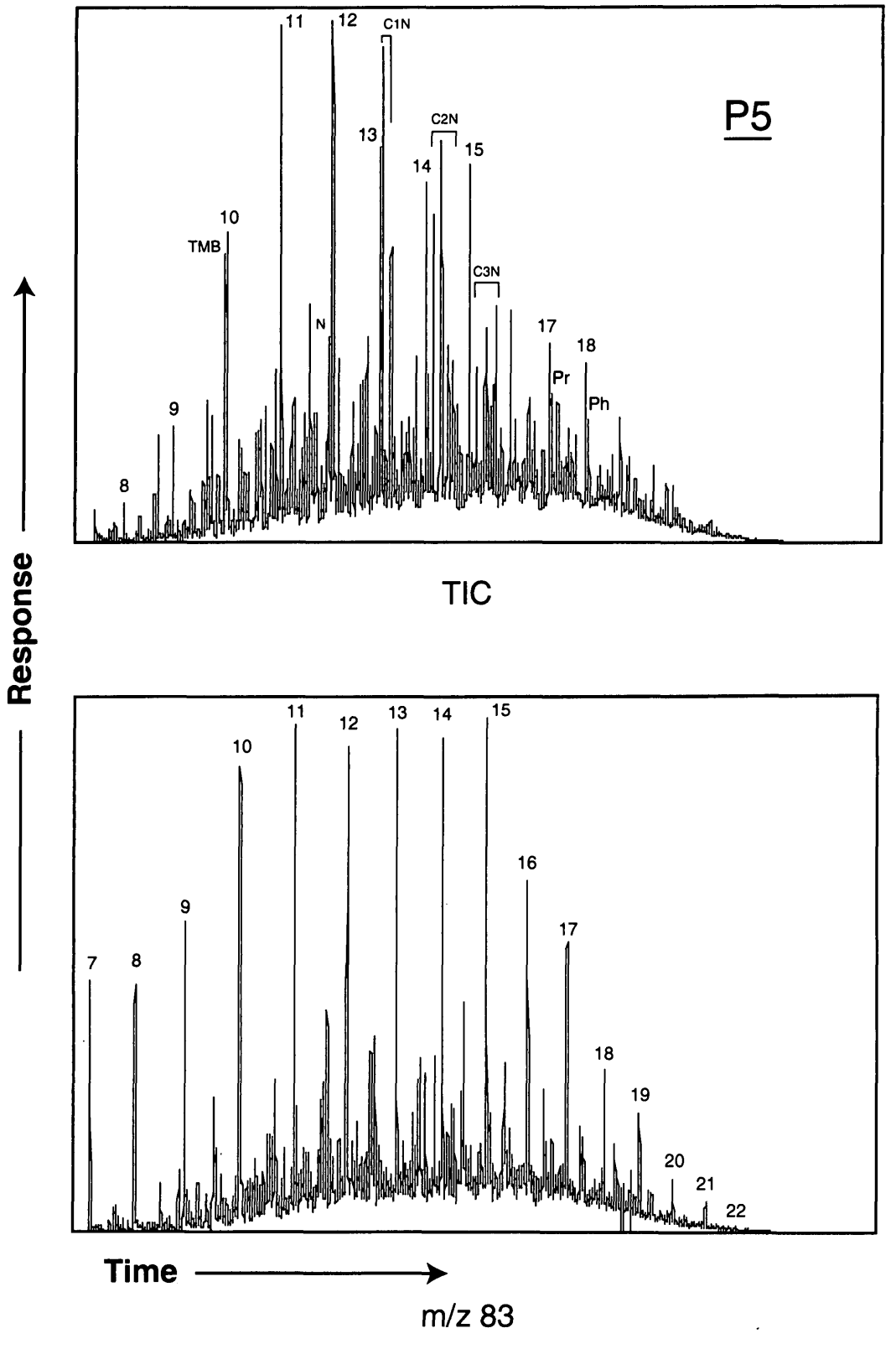

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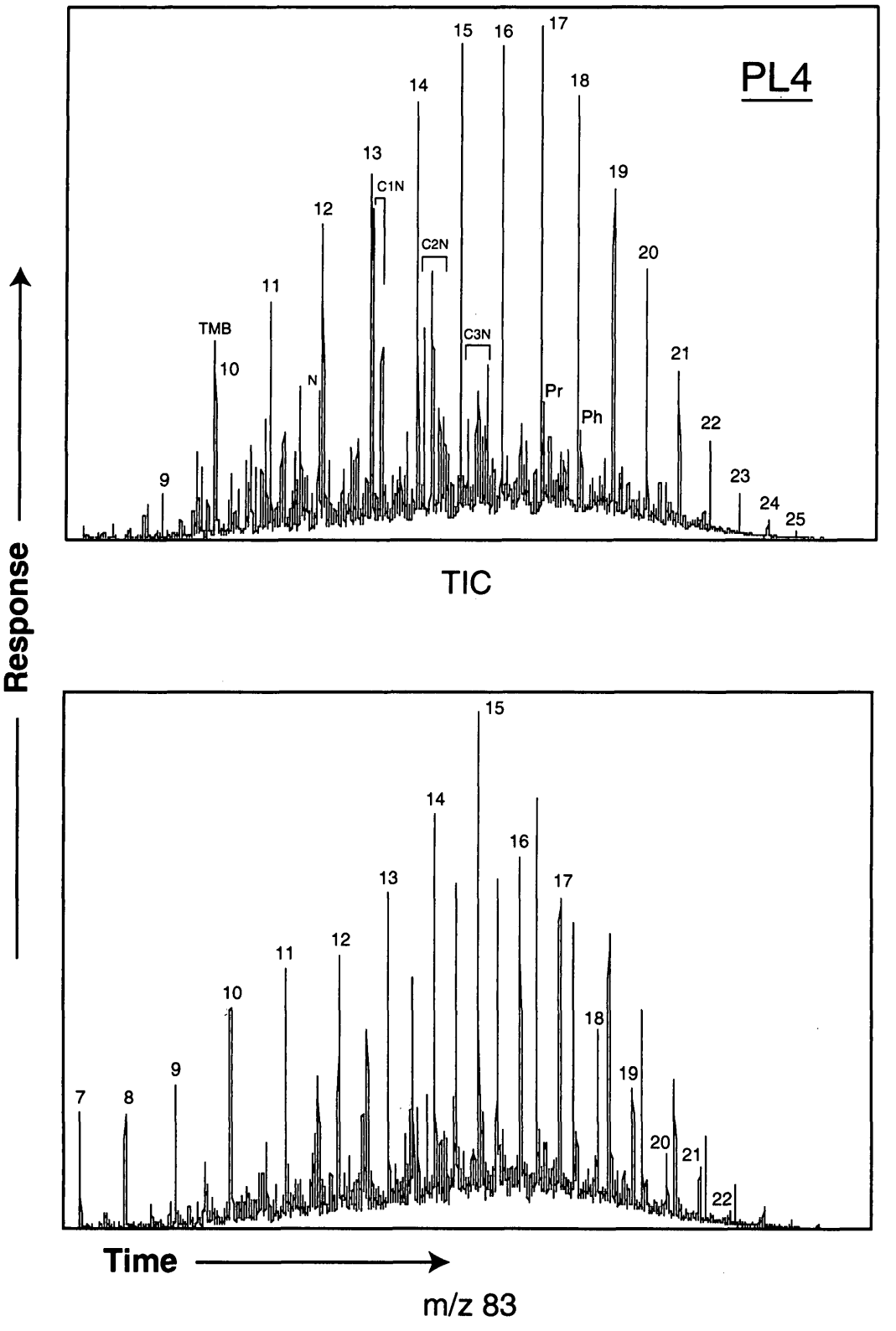

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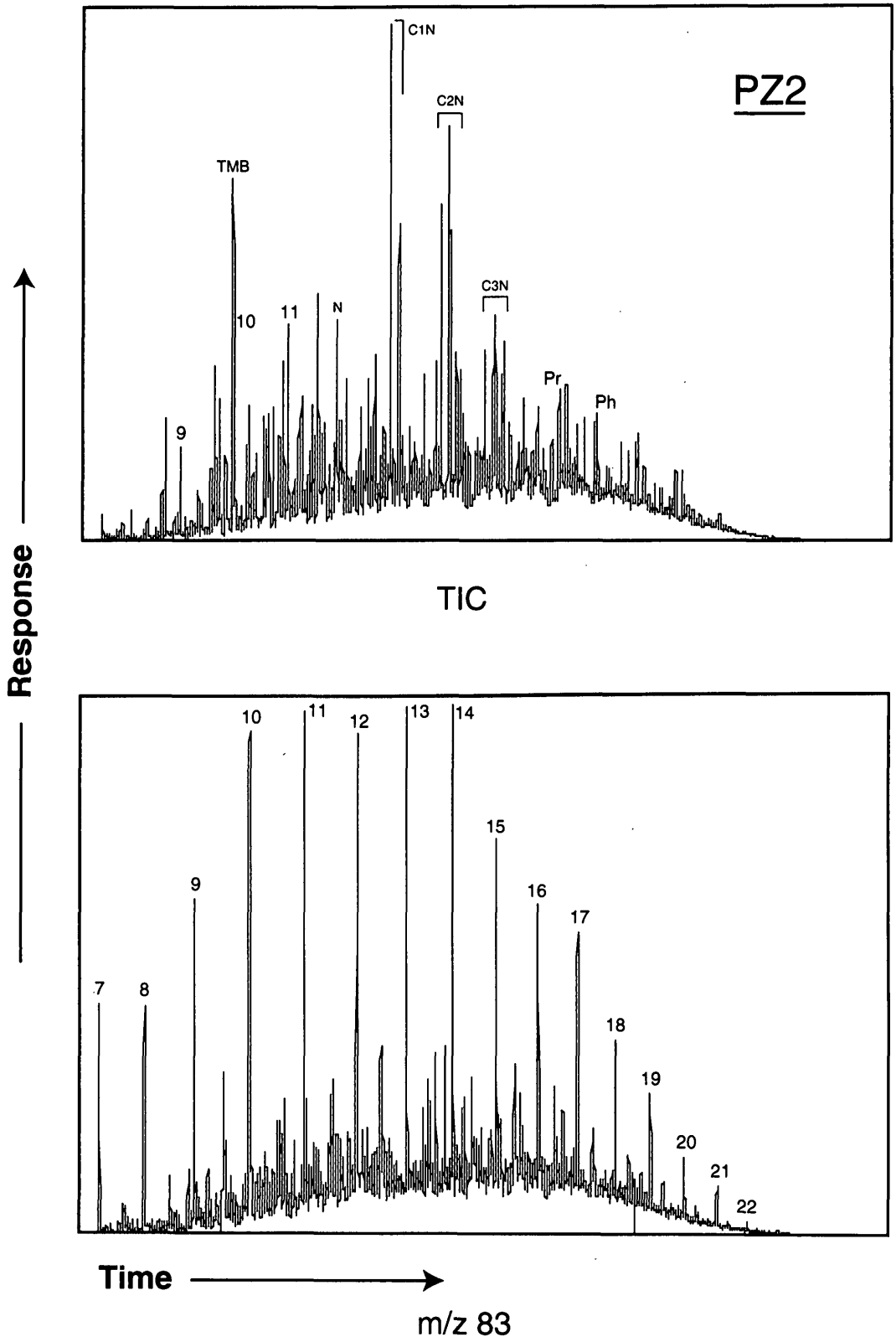

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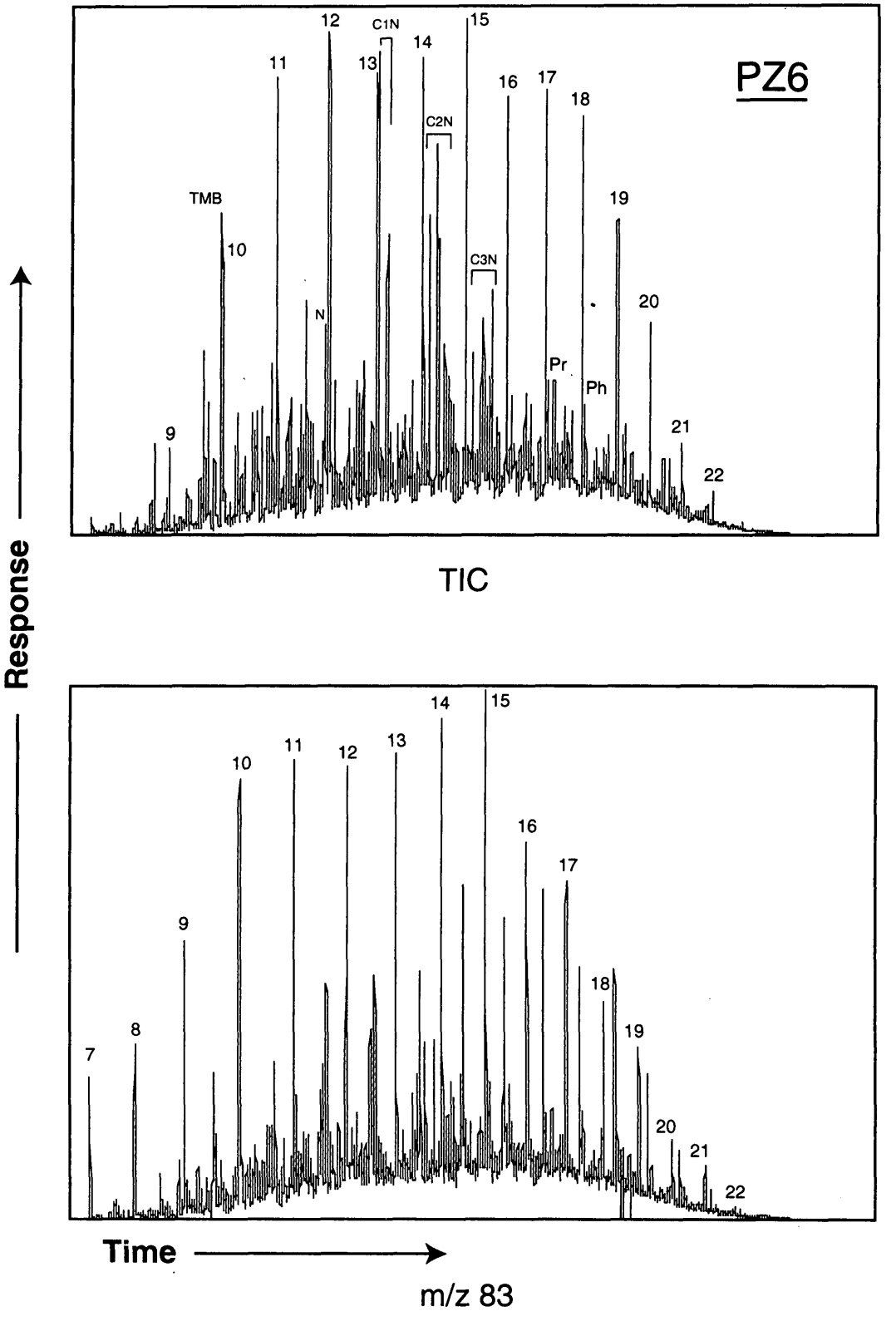

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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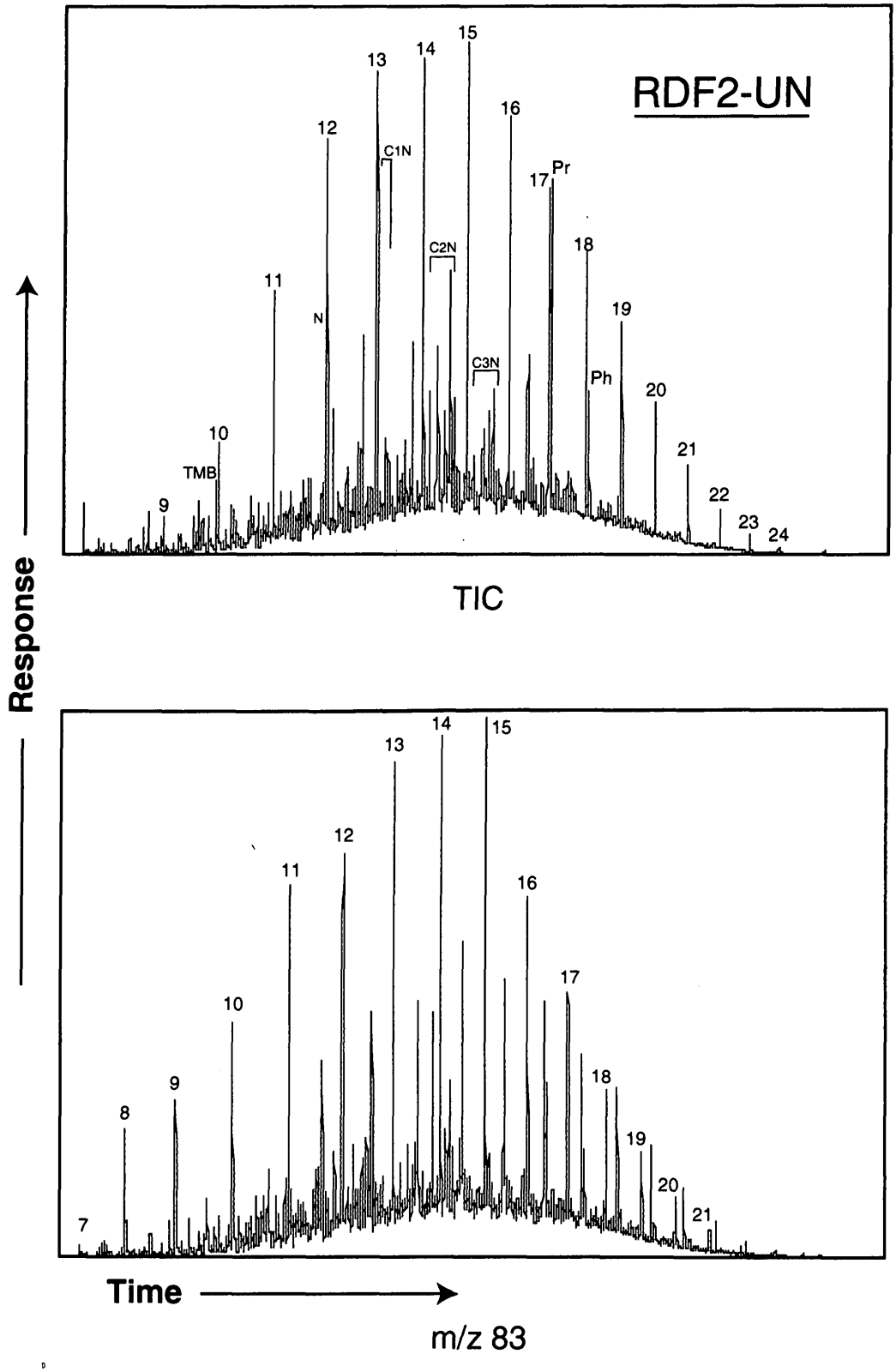

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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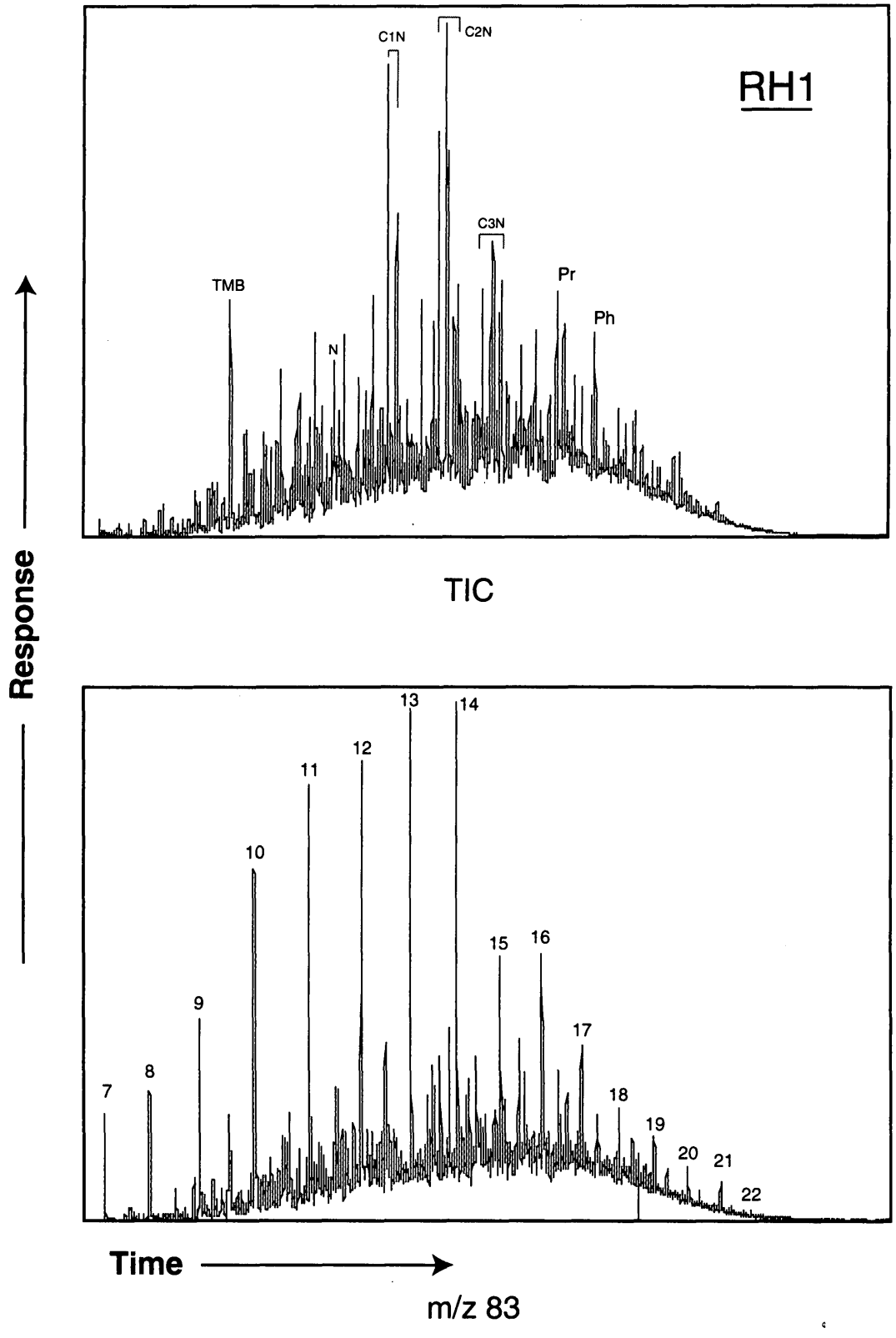

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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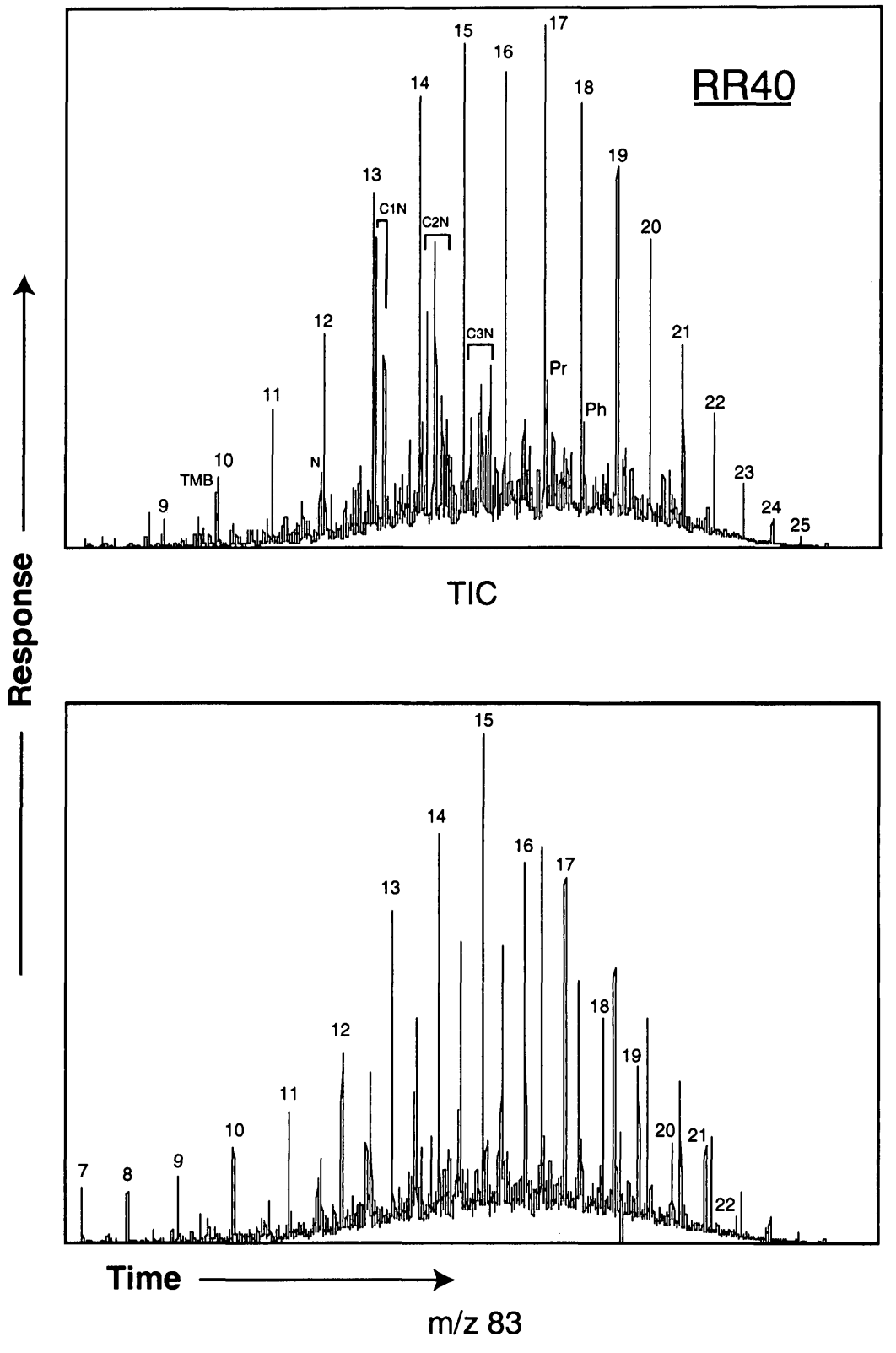

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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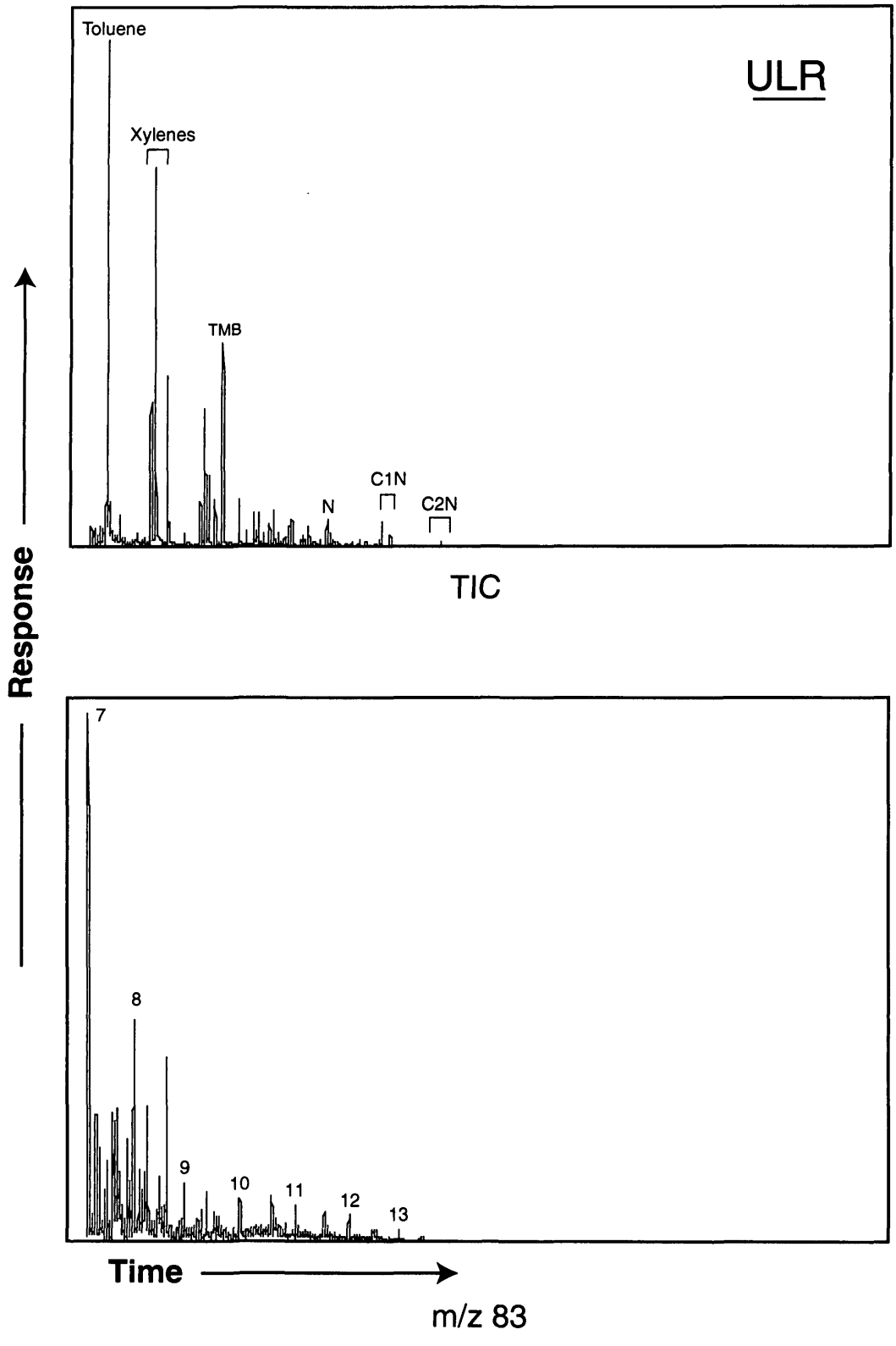

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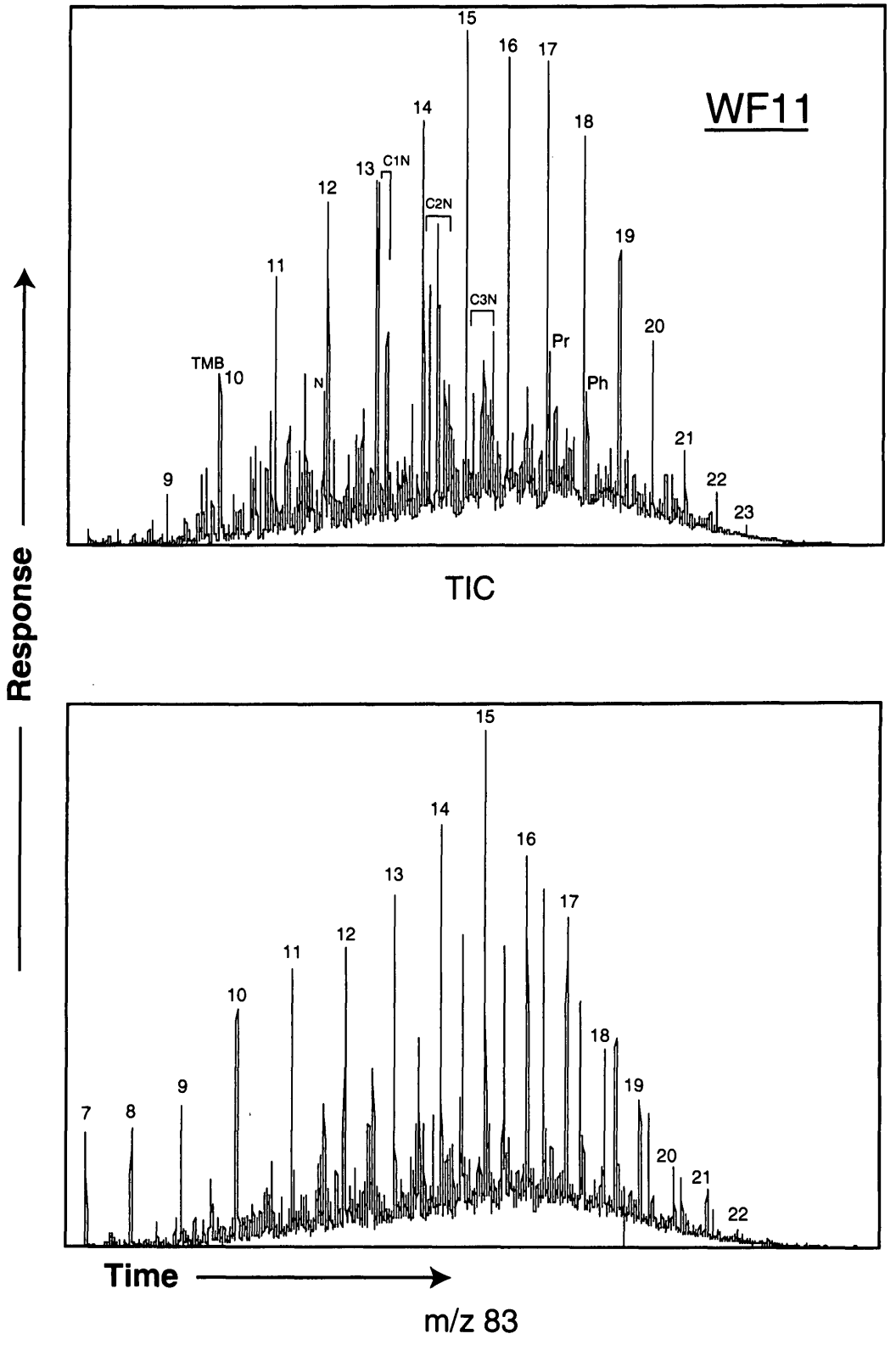

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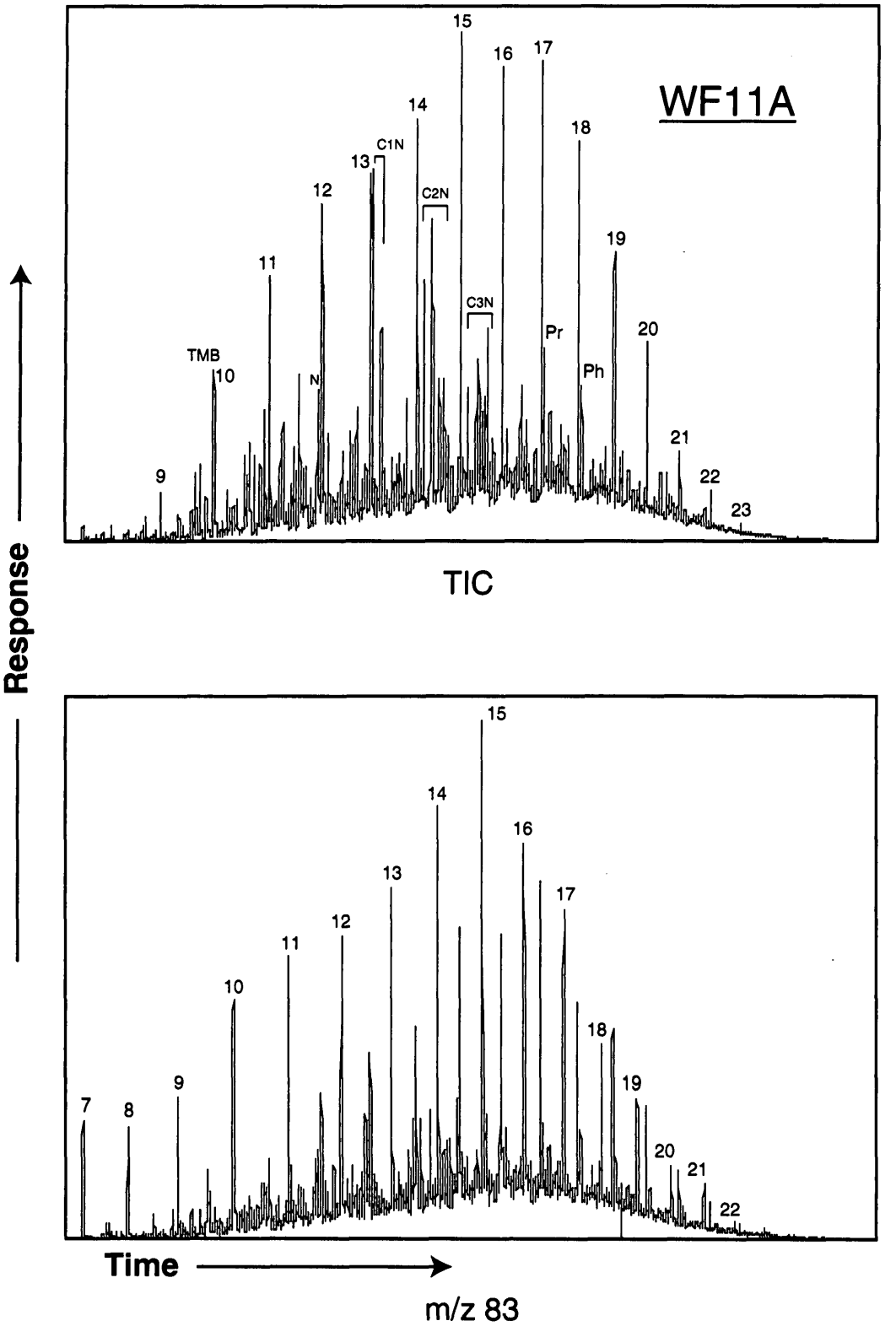

Numbers = homologs in *n*-alkane series (top) and alkylcyclohexane series (bottom).
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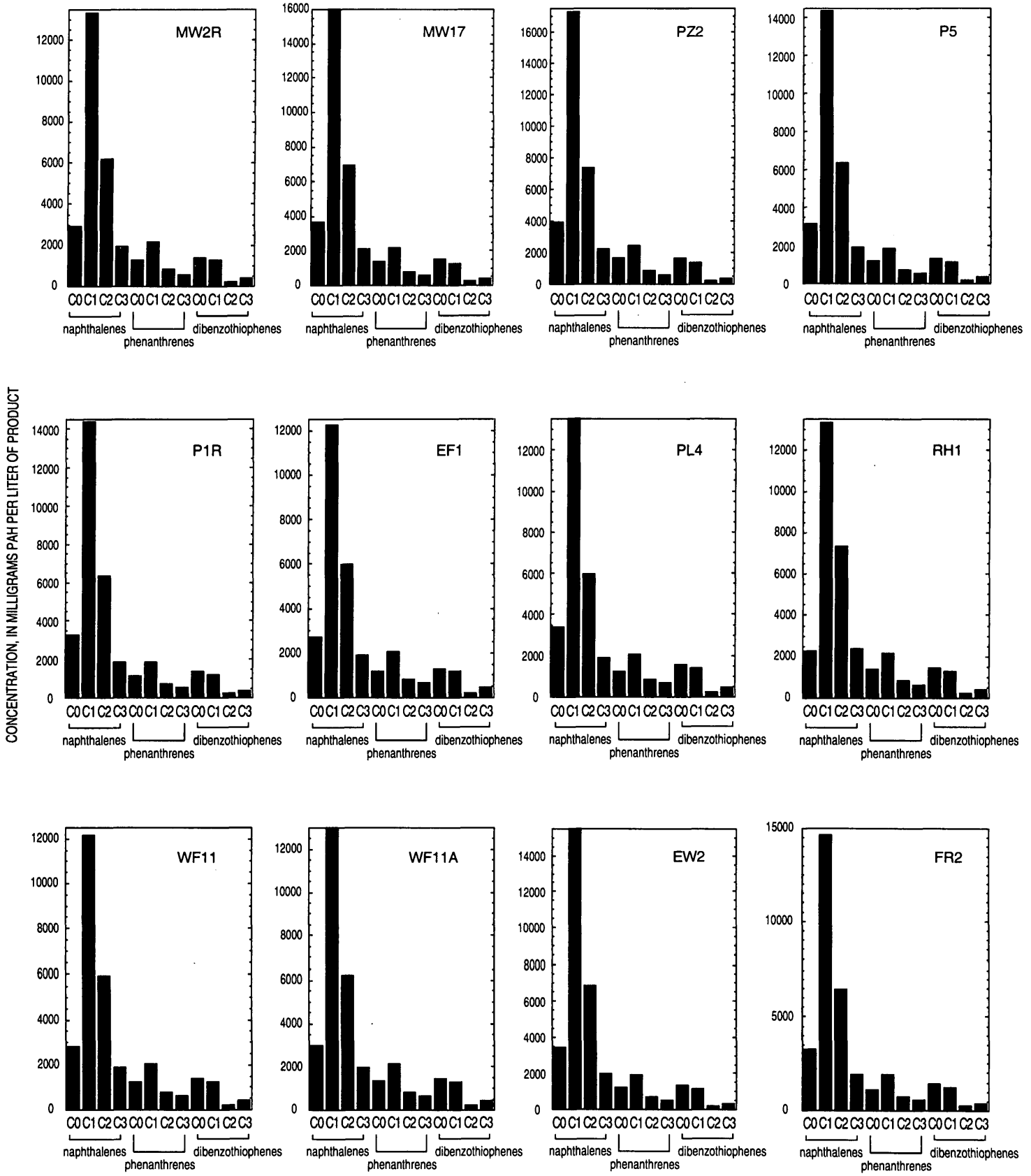
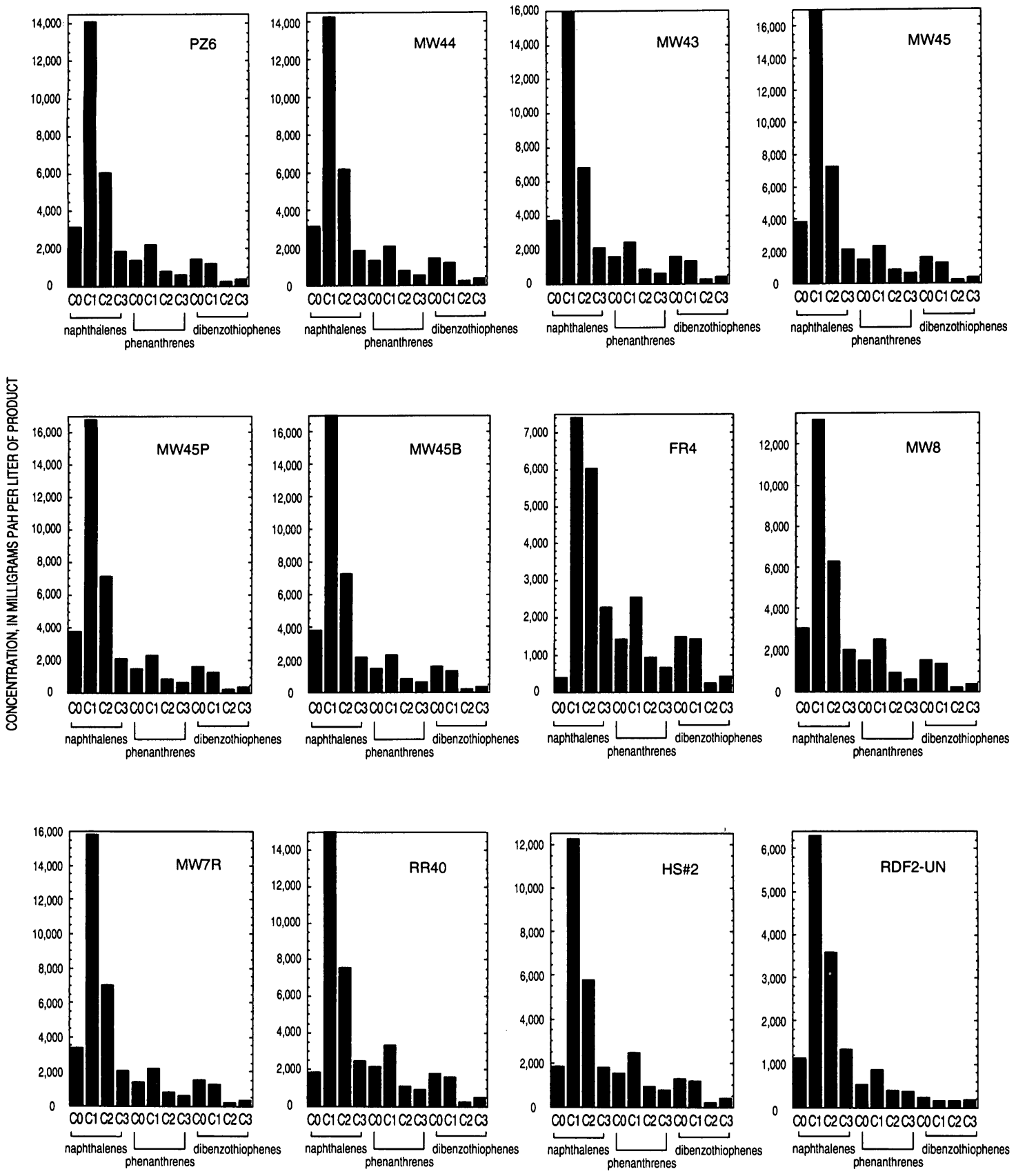
Pr = pristane; Ph = phytane.

APPENDIX H. Concentrations, in milligrams of polycyclic aromatic hydrocarbons per liter of product

Sample identifier	Location or place from which sample was obtained	1,2,4-Trimethyl-benzene	Naphthalene	2-Methyl-naphthalene	1-Methyl-naphthalene	Phenanthrene	Dibenzo-thiophene
			Light nonaqueous phase liquid samples				
MW2R	Railway yard	6,828	2,928	8,236	5,092	1,260	1,388
MW17	Railway yard	8,132	3,652	10,076	6,036	1,356	1,520
PZ2	Railway yard	9,112	3,960	10,788	6,468	1,612	1,652
P5	Railway yard	5,968	3,136	8,956	5,436	1,184	1,316
P1R	Railway yard	7,140	3,264	9,004	5,372	1,132	1,364
EF1	Railway yard-east	4,720	2,684	7,564	4,704	1,196	1,292
PL4	Railway yard-southeast	6,608	3,380	8,588	4,924	1,240	1,560
RH1	Railway yard-southeast	5,024	2,264	7,876	5,472	1,400	1,432
WF11	Railway yard-west	4,412	2,792	7,684	4,472	1,208	1,364
WF11A	Railway yard-west	4,700	2,972	8,240	4,780	1,304	1,416
EW2	Railway yard	9,196	3,404	9,768	5,728	1,196	1,324
FR2	Railway yard	9,540	3,248	9,176	5,476	1,108	1,436
PZ6	North of Main Street	7,244	3,160	8,736	5,344	1,372	1,420
MW44	North of Main Street	7,140	3,160	8,908	5,372	1,320	1,448
MW43	North of Main Street	9,408	3,728	9,936	5,972	1,560	1,580
MW45	North of Main Street	8,368	3,820	10,584	6,372	1,472	1,588
MW45P	North of Main Street	8,724	3,764	10,504	6,292	1,440	1,572
MW45B	North of Main Street	8,676	3,816	10,620	6,360	1,484	1,588
FR4	North of Main Street	1,580	396	4,004	3,420	1,412	1,472
MW8	North of Main Street	8,816	3,012	8,124	5,064	1,488	1,508
MW7R	North of Main Street	7,212	3,336	9,832	5,952	1,372	1,488
			Reference-fuel samples				
RR40	Refinery (current diesel fuel)	1,984	1,864	9,220	5,808	2,164	1,808
HS#2	Refinery (broader refinery-cut fuel)	3,888	1,820	7,484	4,776	1,528	1,292
ULR	Refinery (unleaded regular gasoline)	17,912	1,900	1,892	1,004	120	0
COC	Refinery (crude-oil composite)	3,656	408	1,088	852	252	392
			Restek standard				
RDF2-UN	Restek Corporation	2,487	1,137	3,904	2,391	523	230

APPENDIX I. Concentrations, in milligrams of selected polycyclic aromatic hydrocarbons per liter of product


MW2R
MW17
PZ2
P5
P1R
EF1
PL4
RH1
WF11
WF11A
EW2
FR2
CONCENTRATION, IN MILLIGRAMS PAH PER LITER OF PRODUCT
C0 C1 C2 C3 C0 C1 C2 C3 C0 C1 C2 C3
naphthalenes
phenanthrenes
dibenzothiophenes


CONCENTRATION, IN MILLIGRAMS PAH PER LITER OF PRODUCT
PZ6
MW44
MW43
MW45
MW45P
MW45B
FR4
MW8
MW7R
RR40
HS#2
RDF2-UN
C0 C1 C2 C3 C0 C1 C2 C3 C0 C1 C2 C3
naphthalenes
phenanthrenes
dibenzothiophenes

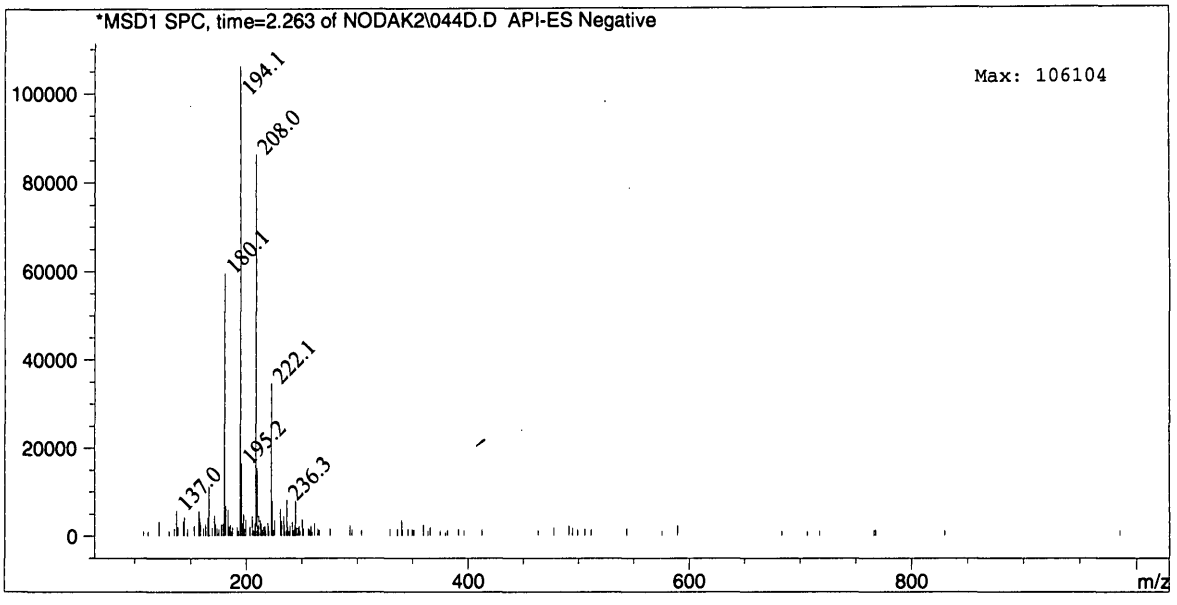
APPENDIX J. Stable carbon isotope ratio data from Zymax Forensics, San Luis Obispo, California

[Isotope ratio data for samples submitted by U.S. Geological Survey, Menlo Park; $\delta^{13}C$, stable carbon isotopes; ‰, per mil; --, no data]

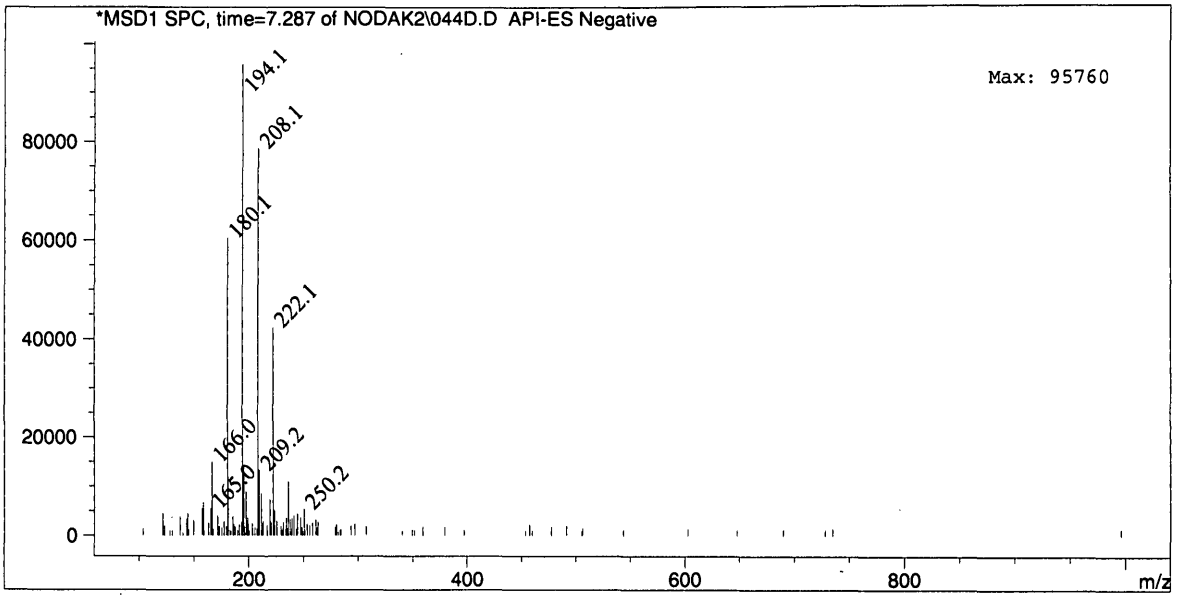
Zymax identifier	Sample identifier	Whole oil	
		$\delta^{13}C$ (‰)	$\delta^{13}C$ (‰) Duplicate
	Light nonaqueous phase liquid samples		
22763-1	MW2R	-28.57	-28.69
22763-2S	MW17	-28.67	--
22763-3	PZ2	-28.62	--
22763-4	P5	-28.80	--
22763-5	P1R	-29.05	--
22763-6	EF1	-29.19	--
22763-7	PL4	-29.60	--
22763-8	RH1	-28.50	--
22763-9	WF11	-29.02	--
22763-10	WF11A	-28.96	--
22763-11	EW2	-28.71	-28.77
22763-12	FR2	-28.68	--
22763-13	PZ6	-28.58	--
22763-14	MW44	-28.74	--
22763-15	MW43	-28.36	--
22763-16	MW45	-28.41	--
22763-17	MW45P	-28.30	--
22763-18	MW45B	-28.32	--
22763-19	FR4	-28.31	--
22763-20	MW8	-28.30	--
22763-21	MW7R	-28.84	-28.78
	Reference-fuel samples		
22763-22	RR40	-29.52	--
22763-23	HS#2	-29.43	--
22763-24	ULR	-29.52	--
22763-25	COC	-29.72	--
22763-26	NSC	-29.64	--
	Quality-assurance samples		
NBS OIL STANDARD		-29.82	--
NBS OIL STANDARD--DUPLICATE		-29.78	--

APPENDIX K. Flow injection/negative electrospray ionization mass spectra

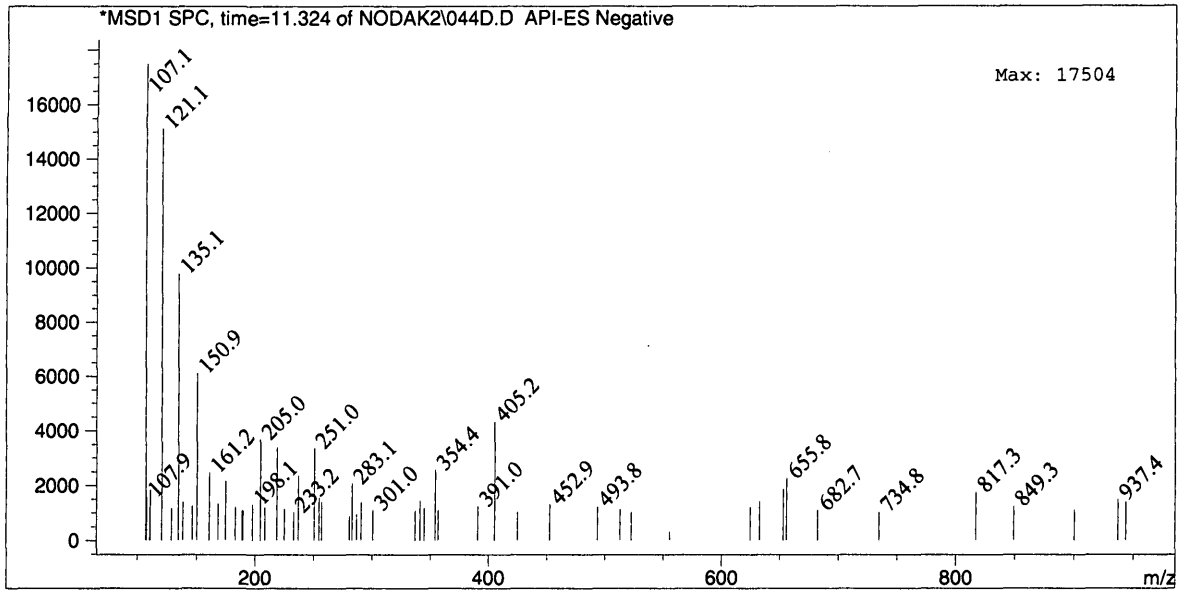
RR40:


*MSD1 SPC, time=2.263 of NODAK2\044D.D API-ES Negative
Max: 106104
194.1
208.0
180.1
222.1
195.2
236.3
137.0
100000
80000
60000
40000
20000
0
200
400
600
800
m/z

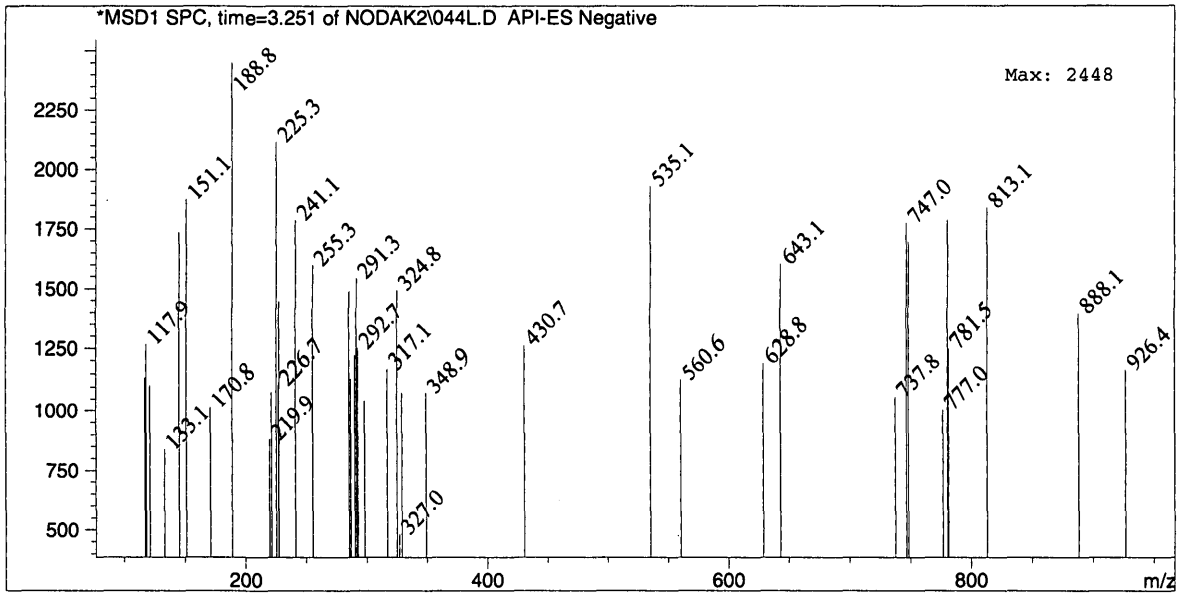
HS#2:


*MSD1 SPC, time=7.287 of NODAK2\044D.D API-ES Negative
Max: 95760
194.1
208.1
180.1
222.1
166.0
209.2
165.0
250.2
80000
60000
40000
20000
0
200
400
600
800
m/z

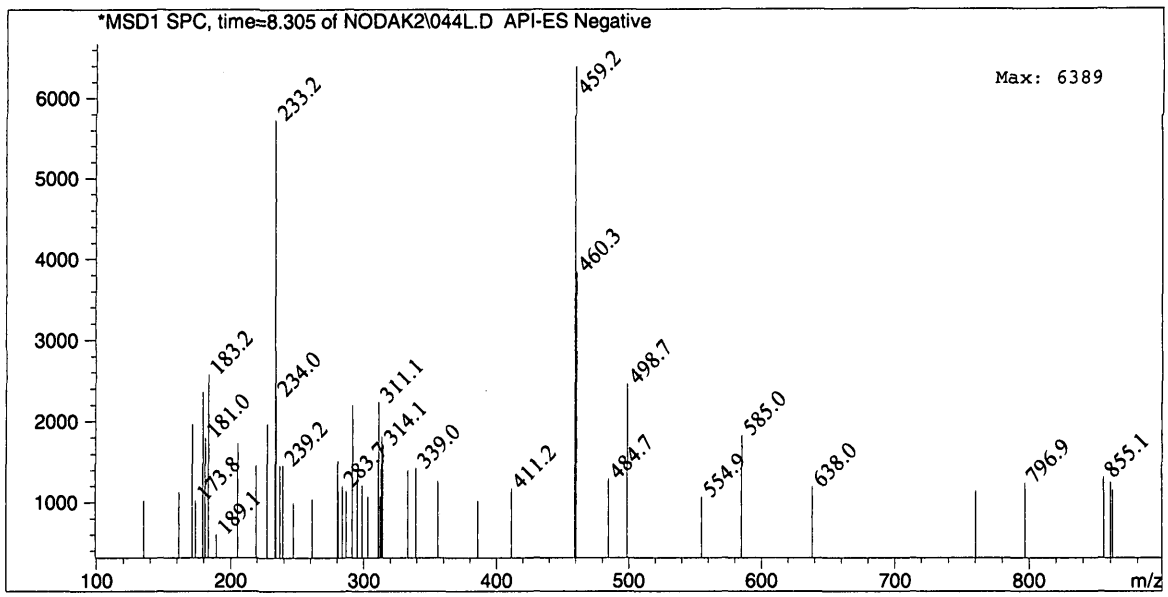
Unleaded Regular:



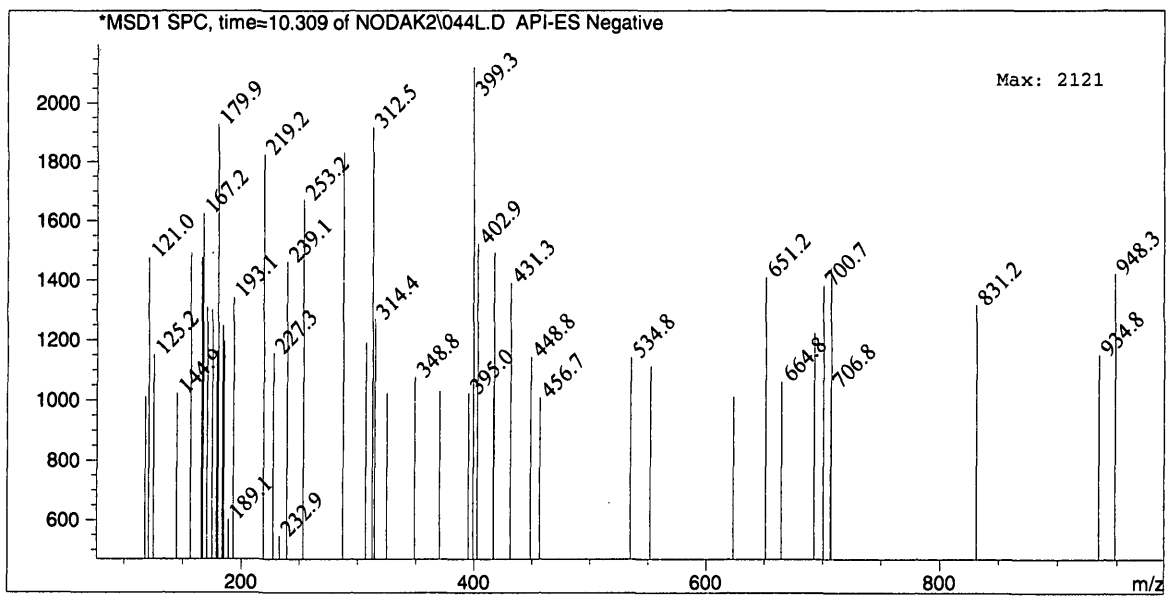
Nalco 5375A:



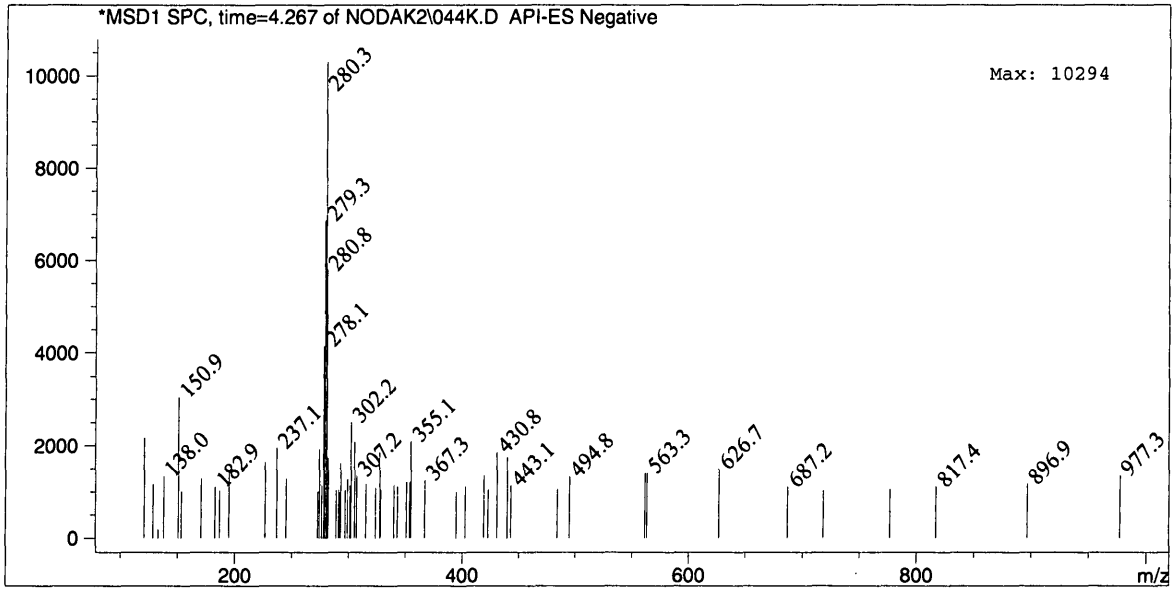
Stadis 450:



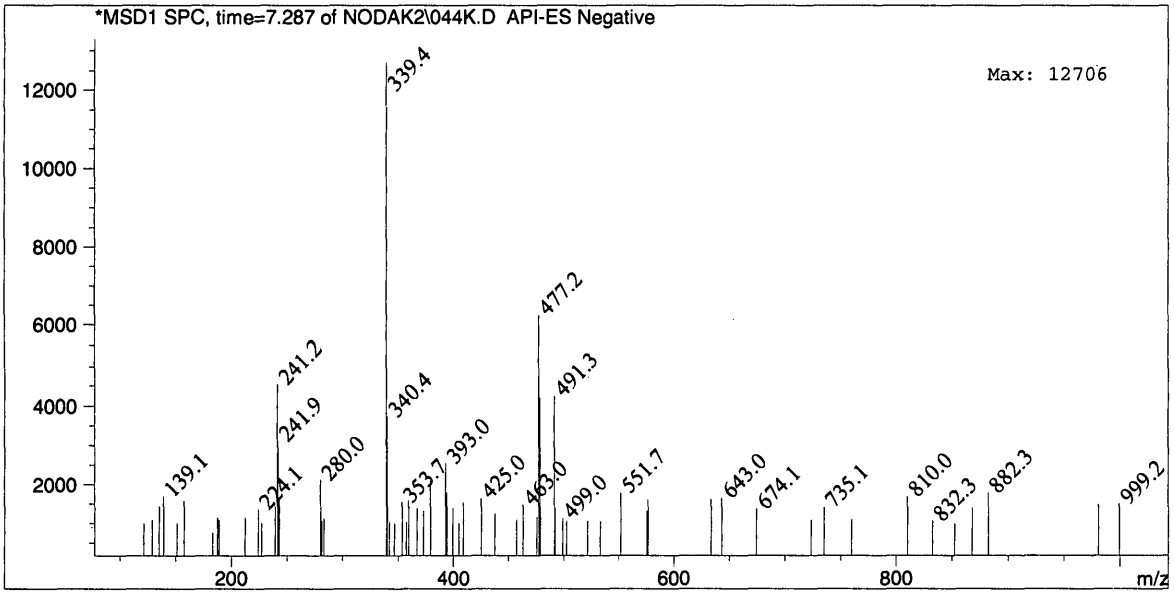
Para Flow 511:



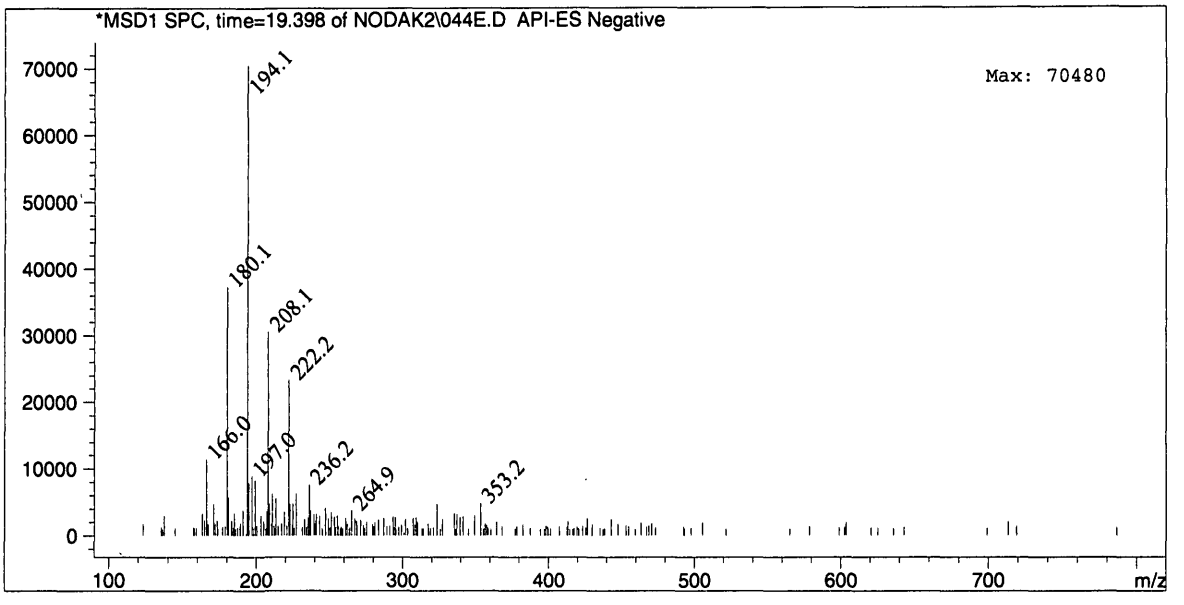
DCI 6A:



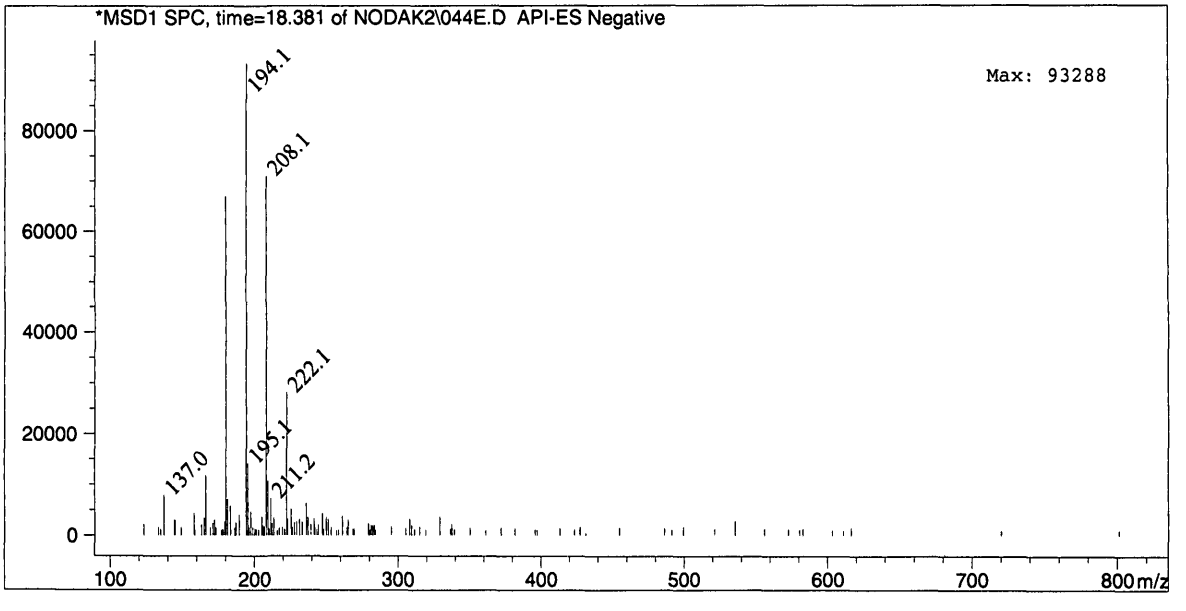
Unisol Red B50:



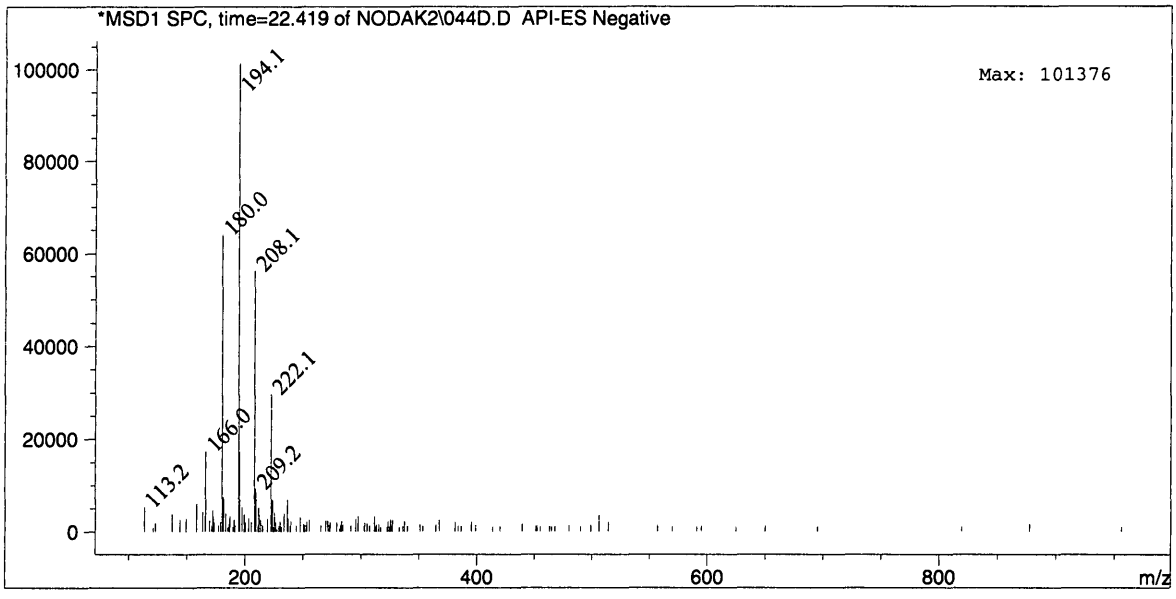
MW2R:


*MSD1 SPC, time=19.398 of NODAK2\044E.D API-ES Negative
Max: 70480
194.1
180.1
208.1
222.2
166.0
197.0
236.2
264.9
353.2
70000
60000
50000
40000
30000
20000
10000
0
100
200
300
400
500
600
700
m/z

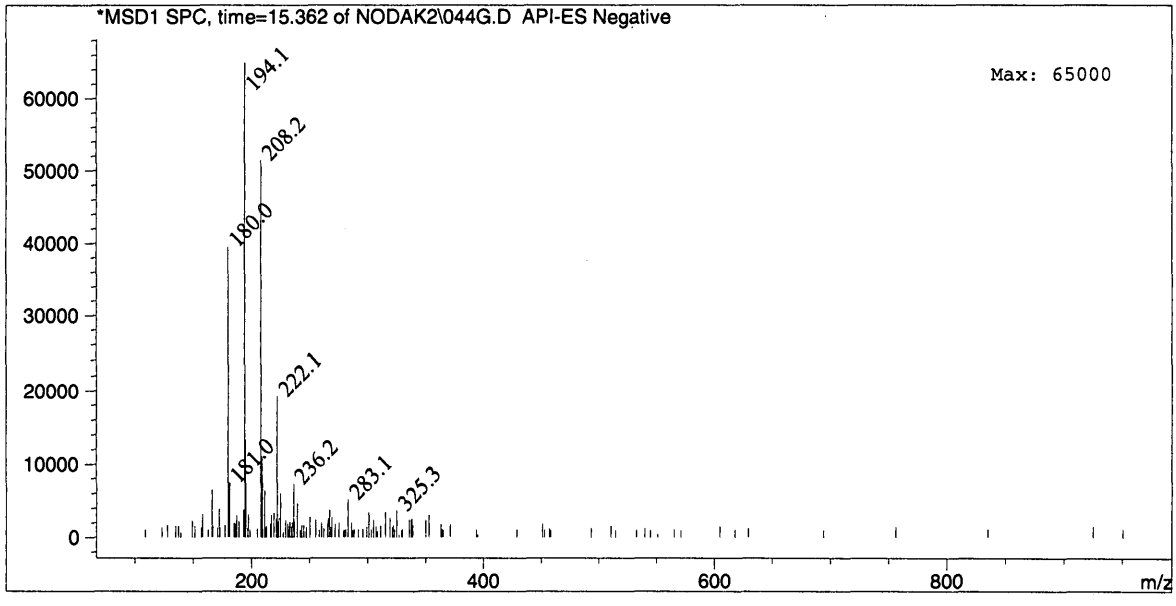
MW17:


*MSD1 SPC, time=18.381 of NODAK2\044E.D API-ES Negative
Max: 93288
194.1
208.1
222.1
195.1
211.2
137.0
80000
60000
40000
20000
0
100
200
300
400
500
600
700
800m/z

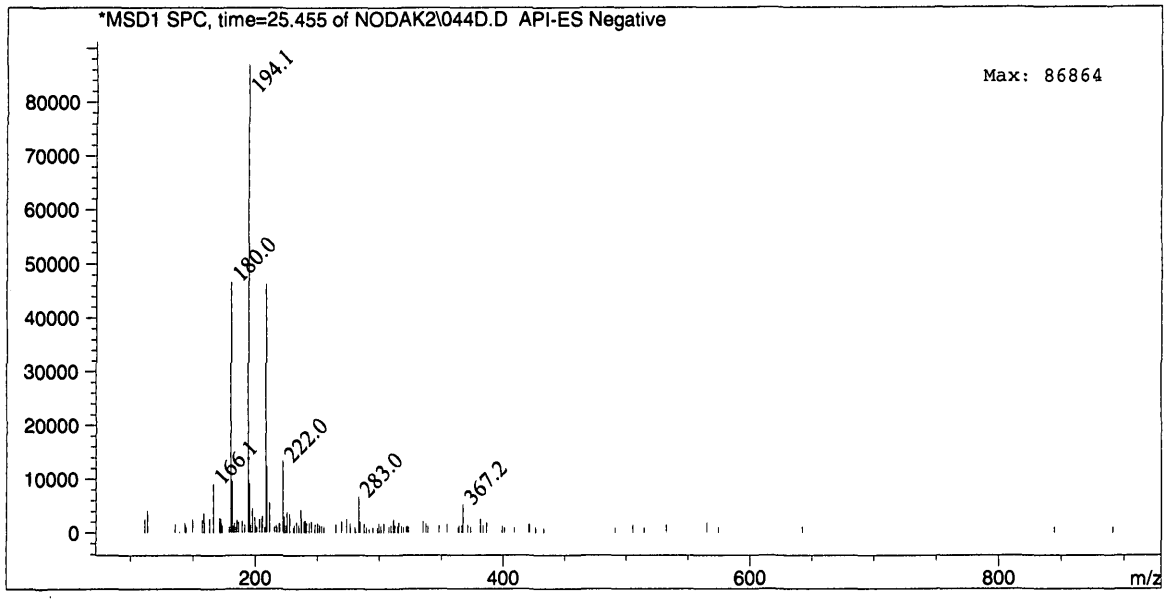
PZ2:


*MSD1 SPC, time=22.419 of NODAK2\044D.D API-ES Negative
Max: 101376
100000
80000
60000
40000
20000
0
194.1
180.0
208.1
222.1
166.0
209.2
113.2
200
400
600
800
m/z

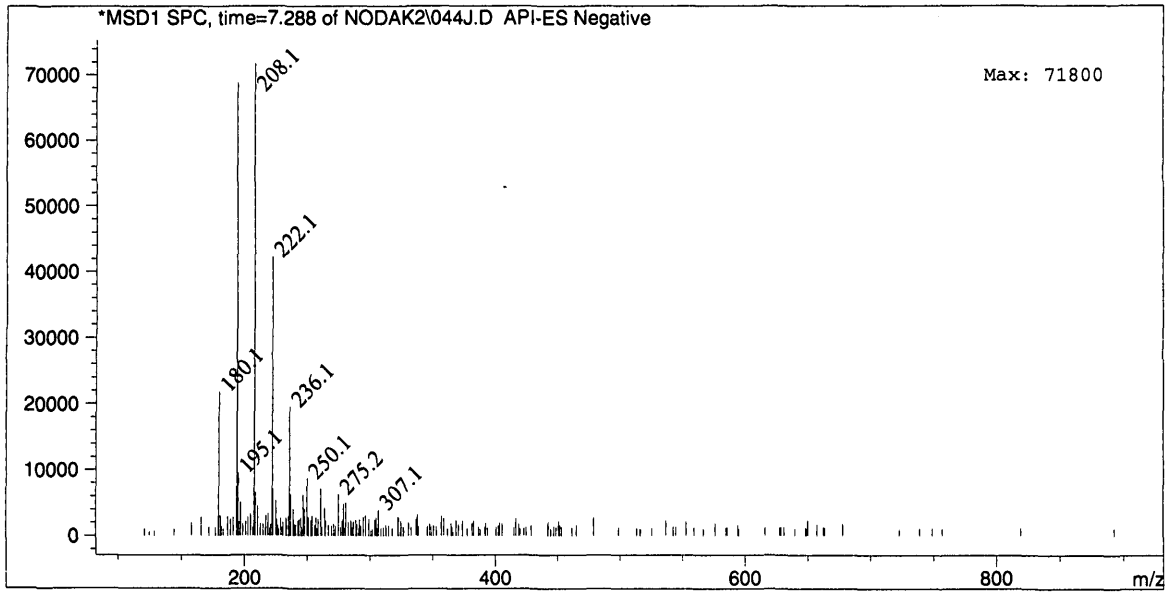
P5:


*MSD1 SPC, time=15.362 of NODAK2\044G.D API-ES Negative
Max: 65000
60000
50000
40000
30000
20000
10000
0
194.1
208.2
180.0
222.1
181.0
236.2
283.1
325.3
200
400
600
800
m/z

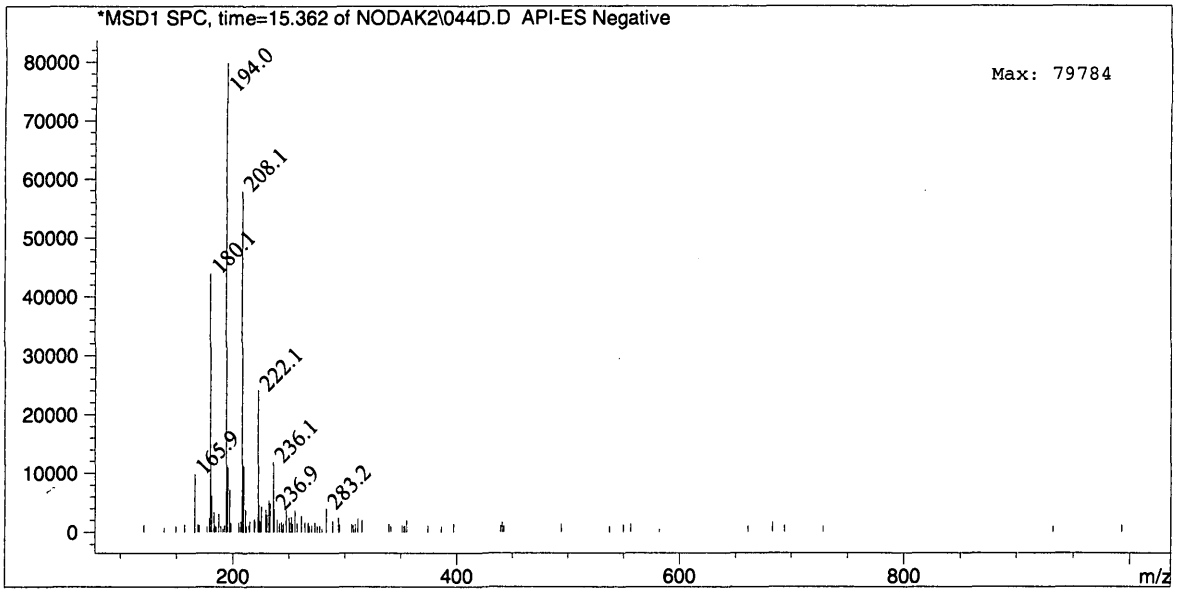
P1R:


*MSD1 SPC, time=25.455 of NODAK2\044D.D API-ES Negative
Max: 86864
194.1
180.0
166.1
222.0
283.0
367.2
80000
70000
60000
50000
40000
30000
20000
10000
0
200
400
600
800
m/z

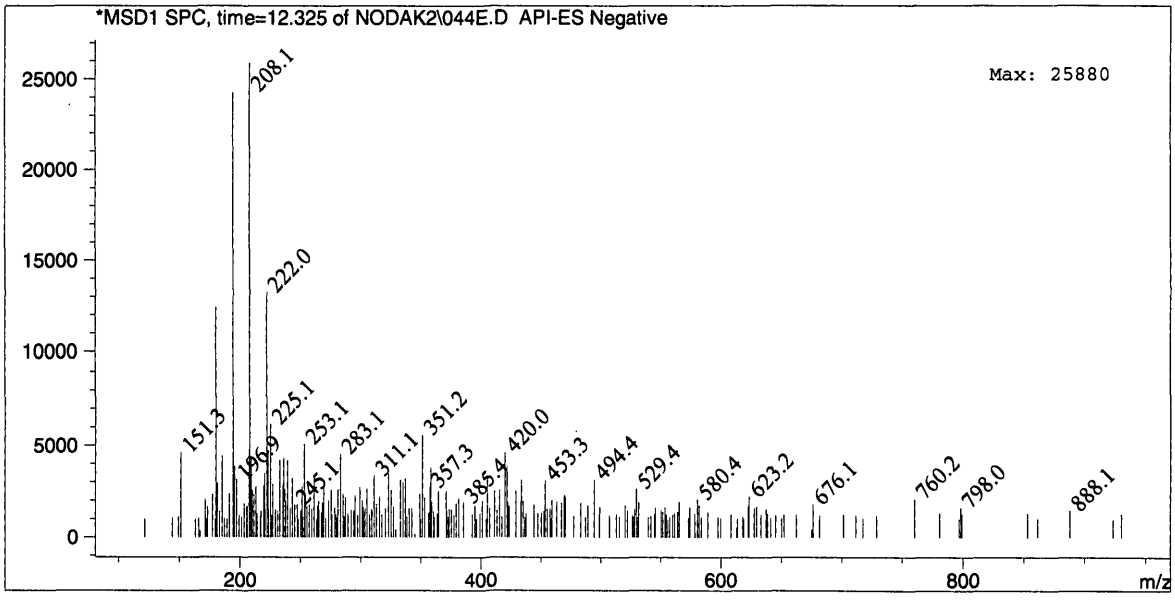
EF1:


*MSD1 SPC, time=7.288 of NODAK2\044J.D API-ES Negative
Max: 71800
208.1
222.1
180.1
236.1
195.1
250.1
275.2
307.1
70000
60000
50000
40000
30000
20000
10000
0
200
400
600
800
m/z

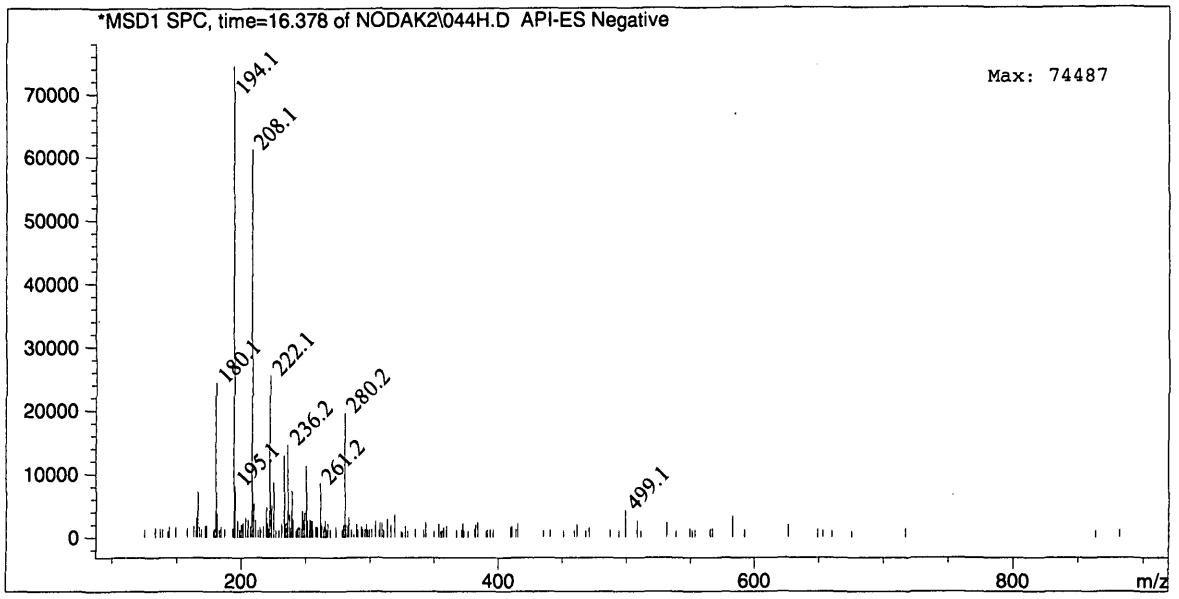
PL4:


*MSD1 SPC, time=15.362 of NODAK2\044D.D API-ES Negative
Max: 79784
194.0
208.1
180.1
222.1
165.9
236.1
236.9
283.2
m/z

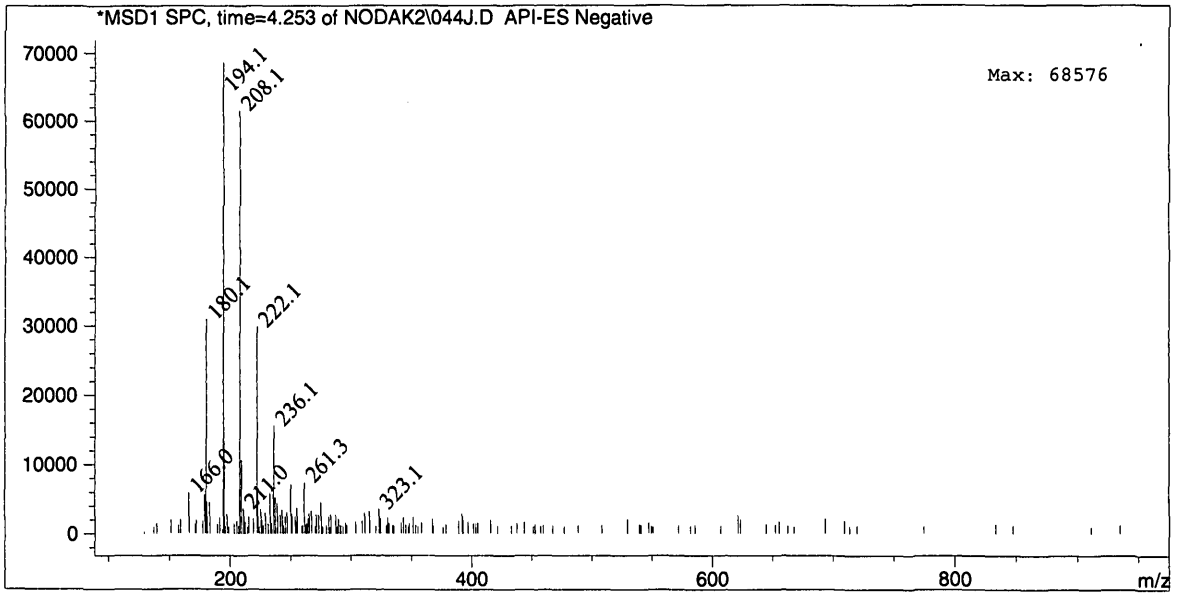
RH1:


*MSD1 SPC, time=12.325 of NODAK2\044E.D API-ES Negative
Max: 25880
208.1
222.0
225.1
151.3
253.1
283.1
351.2
311.1
357.3
420.0
385.4
453.3
494.4
529.4
580.4
623.2
676.1
760.2
798.0
888.1
m/z

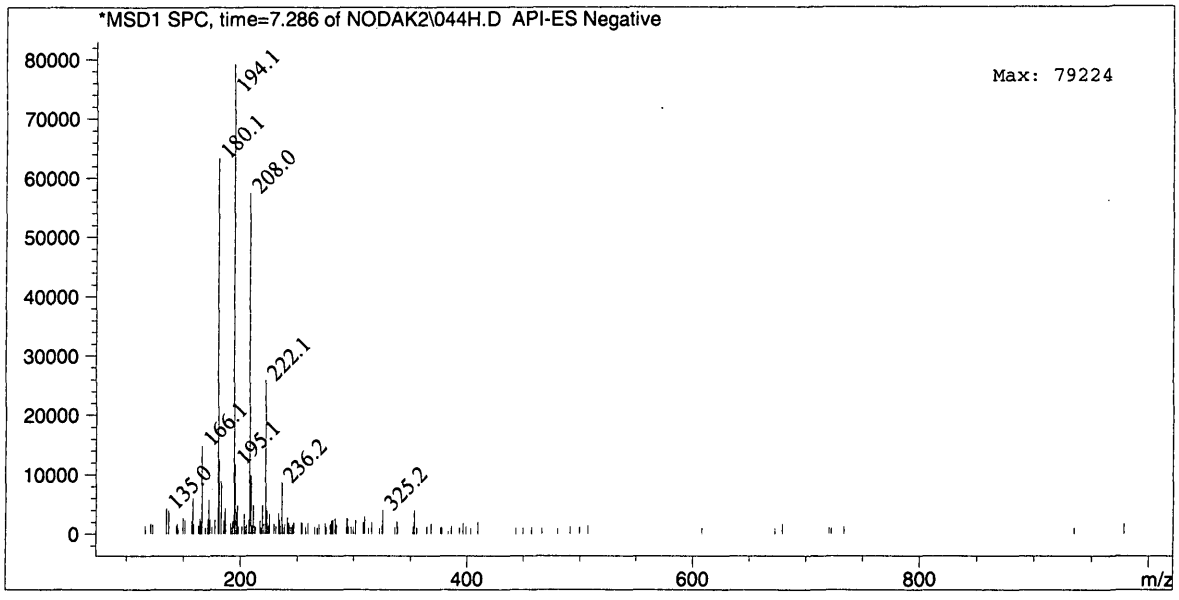
WF11:


*MSD1 SPC, time=16.378 of NODAK2\044H.D API-ES Negative
Max: 74487
194.1
208.1
180.1
222.1
280.2
236.2
195.1
261.2
499.1
70000
60000
50000
40000
30000
20000
10000
0
200
400
600
800
m/z

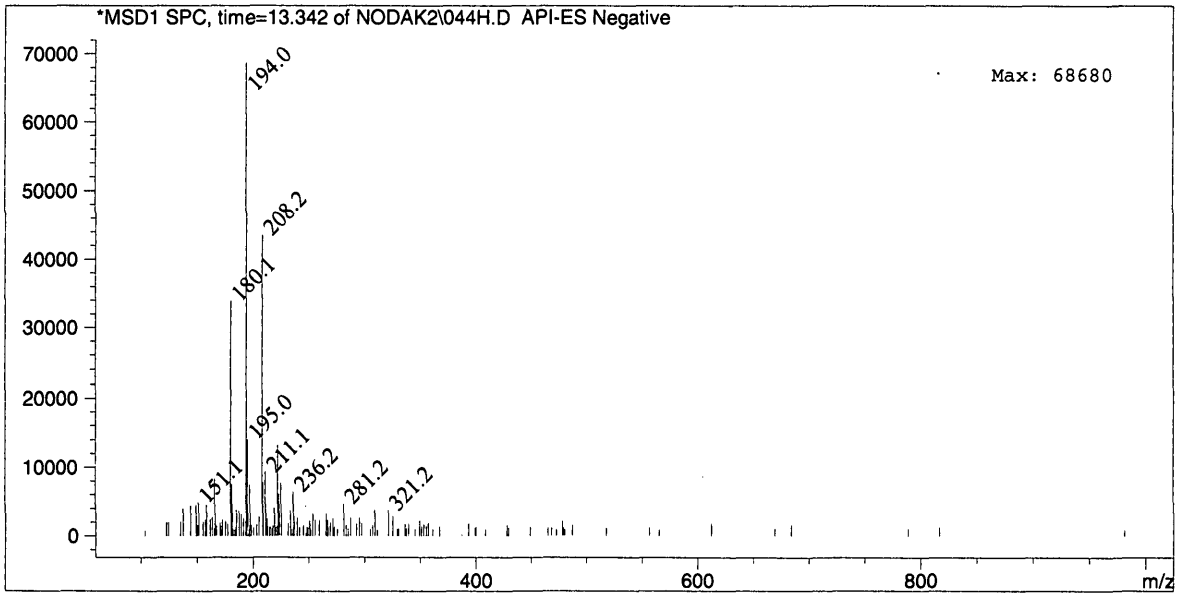
WF11A:


*MSD1 SPC, time=4.253 of NODAK2\044J.D API-ES Negative
Max: 68576
194.1
208.1
180.1
222.1
236.1
166.0
211.0
261.3
323.1
70000
60000
50000
40000
30000
20000
10000
0
200
400
600
800
m/z

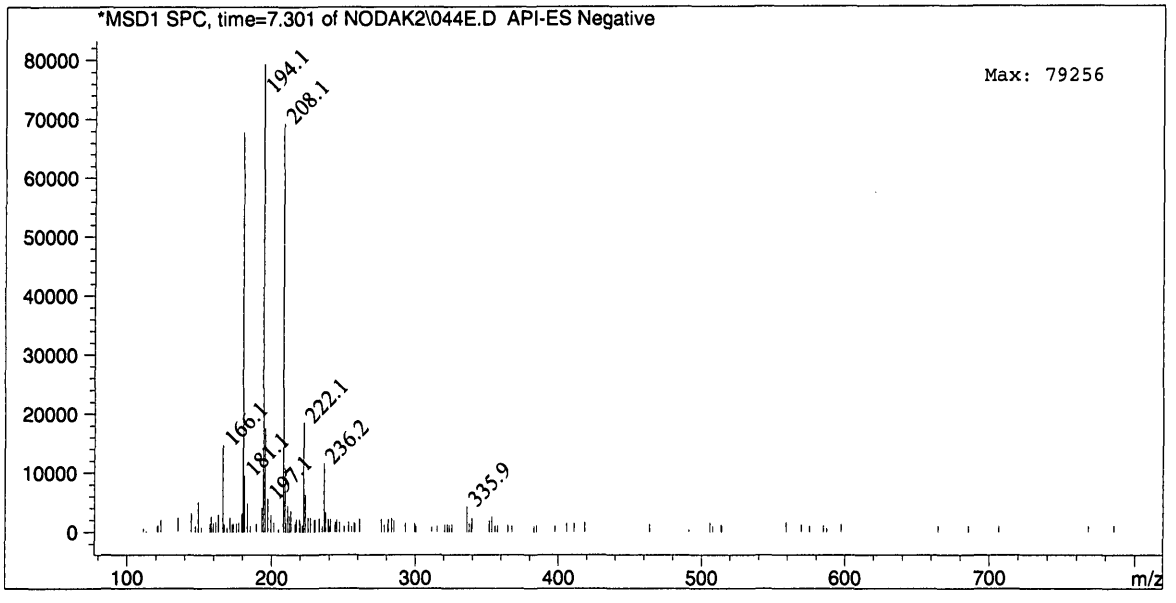
EW2:


*MSD1 SPC, time=7.286 of NODAK2\044H.D API-ES Negative
Max: 79224
80000
70000
60000
50000
40000
30000
20000
10000
0
194.1
180.1
208.0
222.1
166.1
195.1
236.2
135.0
325.2
200
400
600
800
m/z

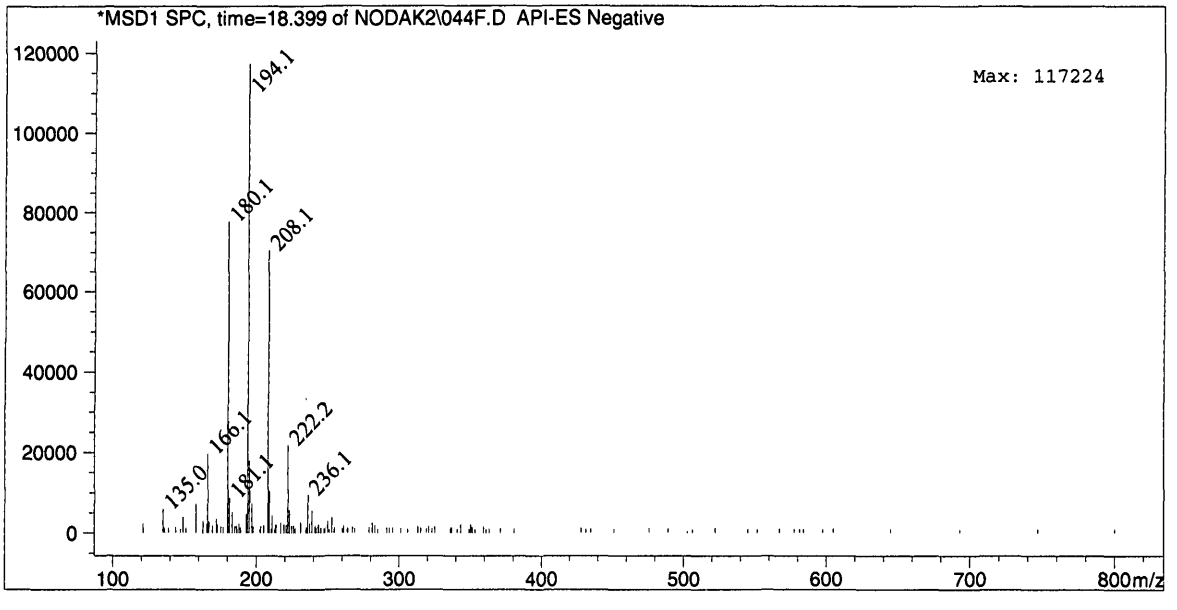
FR2:


*MSD1 SPC, time=13.342 of NODAK2\044H.D API-ES Negative
Max: 68680
70000
60000
50000
40000
30000
20000
10000
0
194.0
208.2
180.1
195.0
211.1
151.1
236.2
281.2
321.2
200
400
600
800
m/z

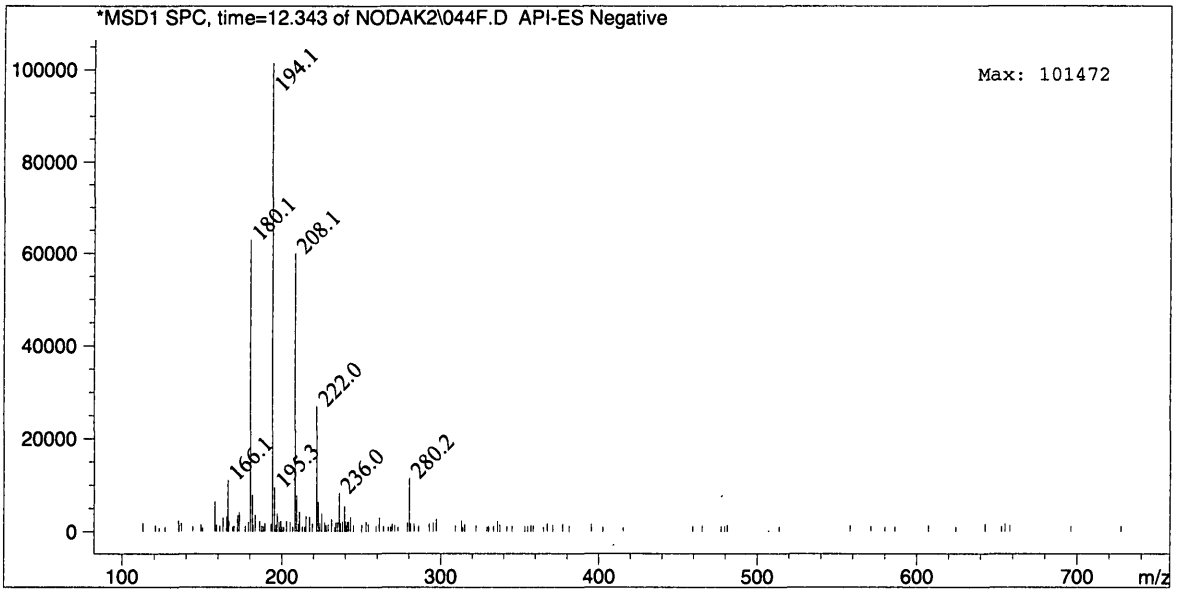
PZ6:


*MSD1 SPC, time=7.301 of NODAK2\044E.D API-ES Negative
Max: 79256
80000
70000
60000
50000
40000
30000
20000
10000
0
194.1
208.1
166.1
181.1
197.1
222.1
236.2
335.9
100
200
300
400
500
600
700
m/z

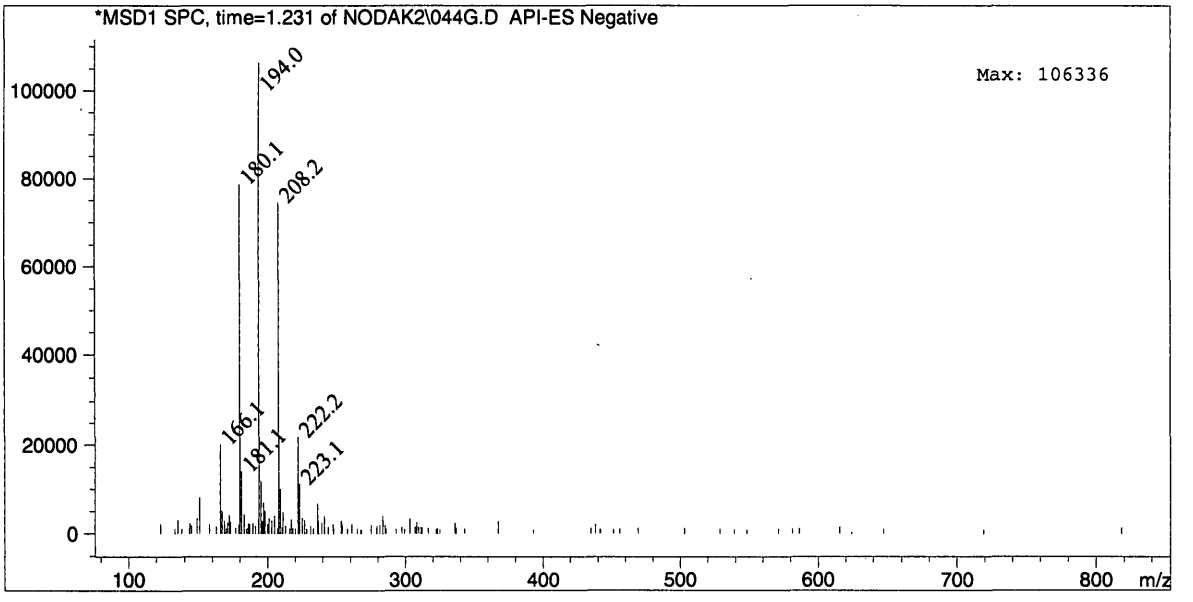
MW44:


*MSD1 SPC, time=18.399 of NODAK2\044F.D API-ES Negative
Max: 117224
120000
100000
80000
60000
40000
20000
0
194.1
180.1
208.1
135.0
166.1
181.1
222.2
236.1
100
200
300
400
500
600
700
800m/z

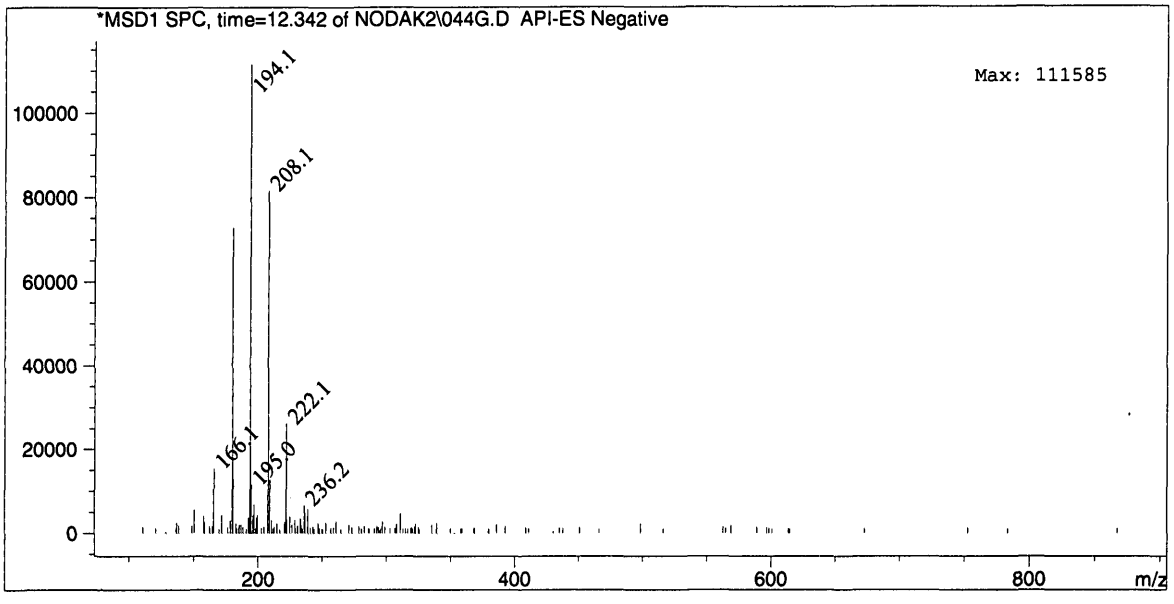
MW43:


*MSD1 SPC, time=12.343 of NODAK2\044F.D API-ES Negative
Max: 101472
100000
80000
60000
40000
20000
0
194.1
180.1
208.1
222.0
166.1
195.3
236.0
280.2
100
200
300
400
500
600
700
m/z

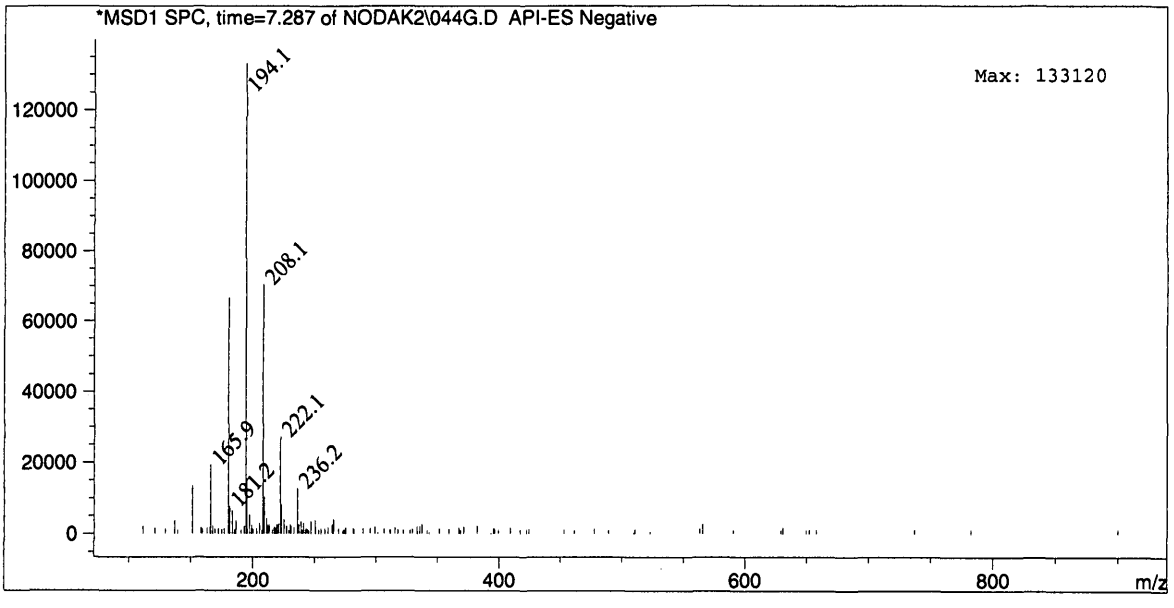
MW45:


*MSD1 SPC, time=1.231 of NODAK2\044G.D API-ES Negative
Max: 106336
100000
80000
60000
40000
20000
0
194.0
180.1
208.2
166.1
181.1
222.2
223.1
100
200
300
400
500
600
700
800
m/z

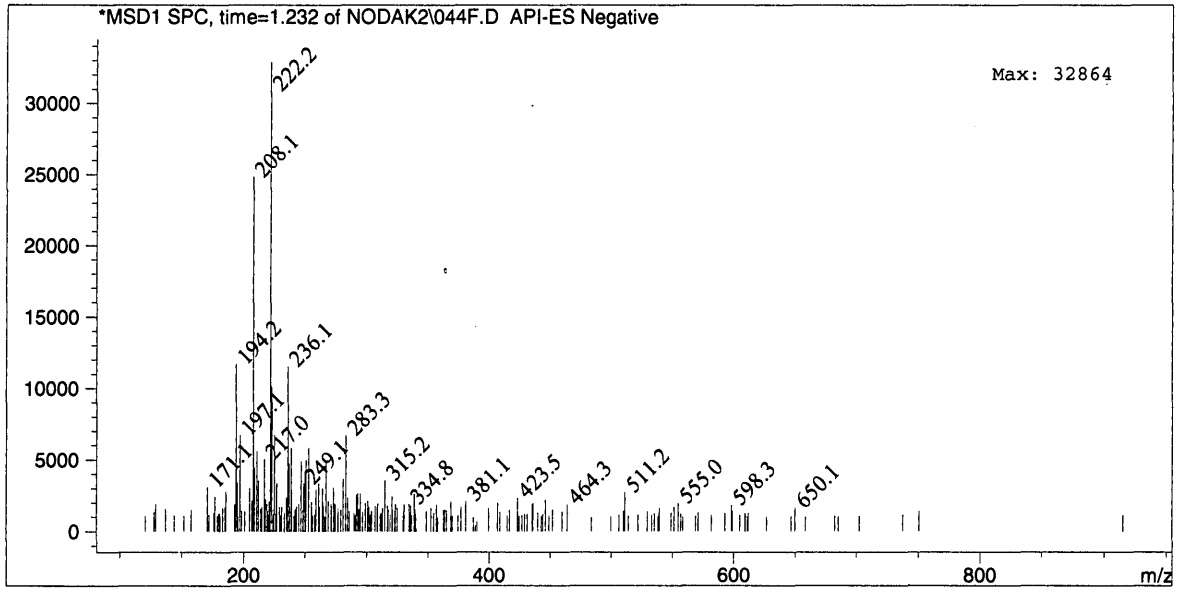
MW45P:


*MSD1 SPC, time=12.342 of NODAK2\044G.D API-ES Negative
Max: 111585
194.1
208.1
222.1
166.1
195.0
236.2
100000
80000
60000
40000
20000
0
200
400
600
800
m/z

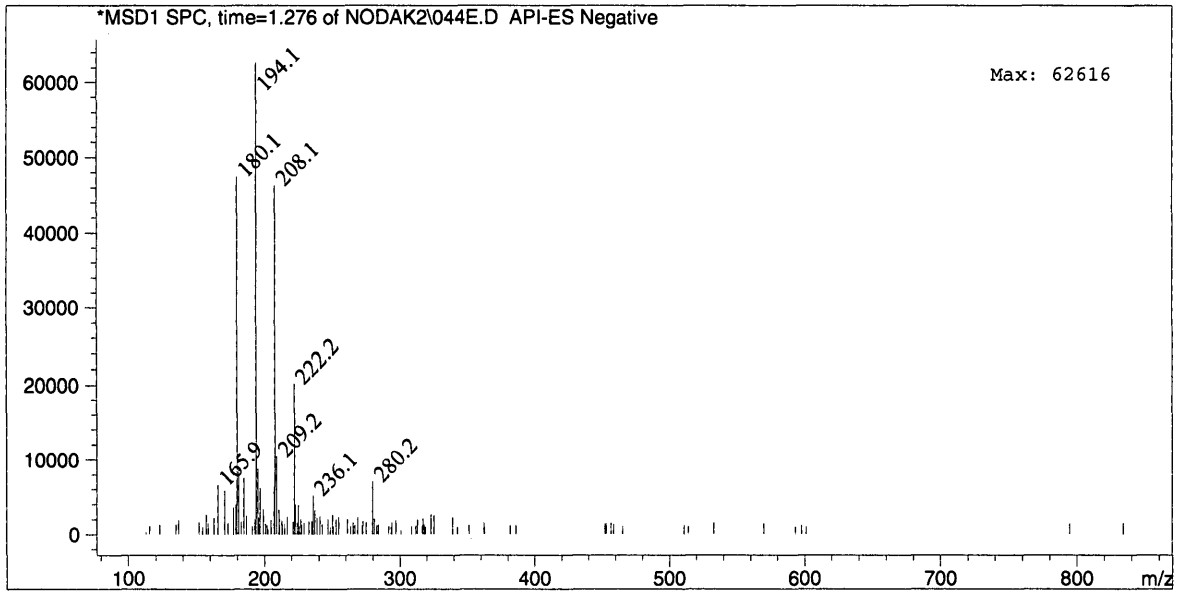
MW45B:


*MSD1 SPC, time=7.287 of NODAK2\044G.D API-ES Negative
Max: 133120
194.1
208.1
222.1
165.9
181.2
236.2
120000
100000
80000
60000
40000
20000
0
200
400
600
800
m/z

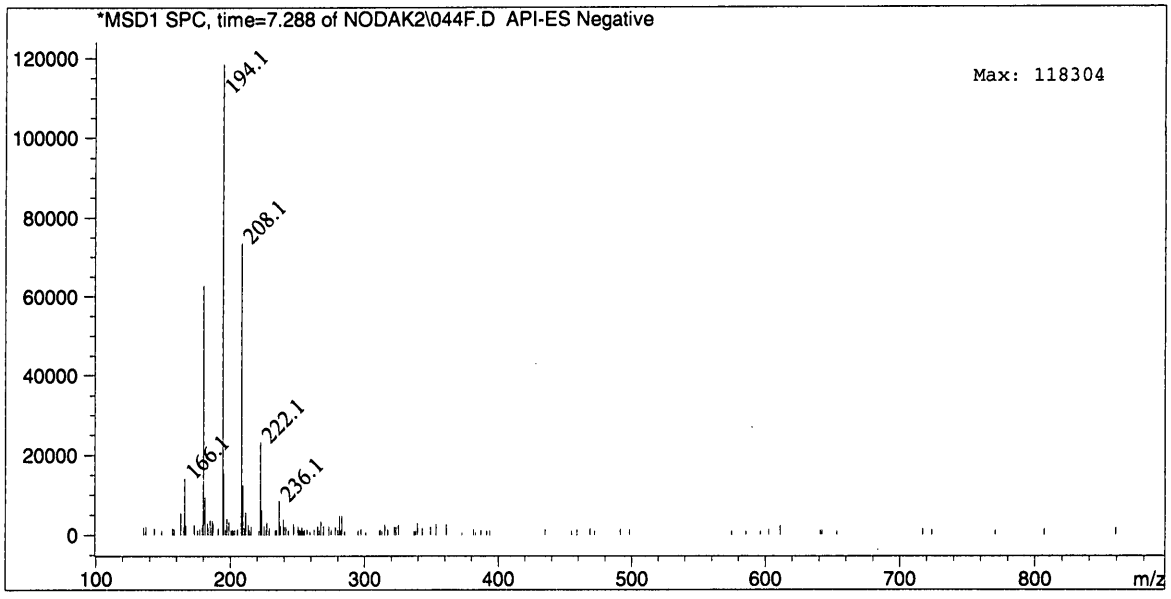
FR4:


*MSD1 SPC, time=1.232 of NODAK2\044F.D API-ES Negative
Max: 32864
222.2
208.1
194.2
236.1
197.1
171.1
217.0
283.3
249.1
315.2
334.8
381.1
423.5
464.3
511.2
555.0
598.3
650.1
30000
25000
20000
15000
10000
5000
0
200
400
600
800
m/z

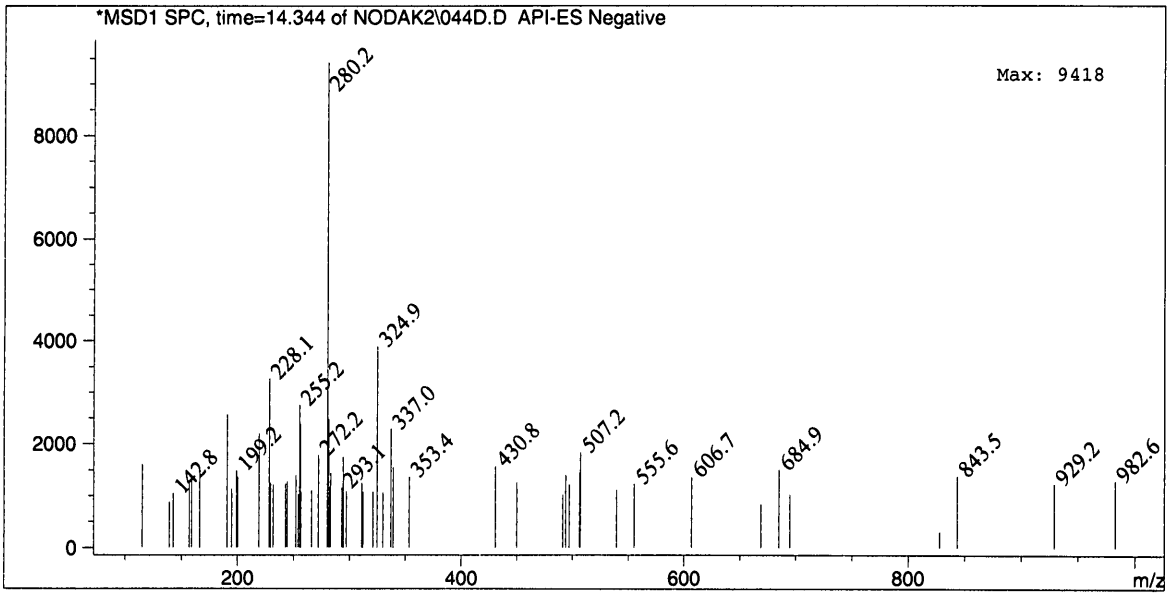
MW8:


*MSD1 SPC, time=1.276 of NODAK2\044E.D API-ES Negative
Max: 62616
194.1
180.1
208.1
222.2
209.2
165.9
236.1
280.2
60000
50000
40000
30000
20000
10000
0
100
200
300
400
500
600
700
800
m/z

MW7R:



Methanol background:



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