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Transferability and Application of Bemidji Site Science

Forensic Work at a Long-term Railroad-Diesel Oil Spill Site in Mandan, ND

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Bemidji Oil Spill

1979 crude oil spill (pipeline rupture)
Pristine environment (no other oil or hydrocarbon background)

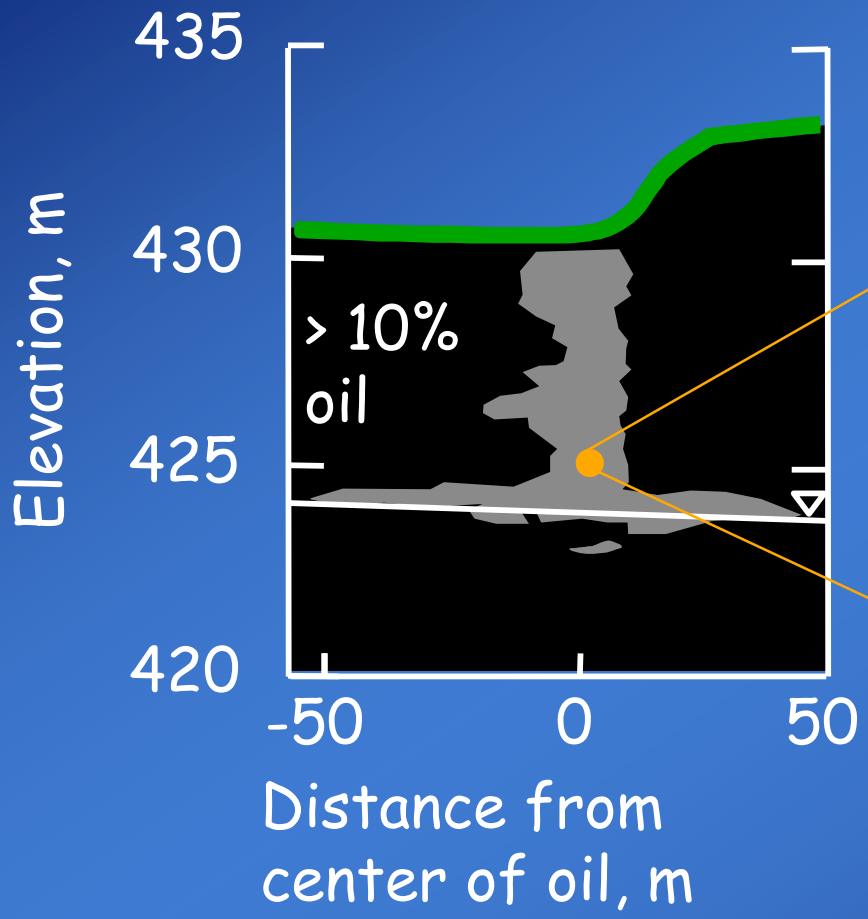
Shallow sandy aquifer, about 7 m to water table USGS study site for >25 years.

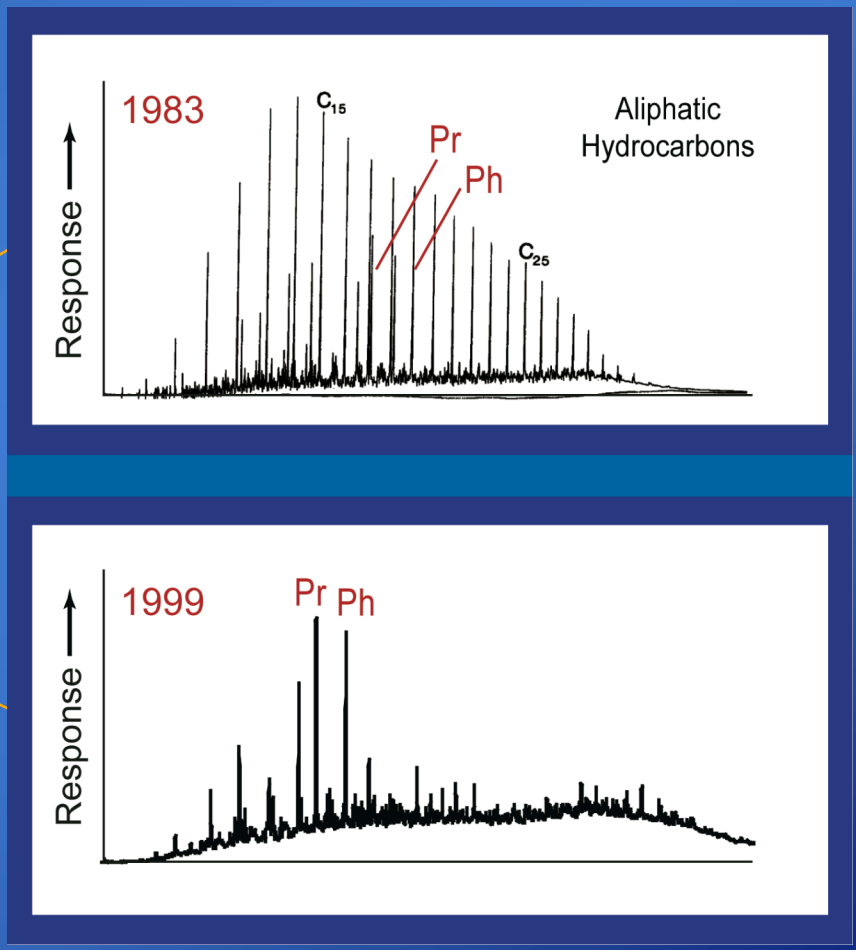
Microbiology shows anaerobic degradation and methanogenesis

Significant findings include the following:

- First to document that the extent of crude oil contamination can be limited by natural attenuation.
- First to document the importance of anaerobic degradation of aromatic hydrocarbons.
- First to document that methanogenesis completely degrades straight-chain hydrocarbons (using the Bemidji microbial consortium).
- Thoroughly mapped the zones of methane production and delineated the types of anaerobic degradation.
- New modeling programs developed to analyze the evolution of the ground-water contaminant plume.
- New techniques such as the development of a “freezing shoe” for collecting undisturbed cores below the water table.
- Unique comprehensive study of the oil distribution in unsaturated and saturated zones.
- Provide fundamental knowledge on remediation with broad carry-over to other unrelated systems.
- Ongoing studies on the limiting factors and molecular progression of methanogenesis.

A comparison of adjacent samples shows significant degradation from 1983 to 1999





Common Fuel Oil Constituents

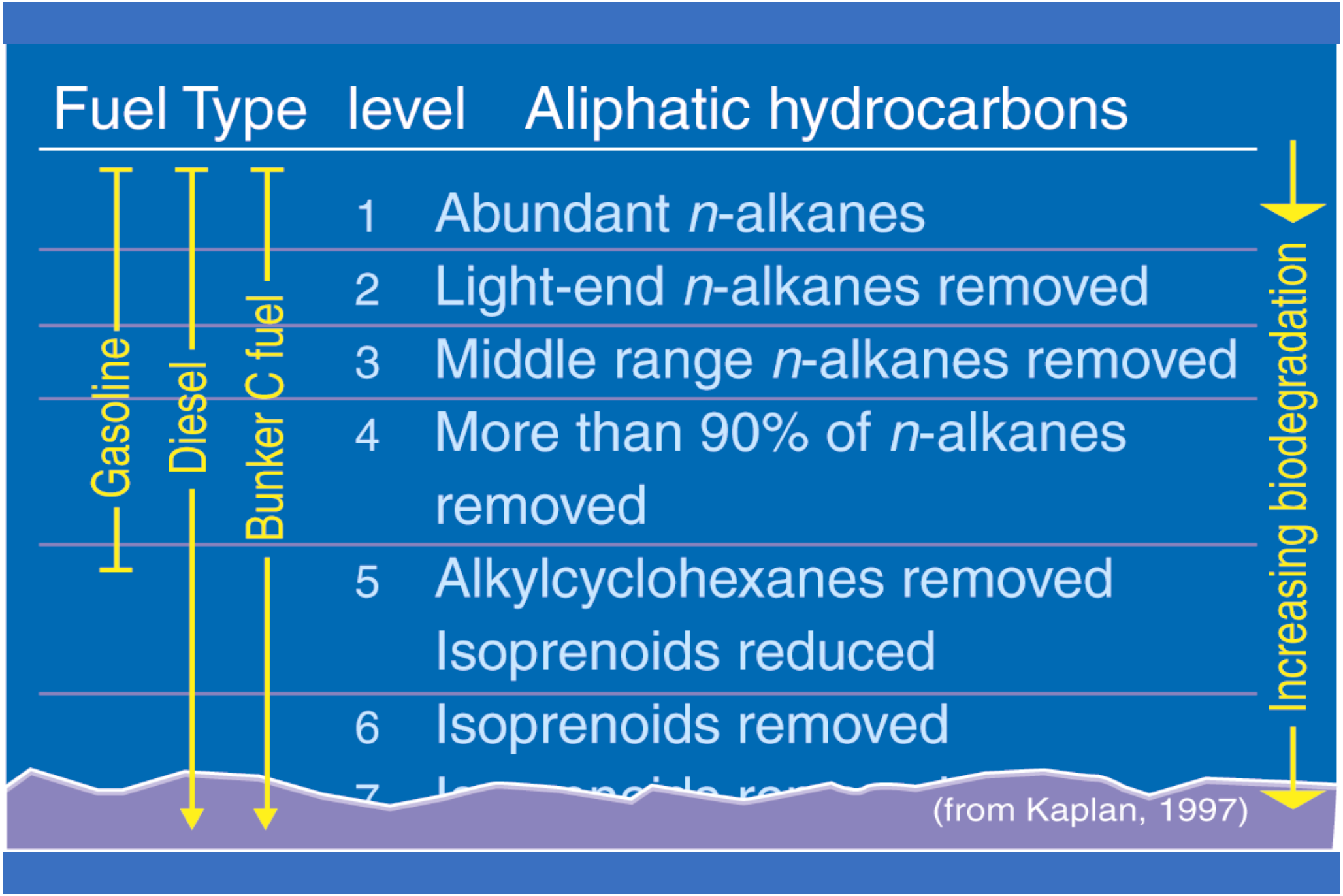
- *n-alkanes*  C_{15}
- isoprenoids  pristane
- n-alkylcyclohexanes  C_{15}

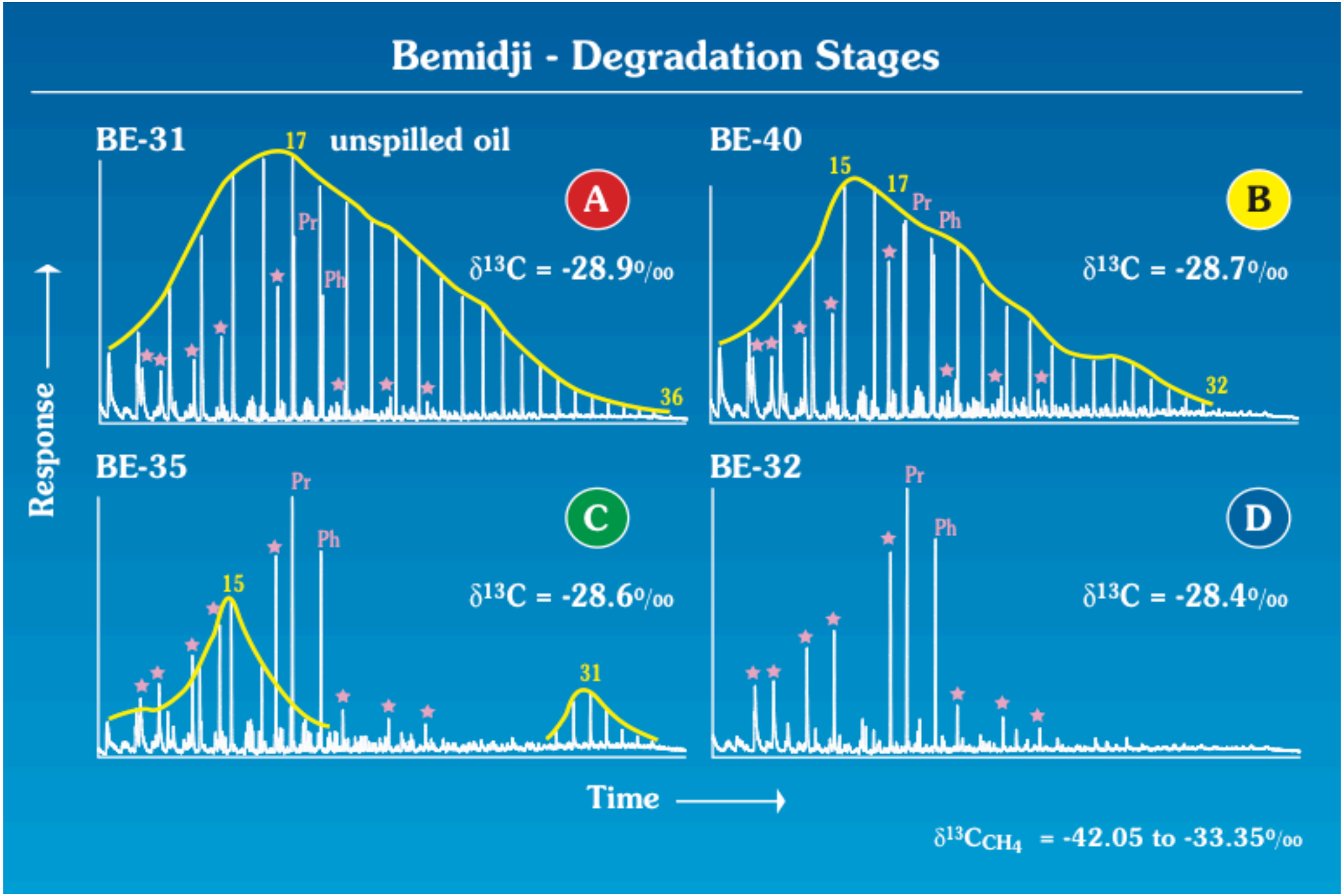
- Volatiles (BTEX) ------> groundwater plume and outside oil body
- Aromatic semi-volatiles ----> little change over time within oil body
- Polars/asphaltenes -----> little change within oil body

Degradation Order

Peters and Moldowan, 1993

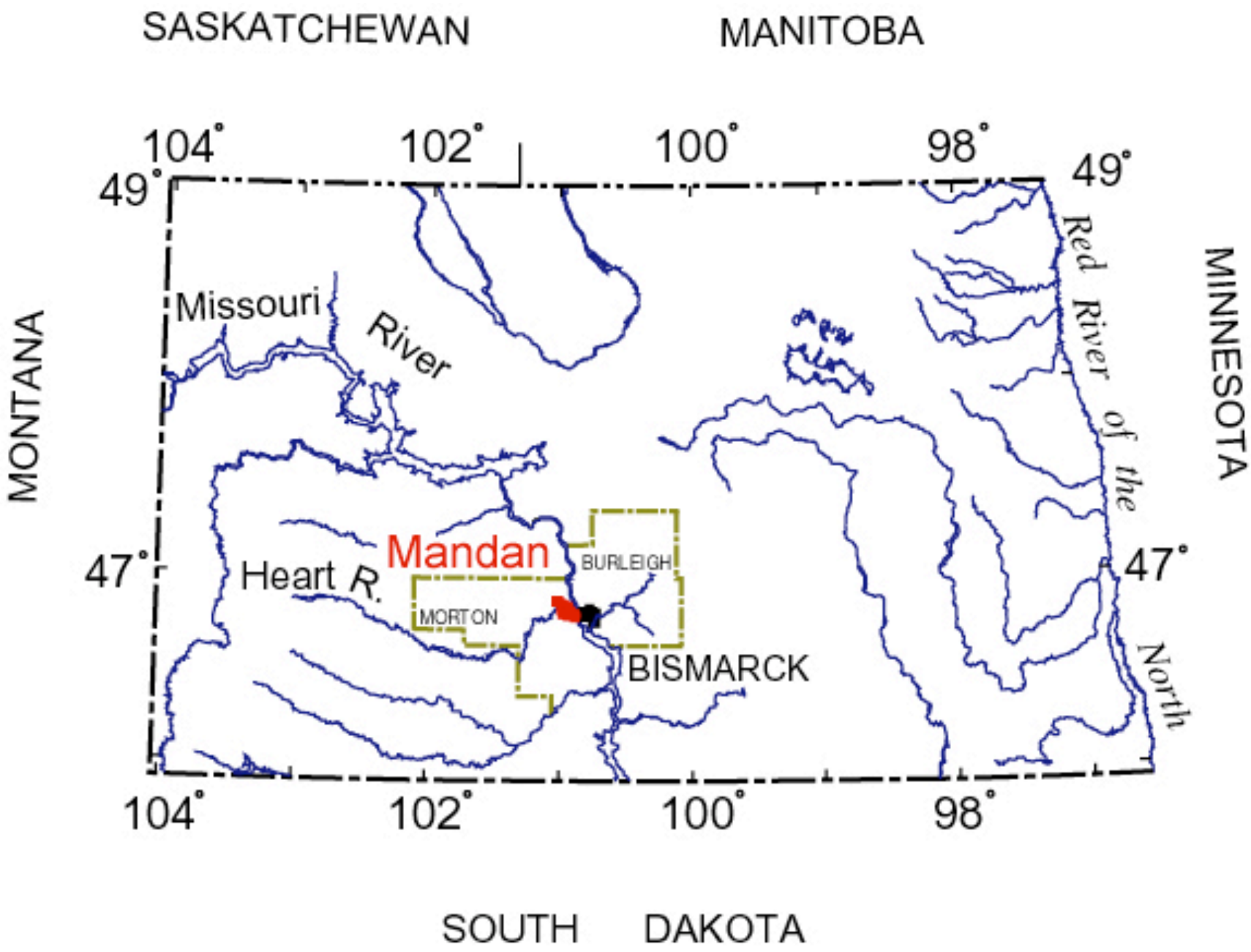
Light	*n*-alkanes
Moderate	isoprenoids, cyclic alkanes lower mol. wt. aromatics
Heavy	steranes, hopanes, aromatics
Very Heavy	diasteranes, aromatics
Severe	aromatic steroids, high mol. wt aromatics

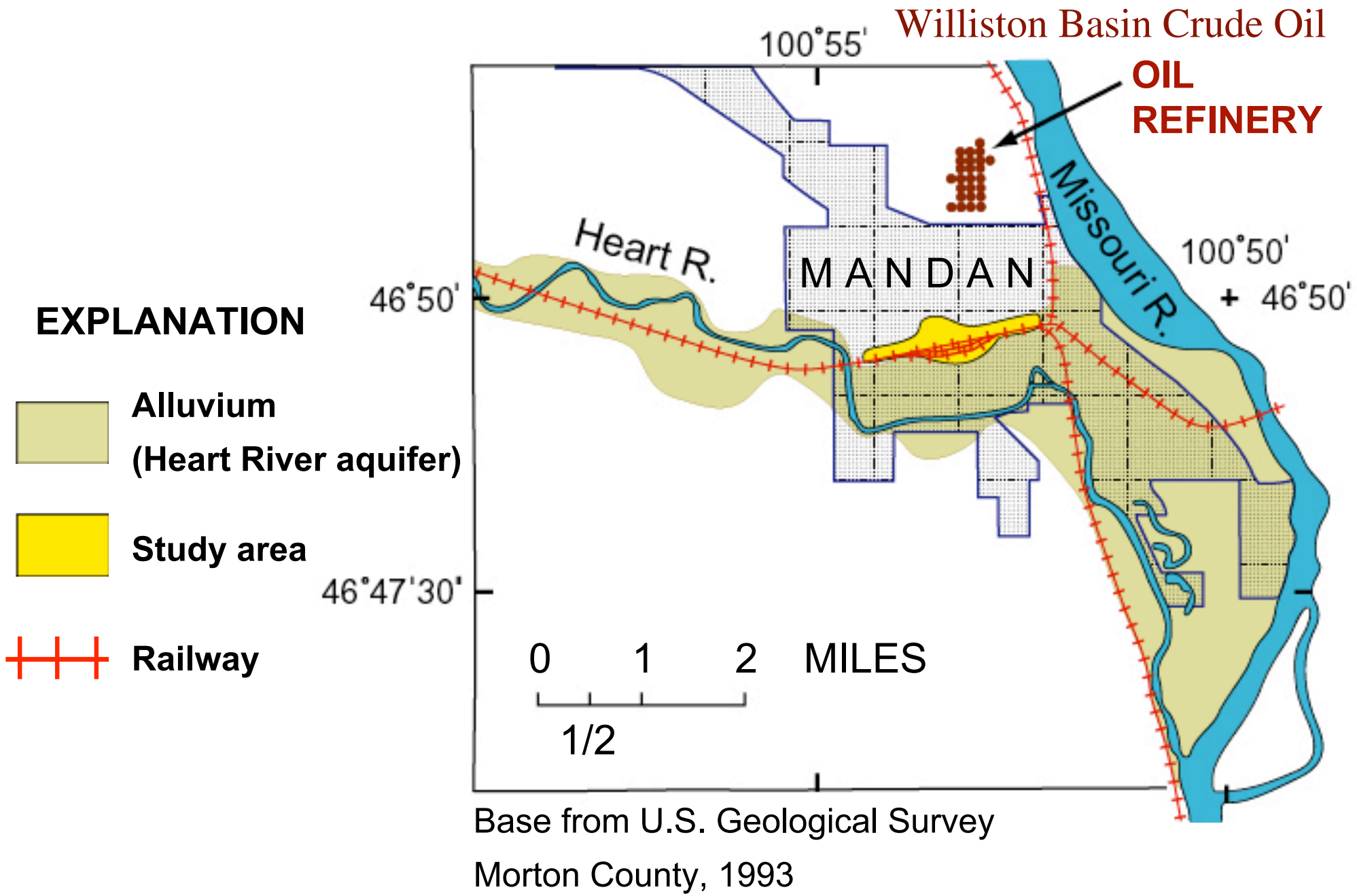

Fuel Type
level
Aliphatic hydrocarbons
Gasoline
Diesel
Bunker C fuel
1 Abundant n-alkanes
2 Light-end n-alkanes removed
3 Middle range n-alkanes removed
4 More than 90% of n-alkanes removed
5 Alkylcyclohexanes removed
Isoprenoids reduced
6 Isoprenoids removed
Increasing biodegradation
(from Kaplan, 1997)


Bemidji - Degradation Stages
BE-31
17
unspilled oil
A
Pr
Ph
δ13C = -28.9o/oo
36
BE-40
15
17
Pr
Ph
B
δ13C = -28.7o/oo
32
Response
BE-35
Pr
Ph
C
15
δ13C = -28.6o/oo
31
BE-32
Pr
Ph
D
δ13C = -28.4o/oo
Time
δ13CCH4 = -42.05 to -33.35o/oo

Bemidji oil samples show:

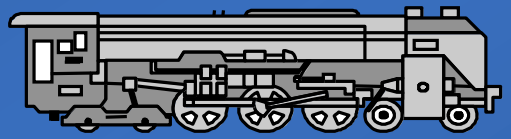
- high end *n*-alkane loss and lower end *n*-alkane enhancement
- heavier $\delta^{13}C$ in area of enhancement indicating some secondary formation of *n*-alkanes


SASKATCHEWAN
MANITOBA
104°
102°
100°
98°
49°
MONTANA
MINNESOTA
Missouri River
Red River of the North
Mandan
BURLEIGH
MORTON
Heart R.
47°
BISMARCK
SOUTH DAKOTA

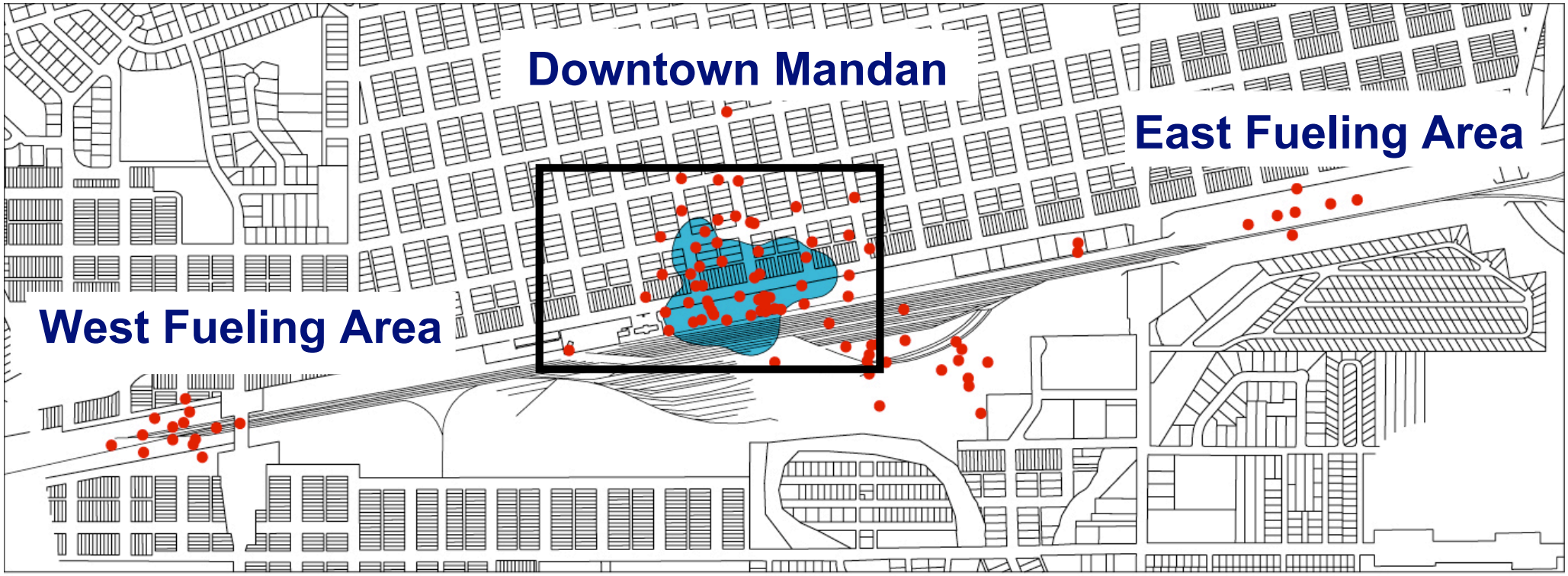

Williston Basin Crude Oil
OIL REFINERY
100°55'
100°50'
46°50'
46°47'30"
Heart R.
MANDAN
Missouri R.
EXPLANATION
Alluvium
(Heart River aquifer)
Study area
Railway
0 1 2 MILES
1/2
Base from U.S. Geological Survey
Morton County, 1993

Problem:

- Chronic spillage of hydrocarbon fuel in Mandan, N.D., 1953-1991



- Estimated 1.5 - 3.0 M gallons of LNAPL floating on water table ~ 20 feet below ground, within alluvial aquifer
- One local refinery crude oil source
- Determine the site hydrology and characterize the hydrocarbon fuel



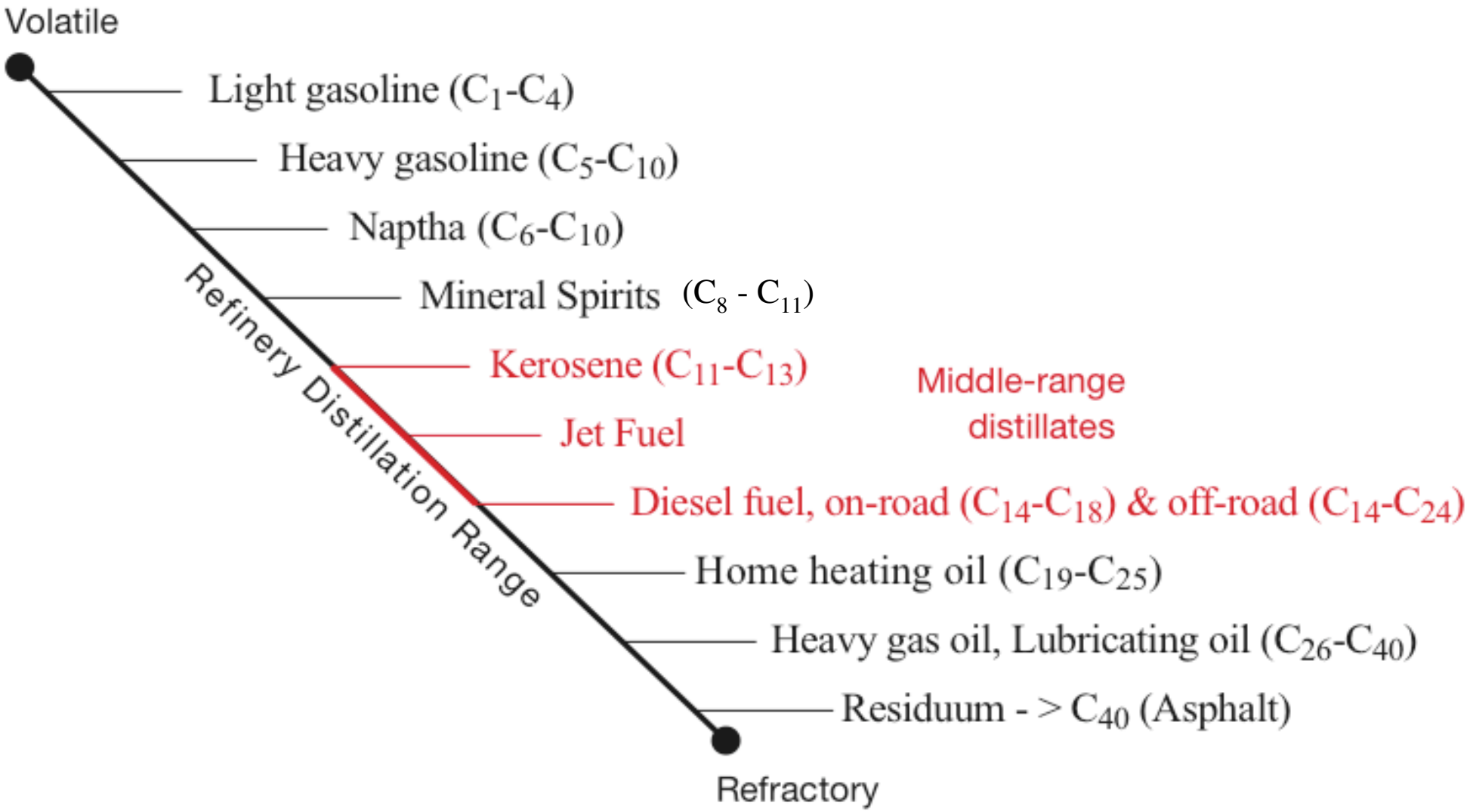
monitoring wells

≈ extent of LNAPL body (November 2000)

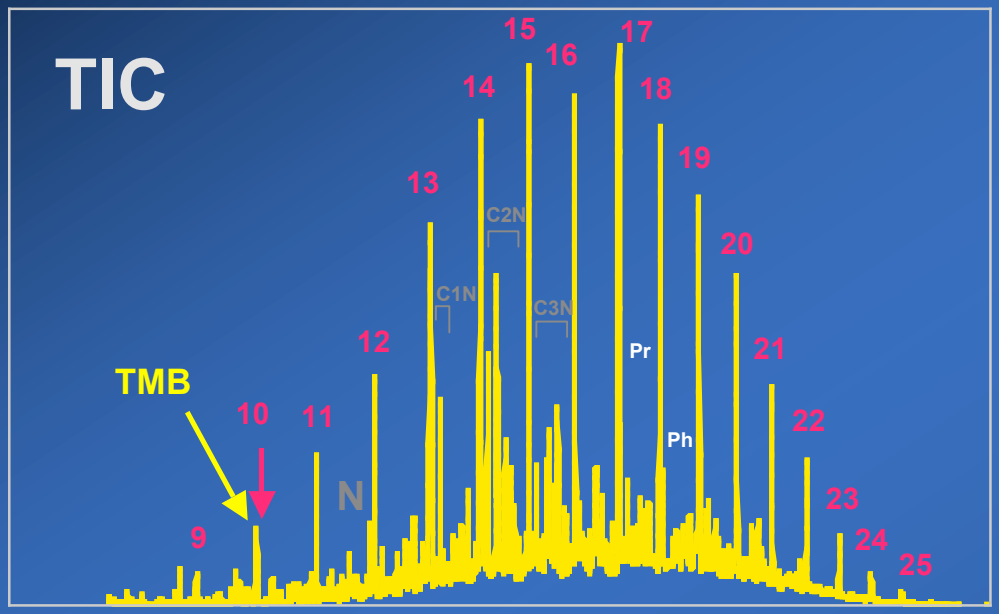
0 1,000 2,000 3,000 4,000 FEET

0 250 500 750 1,000 METERS

What is Diesel Fuel?

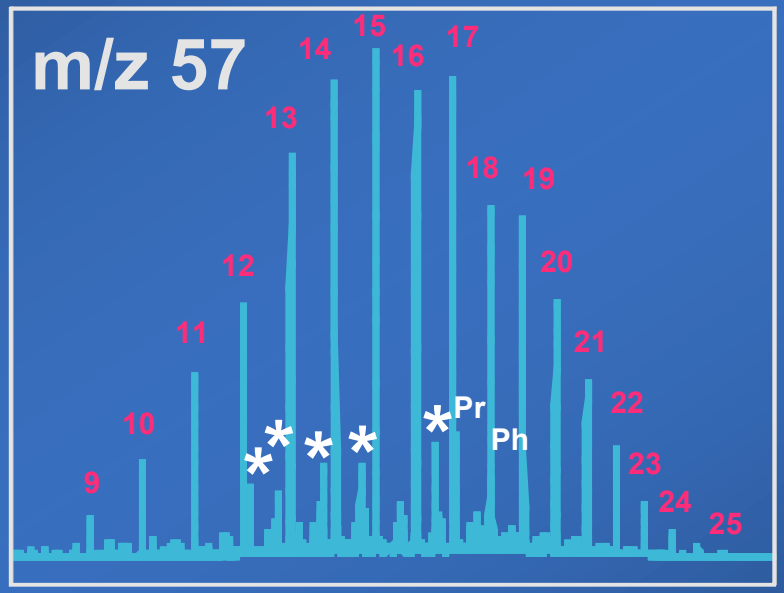


Sample RR40 (diesel fuel)

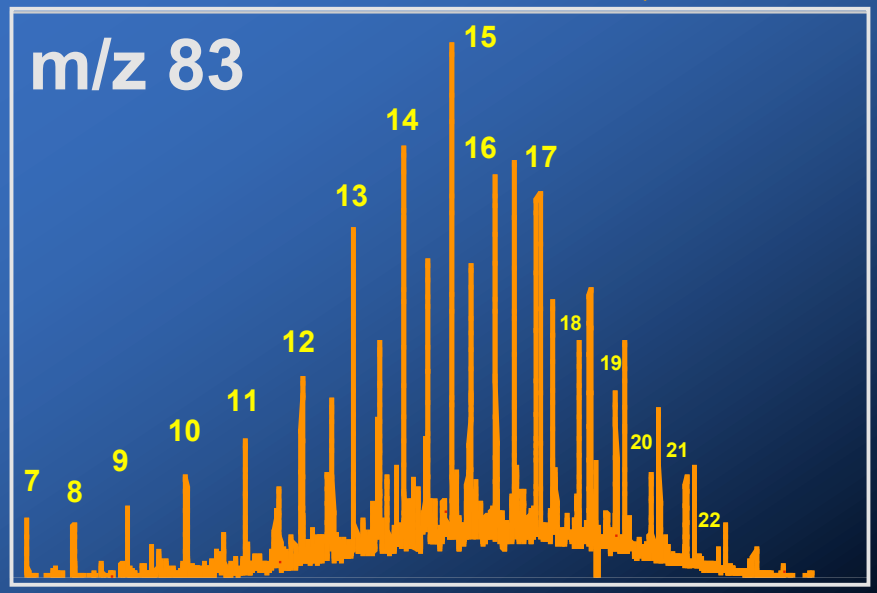


(C_{15})

n-alkanes and isoprenoids



alkylcyclohexanes

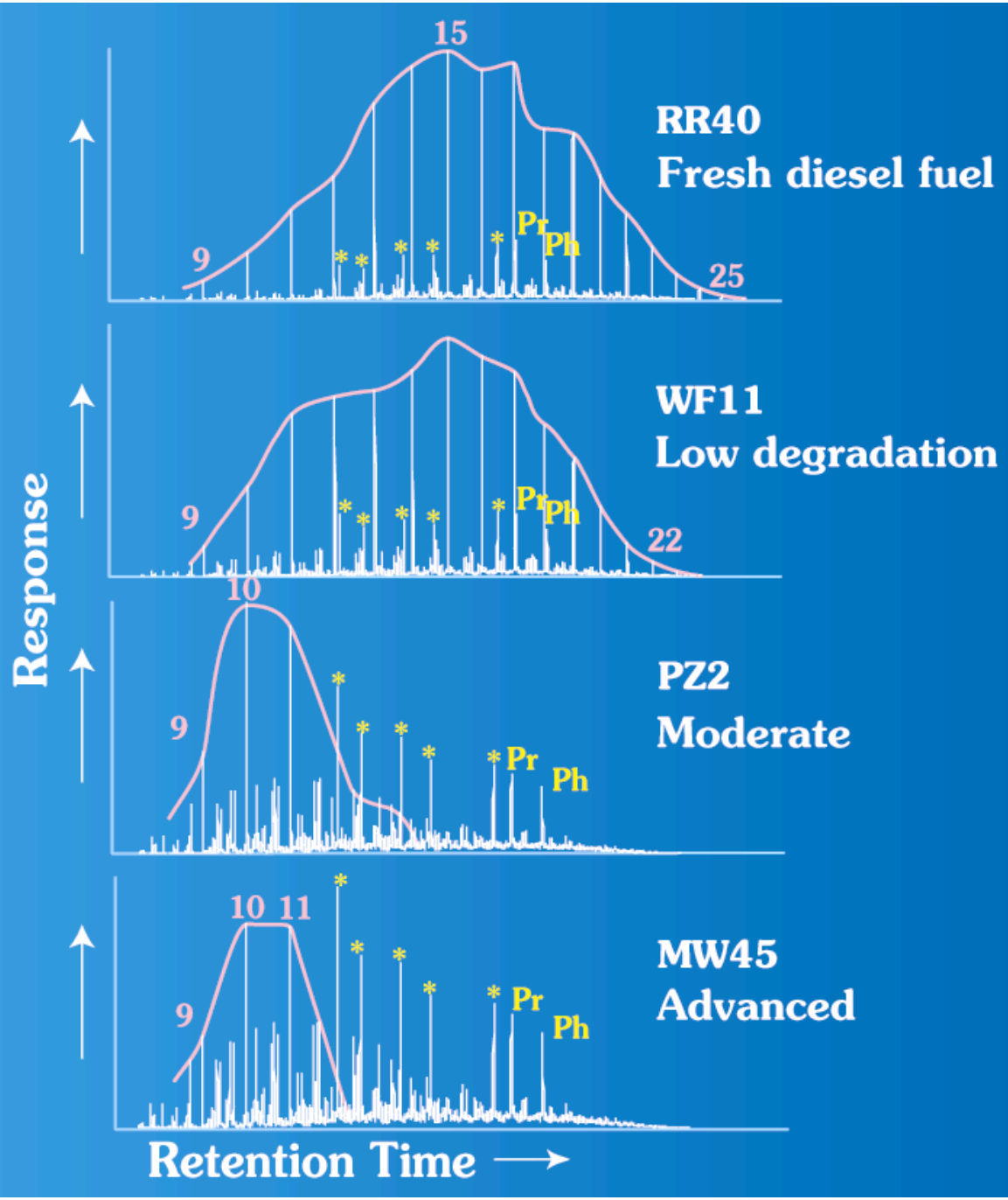


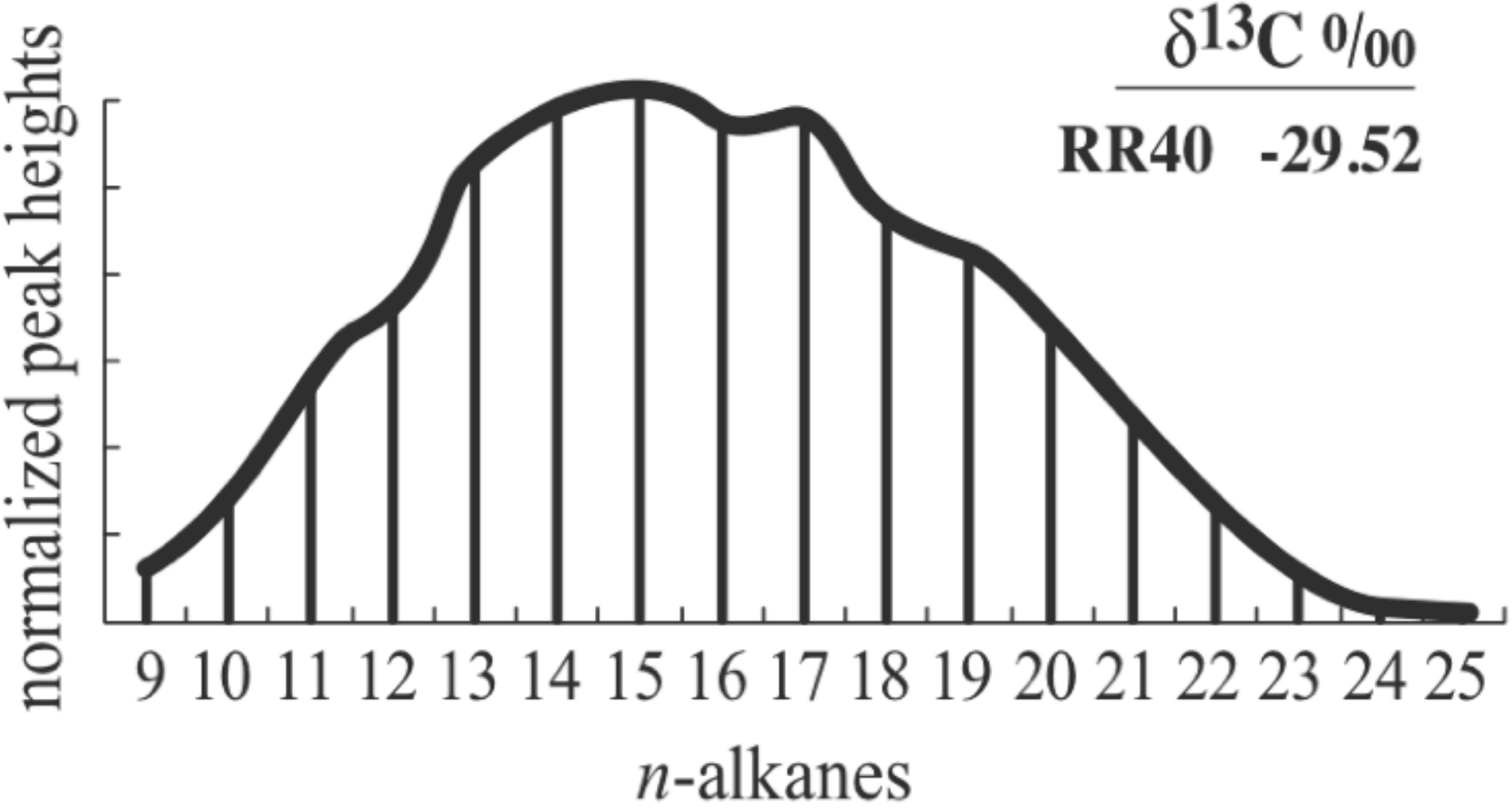
MANDAN Weathering Progression

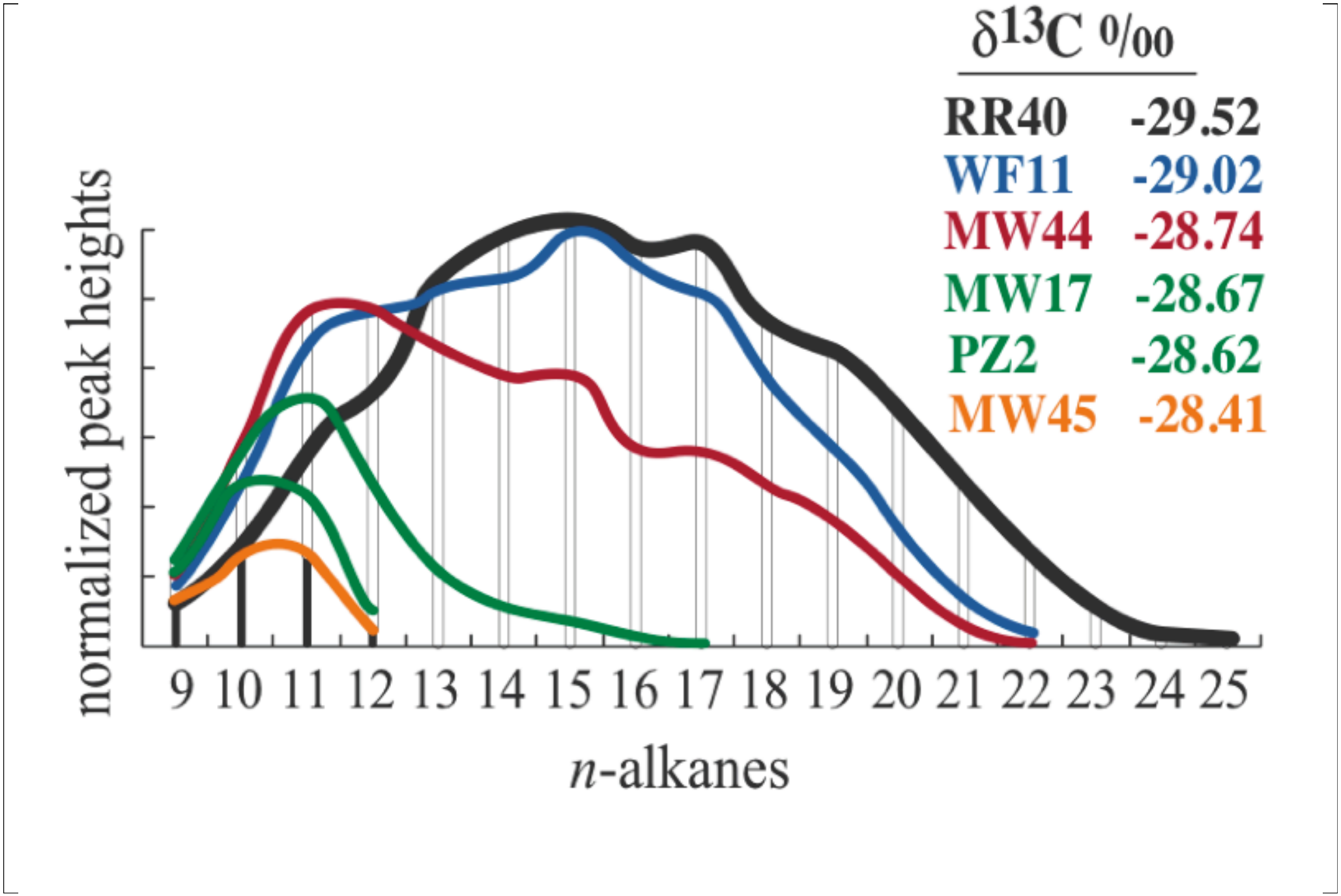
m/z 57

n-alkanes

isoprenoids*




δ13C 0/00
RR40 -29.52
normalized peak heights
9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
n-alkanes


δ13C ‰
RR40 -29.52
WF11 -29.02
MW44 -28.74
MW17 -28.67
PZ2 -28.62
MW45 -28.41
normalized peak heights
9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
n-alkanes

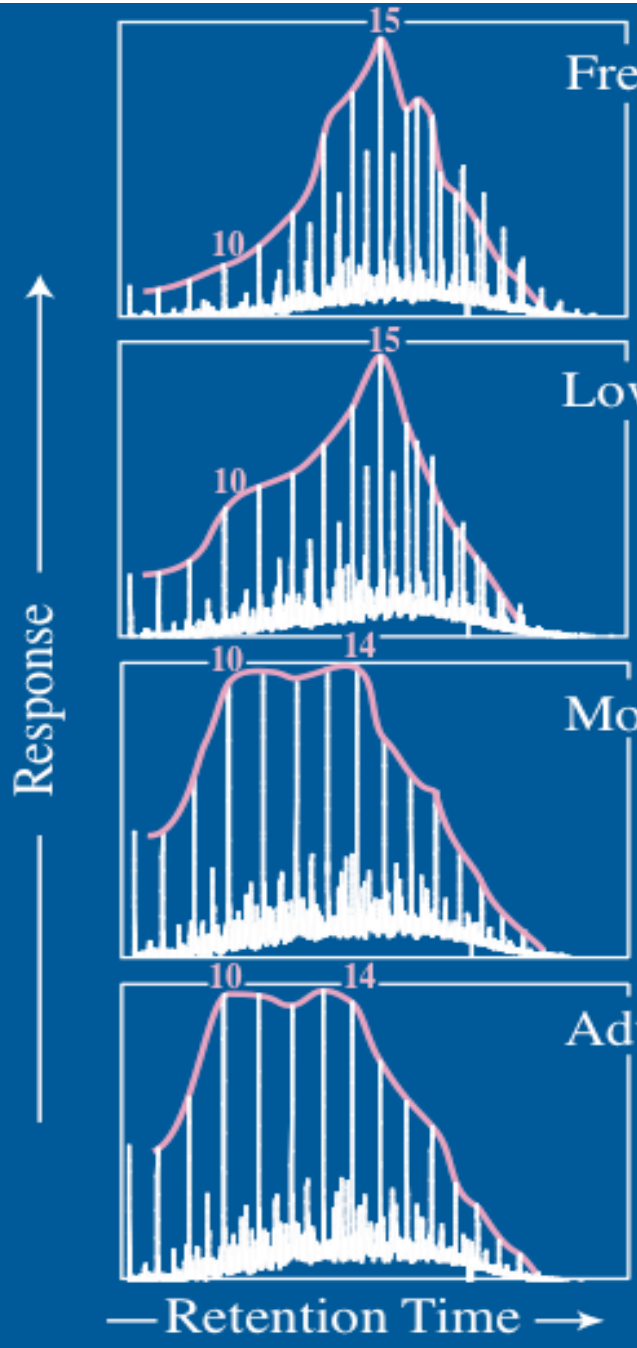
Alkyl-CHs in some refinery mid-range fuels

	CH range	CH max
RR diesel (RR40)	C_7 - C_{24}	C_{15}
Mineral spirits	C_8 - C_{11}	C_9, C_{10}
Kerosene	C_7 - C_{15}	C_{12}
Diesel fuel #1	C_7 - C_{20}	C_{11}

(from Kaplan, 1997)

MANDAN

n-alkylcyclohexanes
(m/z 83)

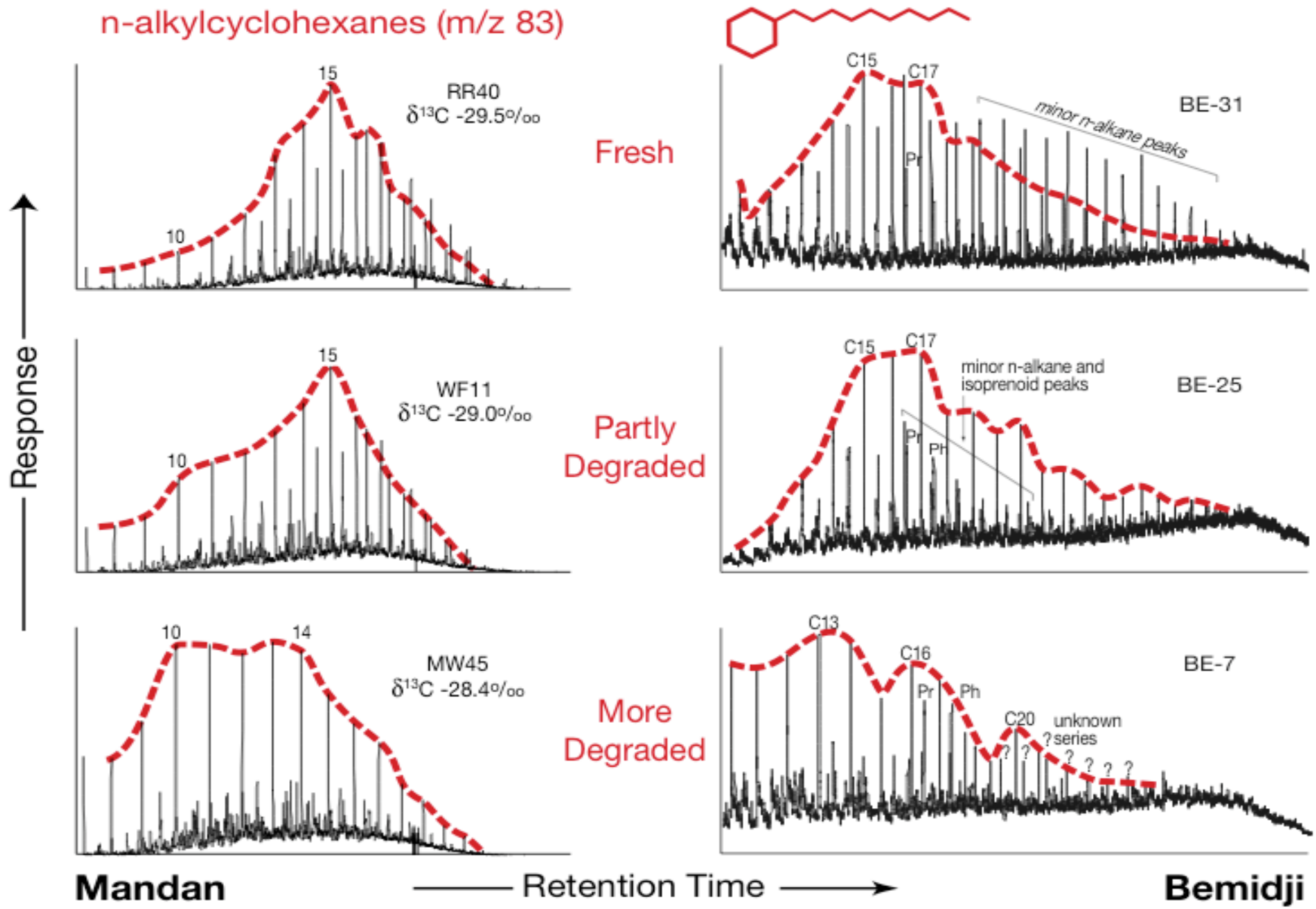


RR40
$\delta^{13}C$ -29.5‰

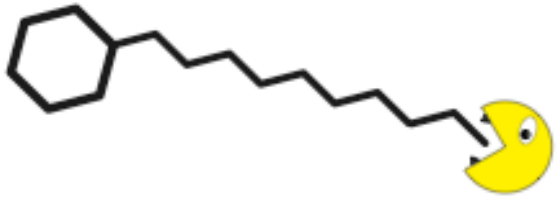
WF11
$\delta^{13}C$ -29.0‰

PZ2
$\delta^{13}C$ -28.7‰

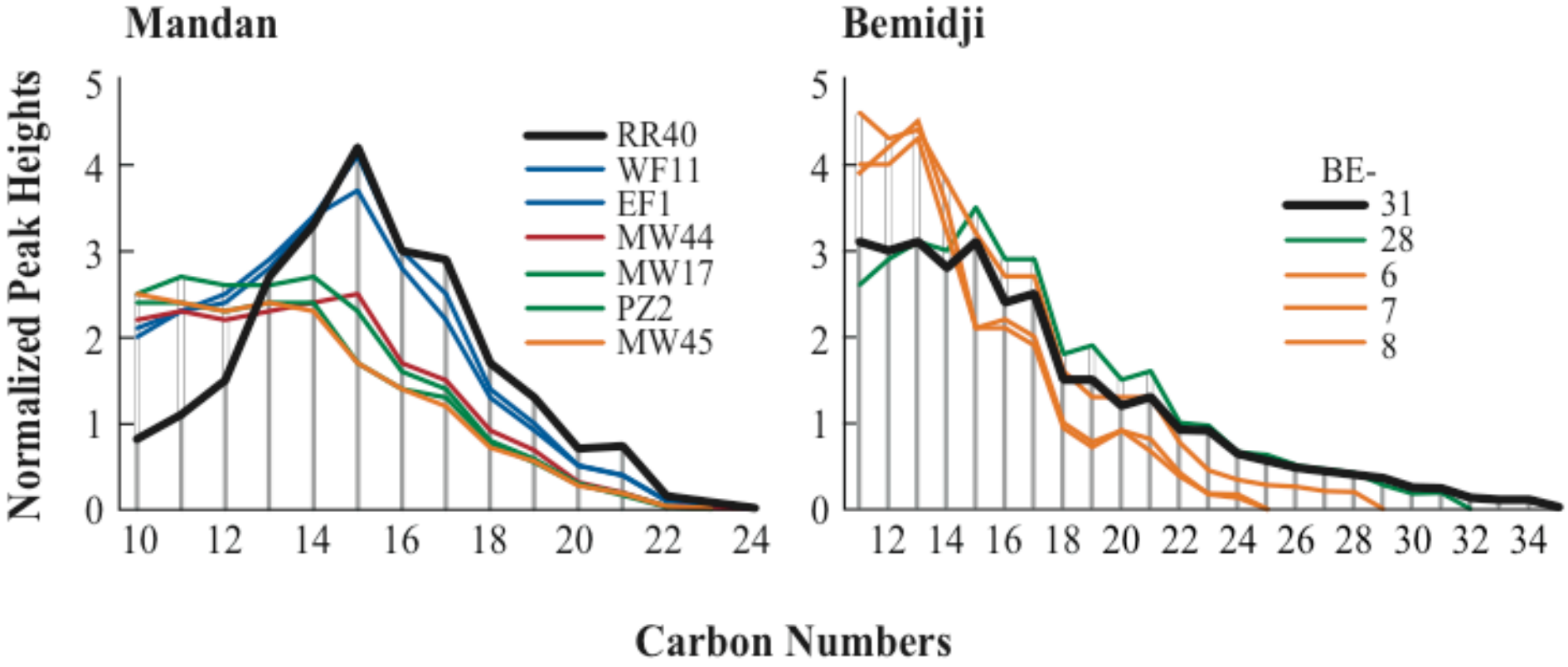
MW45
$\delta^{13}C$ -28.4‰


n-alkylcyclohexanes (m/z 83)
Response
15
10
RR40
δ13C -29.5o/oo
Fresh
C15
C17
Pr
minor n-alkane peaks
BE-31
15
10
WF11
δ13C -29.0o/oo
Partly
Degraded
C15
C17
minor n-alkane and
isoprenoid peaks
Pr
Ph
BE-25
10
14
MW45
δ13C -28.4o/oo
More
Degraded
C13
C16
Pr
Ph
C20
unknown
? series
BE-7
Mandan
Retention Time
Bemidji

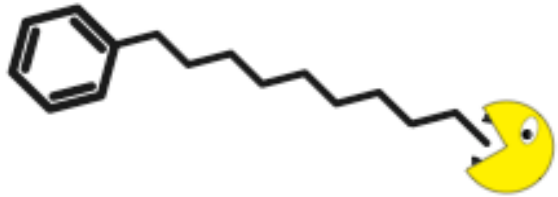
Normalized peaks



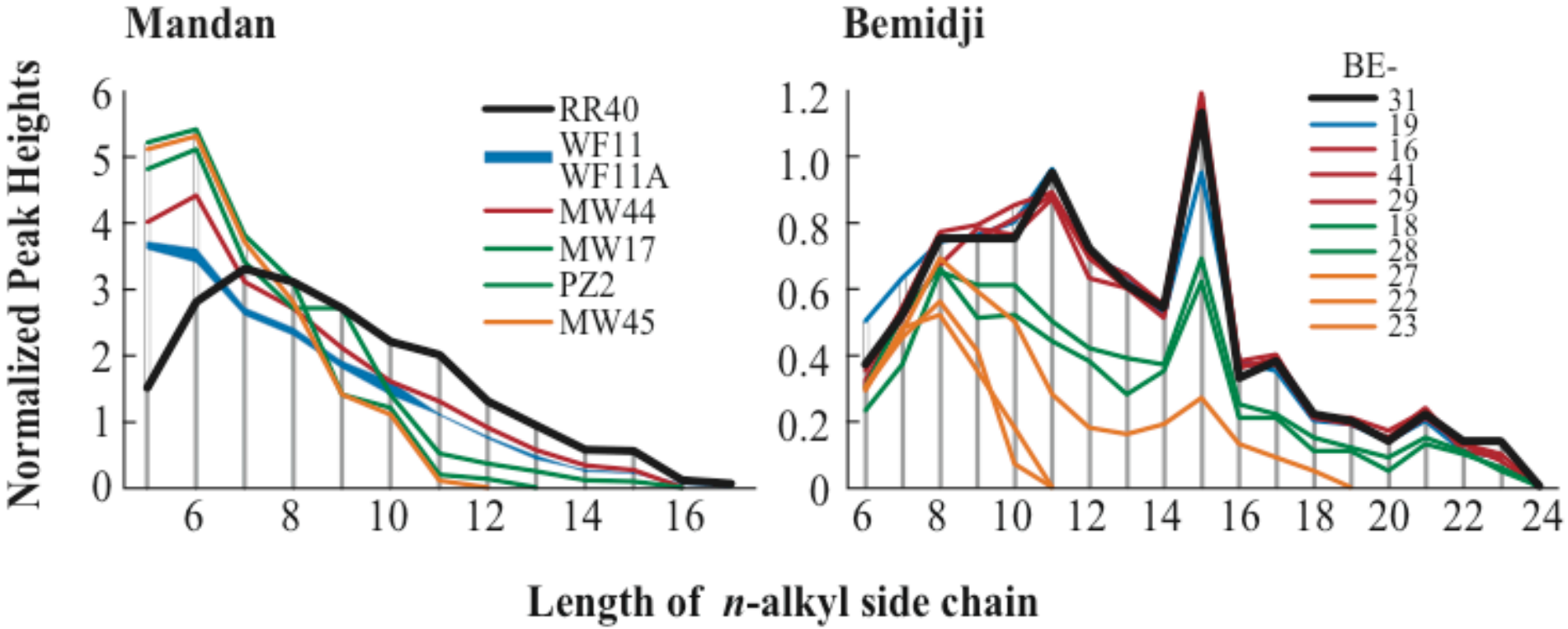
n-alkyl CHs



Normalized peaks



n-alkyl benzenes



Evidence that LNAPL spill is primarily RR off-road diesel and not admixture with other fuels:

1. Gasoline - No evidence of gasoline marker (iso-octane) except at one shallow outlying site.
2. Kerosene - Although *n*-alkane + *n* -alkyl CH patterns seem to indicate admixture, this research shows that the methanogenic degradation progression mimics its presence. Ratios of recalcitrant (non-degraded) constituents (e.g., Pr/Ph) show no kerosene present.
3. On-road diesel - PAH profiles do not fit.

Conclusions of Research Study

- All sites from downtown Mandan contain diesel fuel, consistent with railroad off-road diesel, at varying stages of biodegradation
- Related to episodic deposition over long time period
- Source of the diesel was the fuel used continually over 50 years supplied by the local refinery.

Challenges and Litigation - Results

July 2004. Lawsuit between railroad and NDDH and the State of ND settled out-of-court for $30.25 million (large$t environmental $ettlement in ND hi$tory).

Acknowledgements

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Further detail in USGS WRIR 01-4108

Report prepared and published as USGS WRIR 01-4108

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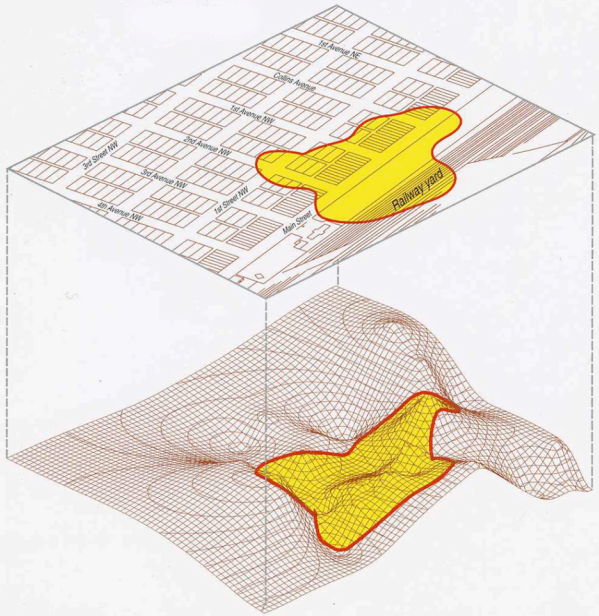
In cooperation with the North Dakota Department of Health

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



U.S. Department of the Interior
U.S. Geological Survey

WHY IS THIS IMPORTANT?

1. New and exciting patterns of hydrocarbon biodegradation under methanogenic conditions are emerging
2. Degradation involves non-polar intermediates
3. This pathway should be of interest in:
   - studies of microbial metabolite formation in anoxic environments
   - Descriptive Geochemistry, where anaerobic degradation processes are still being worked out
   - Forensic & Environmental Geochemistry where the progression may mimic lighter distillery products, or admixture, and lead to erroneous source attributions

Citations

Hostettler, F.D., Rostad, C.E., Kvenvolden, K.A., Delin, G.N., Putnam, L.D., Kolak, J.J., Chaplin, B.P., and Schaap, B.D., 2001, Hydrologic setting and geochemical characterization of free-phase hydrocarbons in the alluvial aquifer at Mandan, North Dakota, November 2000: U.S. Geological Survey Water-Resources Investigations Report 01-4108, 117 p.

Hostettler, F.D. and Kvenvolden, K.A., 2002, Alkylcyclohexanes in Environmental Geochemistry. Environmental Forensics, v. 3/3-4, p. 293-301.

Bekins, B.A., Hostettler, F.D., Herkelrath, W.N., Delin, G.N., Warren, E., and Essaid, H.I., 2005, Progression of methanogenic degradation of crude oil in the subsurface. Environmental Geosciences, v. 12, p. 1-14.

Hostettler, F.D., Wang, Y., Huang, Y., Cao, W., Bekins, B.A., Rostad, C.E., Kulpa, C.F., and Laursen, A., 2007, Forensic fingerprinting of oil-spill hydrocarbons in a methanogenic environment—Mandan, ND and Bemidji, MN. Environmental Forensics, v. 8, p. 139-153.

Rostad, C.E. and Hostettler, F.D., 2007. Profiling refined hydrocarbon fuels using polar components. Environmental Forensics, v. 8, p. 129-137.

Hostettler, F.D., Bekins, B.A., Rostad, C.E., and Herkelrath, W.N., 2008, Response to Commentary on observed methanogenic biodegradation progressions. Environmental Forensics, v. 9, p. 121-126.