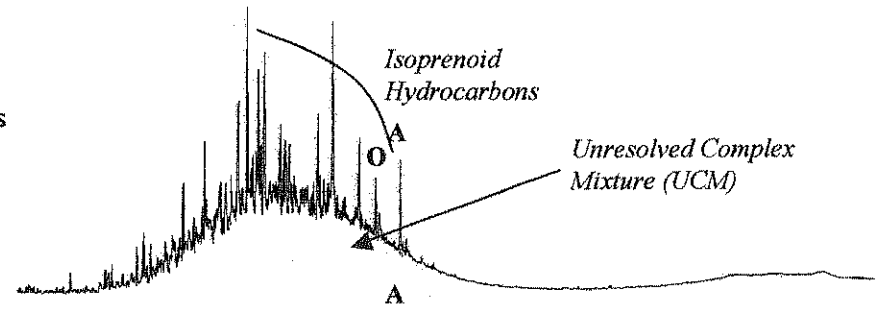
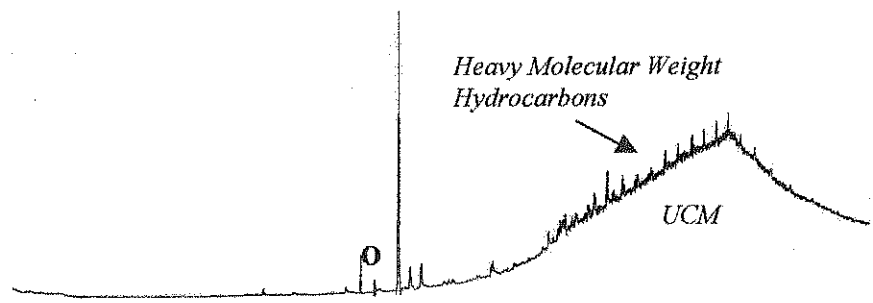
Figure 2.
Selected High Resolution Hydrocarbon Fingerprints

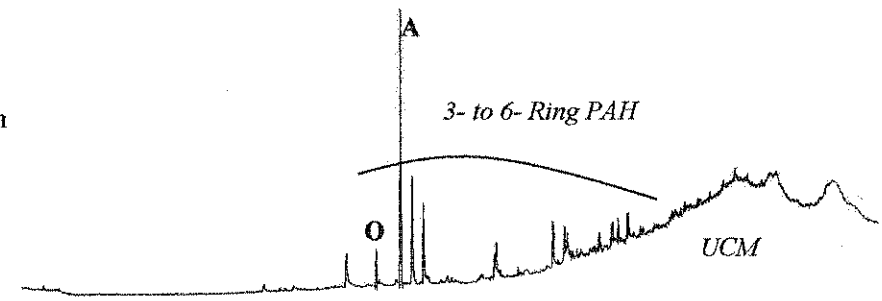
2a. SO11
Middle Distillate
Presence of isoprenoids and absence of normal alkanes indicates biodegradation.



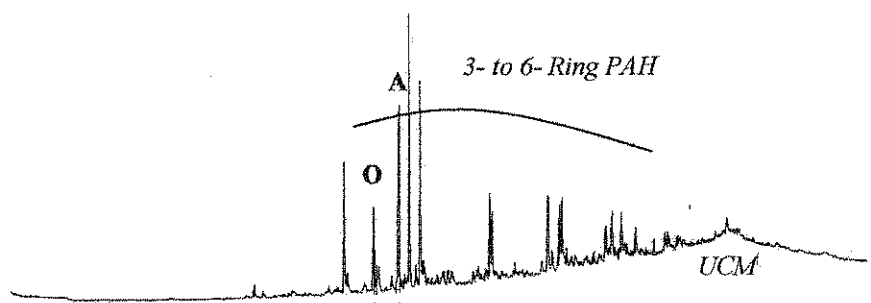
2b. SO15
Residual Petroleum
Heavy molecular weight compounds are consistent with asphalt or other residual petroleum.



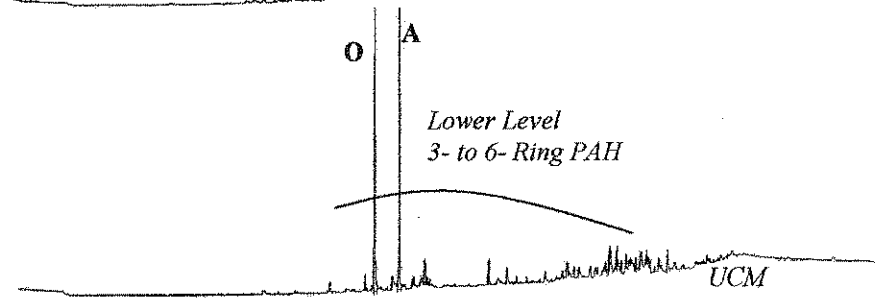
2c. OF93
Parking Lot Runoff
Pyrogenic PAH and late eluting UCM is a typical signature of urban runoff.



2d. 471
Urban Sediment
Enriched pyrogenic PAH and late eluting UCM is a typical signature of urban runoff.



2e. JPC03
Sediment
Lower level pyrogenic PAH and late eluting UCM is typical of runoff from less urban area and offshore locations.



O-terphenyl (**O**) and 5a-Androstane (**A**) are QC compounds that should otherwise be ignored for fingerprinting purposes

Figure 3.
PAH Analyte Patterns

3a. SO11
Middle Distillate
Enriched in 2- and 3-ring PAH with a petrogenic profile.

3b. S015
Residual Petroleum
Wide PAH range (2- to 6-rings) with mixed petrogenic and pyrogenic profiles. This pattern is consistent with a partially combusted crude or heavy fuel oil.

3c. OF93
Parking Lot Runoff
Pyrogenic 3- and 4- ring PAH with strong 5- and 6- ring PAH presence. This pattern is consistent with atmospheric fallout (see Fig 4e) that accumulates in the sediment matrix.

3d. 471
Urban Sediment
Similar to Fig 3c with slightly lower parent relative to alkylated PAH. This slight reduction in parent PAH is consistent with environmental weathering.

3e. JPC03
Sediment
Similar to Fig 3d with more pronounced reduction in parent PAH indicative of more advanced weathering.

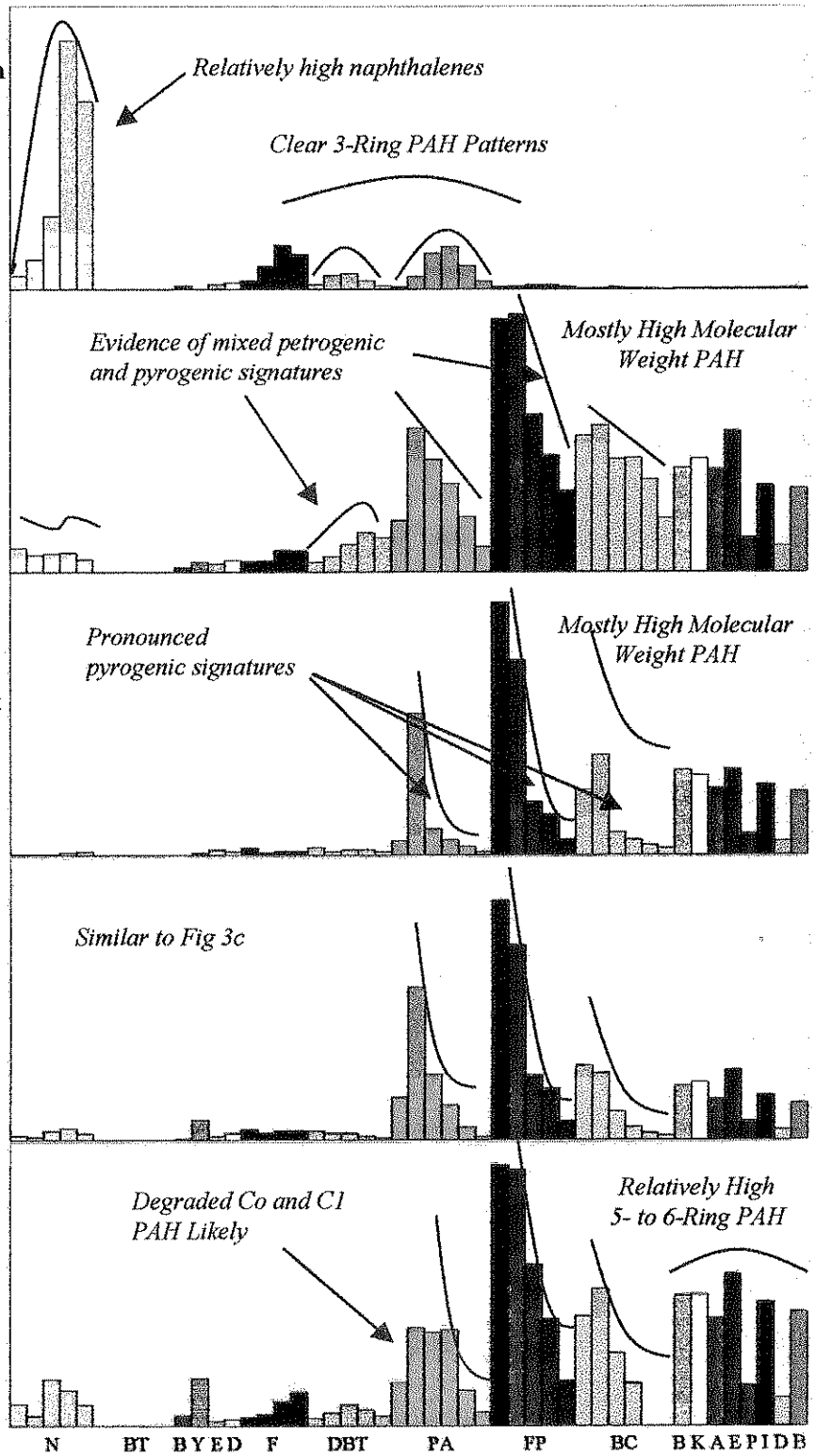
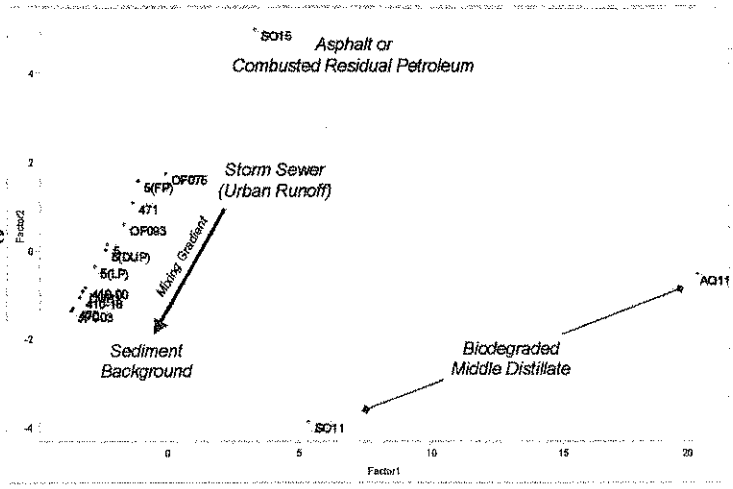
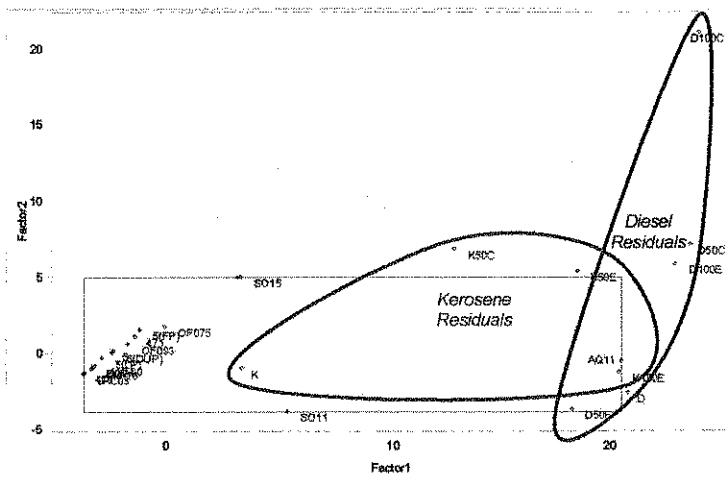


Figure 5.
Principal Components Analysis of PAH Analyte Ratios In Field and Reference Samples

5a. Sample Groupings (PCA Scores Plot).
The middle distillates were located in the lower right due to petrogenic 2- and 3-ring PAH. The residual petroleum exhibited a mixed petro- and pyrogenic PAH pattern with a bias towards 4- to 6-ring PAH. The sediments were fairly similar differing mostly in the relative abundances of 4- through 6-ring PAH.



5b. Sample Grouping (PCA Scores Plot Modified)
Plot 5a shown with selected kerosene and diesel reference materials. Sample AQ11 clustered with the diesel samples while SO-11 plotted to the lower left due to the enriched 2-ring PAH – indicating a light diesel source material with slight evaporation effects in AQ-11. Like SO-11 and AQ-11, the reference materials were distinct from the sediment samples.



5c. Analyte Groupings (PCA Loadings Plot).
Principal components 1 (x-axis) and 2 (y-axis) contain 87% and 9% of the variability, respectively. The PAH concentration data illustrate three primary types of field samples: pyrogenic urban runoff, residual petroleum, and middle distillate.

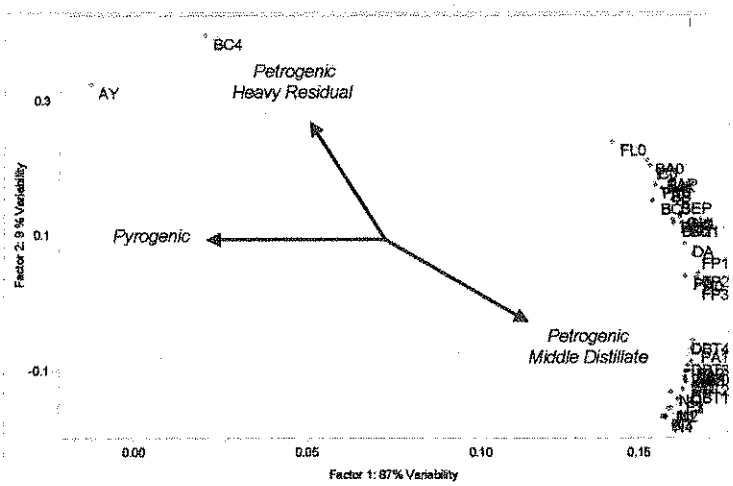
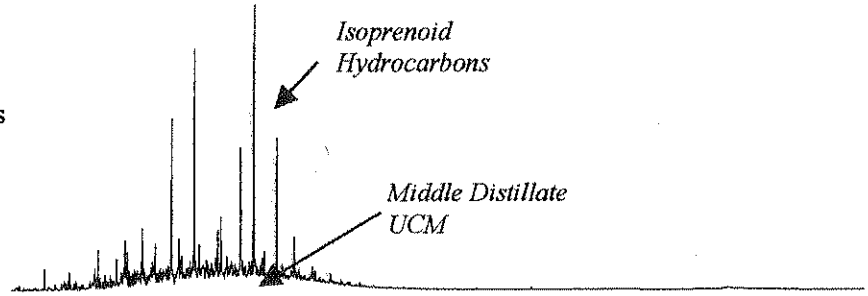
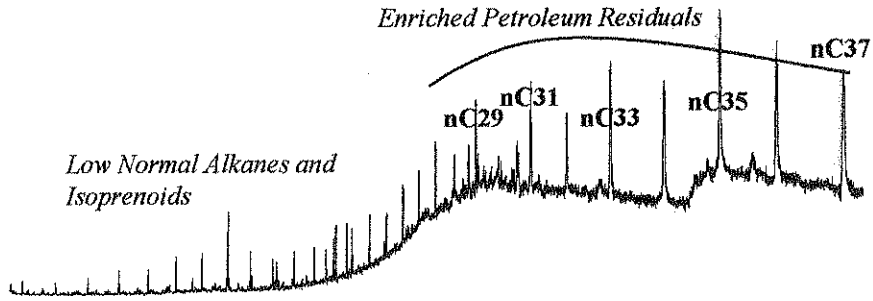


Figure 6.
Normal Alkane Fingerprints (GC/MS m/z 85)

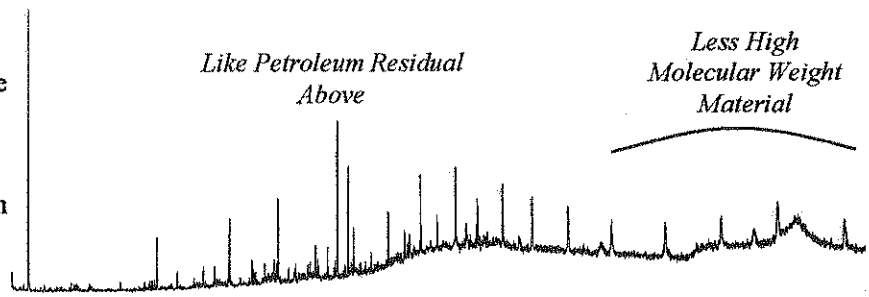
6a. SO11
Middle Distillate
Presence of isoprenoids and absence of normal alkanes indicates biodegradation.



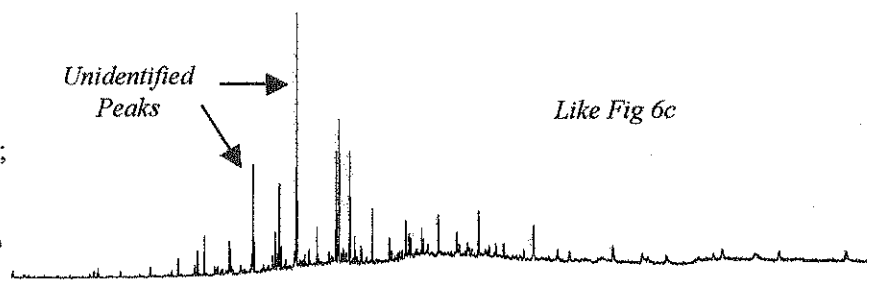
6b. S015
Residual Petroleum
Heavy molecular weight compounds are consistent with asphalt or other residual petroleum. Heavy odd carbon number preference observed may indicate unique petroleum source.



6c. OF93
Parking Lot Runoff
Wide range normal alkanes and late eluting UCM is a typical signature of urban runoff. This petroleum pattern is very low relative to the pyrogenic PAH pattern described in Fig 3c.



6d. 471
Urban Sediment
When the unidentified peaks are removed from the pattern, similarities with Fig 6c are evident; i.e., wide range normal alkanes with a late eluting UCM. This petroleum pattern is low relative to the pyrogenic pattern in Fig 3d.



6e. JPC03
Sediment
Residual petroleum pattern is low relative to the pyrogenic PAH patterns described in Fig 3e. The lower level of light hydrocarbons could indicate greater weathering than Fig 6d. Pattern without sulfur peaks is in Attachment 6.

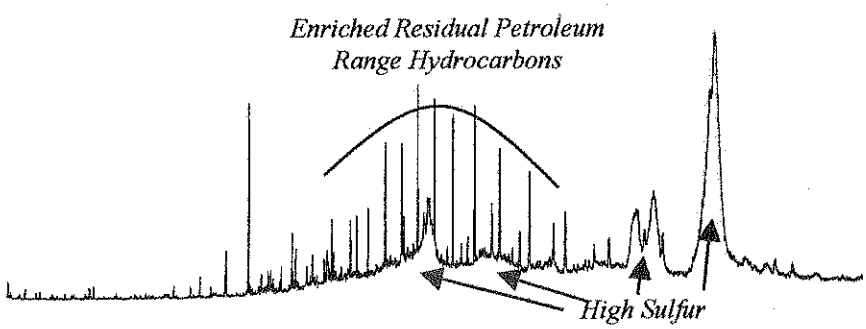
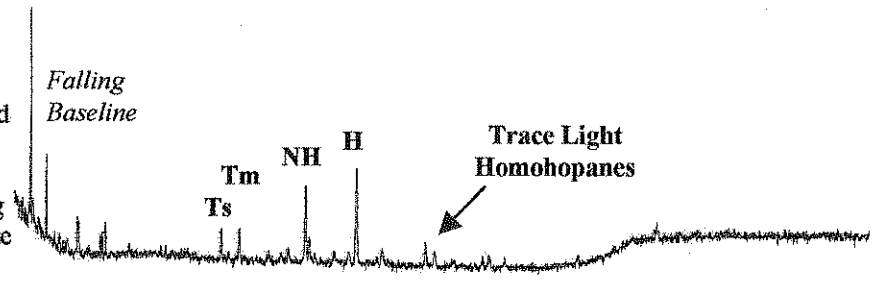
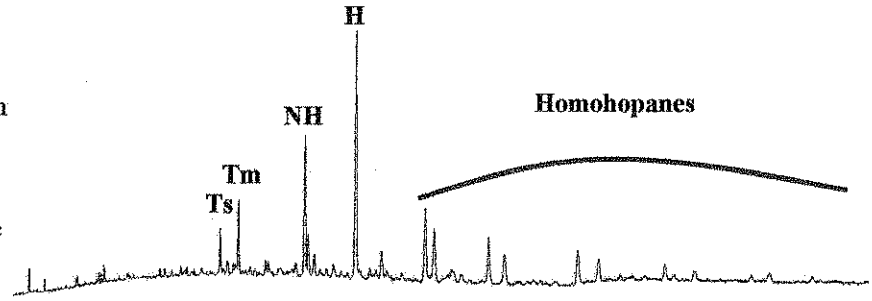


Figure 7.
Terpane Biomarker Fingerprints

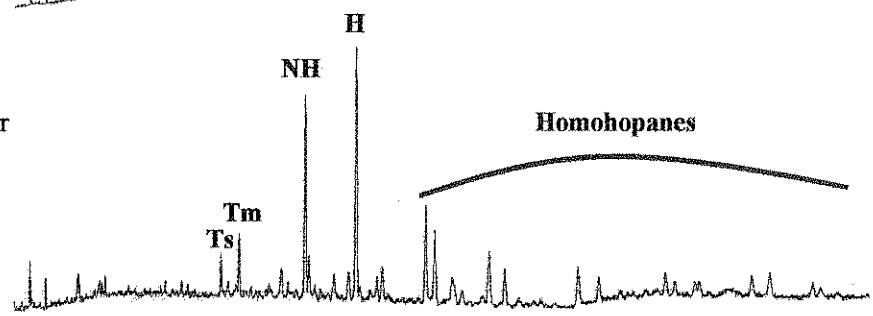
7a. SO11
Middle Distillate
The end of the distillation run is revealed by the falling baseline and trace, light homohopanes. The relative abundances of Ts to Tm and NH to H appear unique among these samples and indicate a unique petroleum origin.



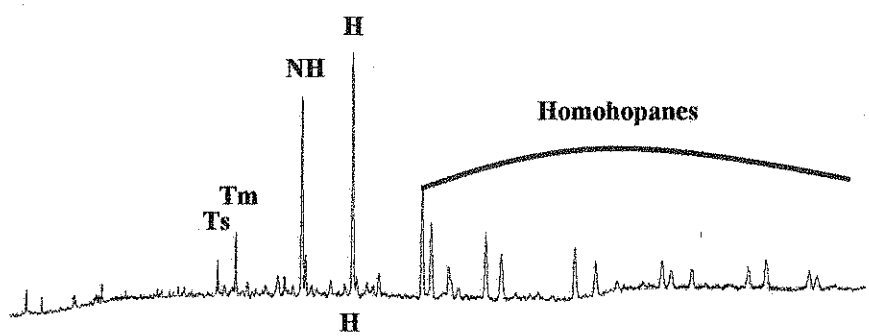
7b. SO15
Residual Petroleum
Heavy molecular weight petroleum revealed by a full range of triterpanes. The low relative abundance of NH to H may indicate a unique petroleum source among the field samples.



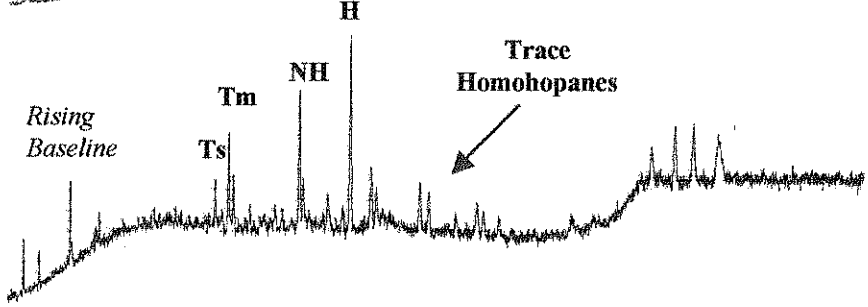
7c. OF93
Parking Lot Runoff
Similar to Fig 6b, except the higher relative abundance of NH to H differentiated this petroleum material from that in SO15.



7d. 471
Urban Sediment
Similar to Fig 6c.



7e. JPC03
Sediment
Similar to Fig 6c, except the relative abundance of Ts to Tm may be low. The triterpanes are present at trace concentrations as evidenced by the rising initial baseline and homohopanes below the detection limit.



Ts = 18α(*H*),21β(*H*)-22,29,30-trisnorhopane Tm = 17α(*H*),21β(*H*)-22,29,30-trisnorhopane
NH = 17α(*H*),21β(*H*)-30-norhopane H = 17α(*H*),21β(*H*)-hopane