

PS Soil Hydrocarbon Alteration: Solid Phase versus Gas Phase Hydrocarbon Detection*

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Abstract

The main assumption that drives surface exploration techniques is that hydrocarbon gases from the reservoir seep to the surface where they are detected and measured by various methods. This investigation puts forth the alternative explanation that the hydrocarbon anomalies being detected at the surface come from soil organics altered by seeping reservoir hydrocarbons rather than by the direct measurement of the reservoir hydrocarbons.

Surface soil hydrocarbons are ubiquitous and occur in an infinite number of configurations. Because of the diversity of compounds present in near surface soils, Humic and Fulvic acids are the primary compounds of interest. Altered carbohydrates and proteins also contribute to the surface geochemical signature. The soluble Fulvic acids appear to be the source of most measured hydrocarbon anomalies while the non-water soluble Humic acids contribute when degraded chemically or physically. Condensation and addition reactions between Fulvic acids and the available free alkanes are the pathways to altered hydrocarbon signatures found over oil and gas reservoirs. The physical and chemical properties of these two types of soil organic matter account for many of the surface geochemical phenomena observed.

The soluble altered Fulvic acids are measured in aqueous phase by UV-Vis Spectroscopy. UV-Vis absorbance spectra of soil hydrocarbons correlate well with thermally desorbed gas phase soil hydrocarbons. GC/MS was used to identify potential sources of measurable solid, aqueous, and gas phase soil hydrocarbons.

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Introduction

Surface geochemistry as applied to oil and gas exploration is the search for surface and near surface direct indications of the microseepage of hydrocarbons from an oil or gas reservoir. Devolatilization and thermal degradation of oils produce a continual leakage of light hydrocarbon components from the reservoir. All viable methods of surface geochemistry depend on various mechanisms of hydrocarbon migration from the reservoir, with a primary vertical vector with little lateral offset or dispersion.

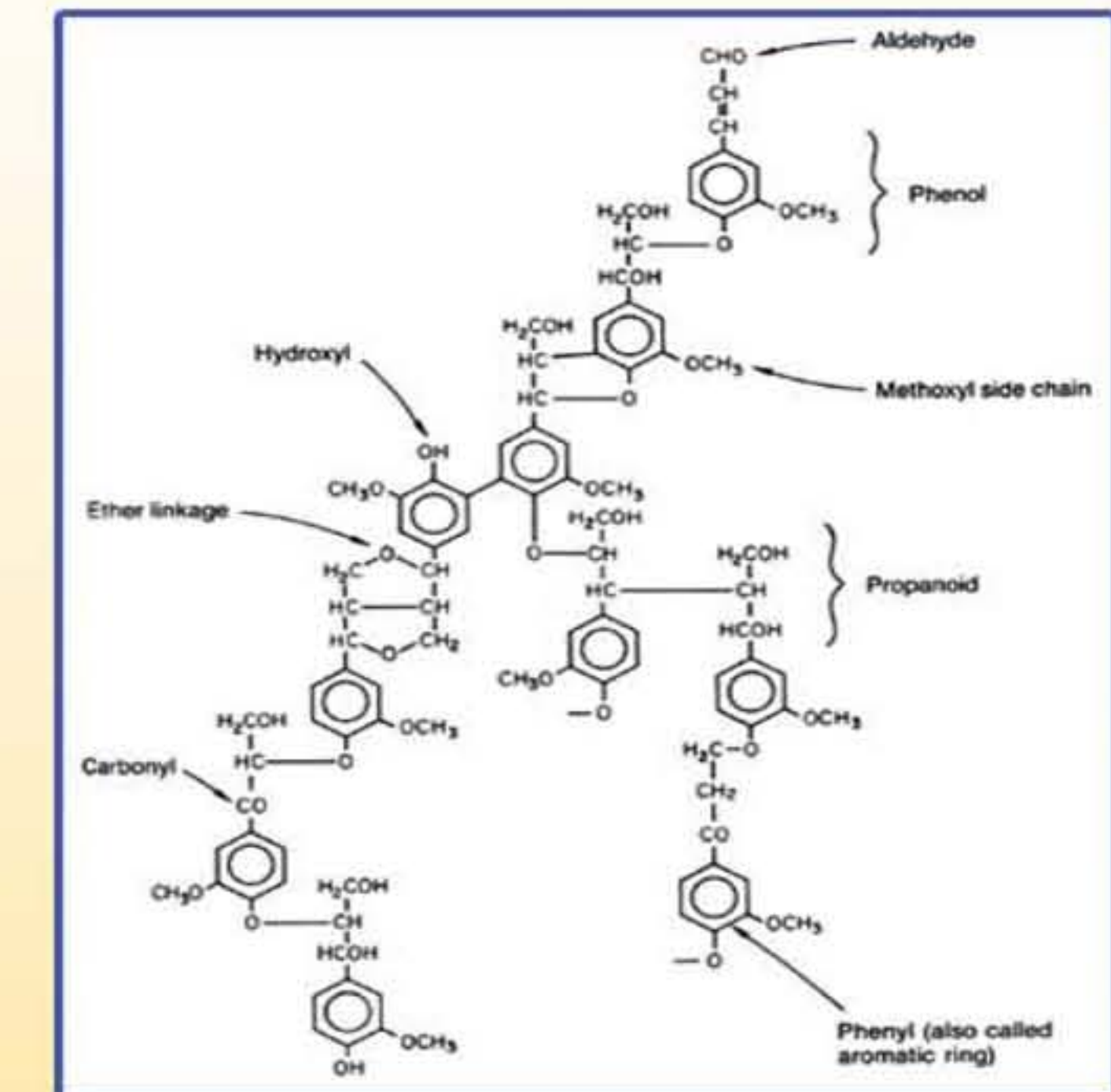


Figure 1. Basic lignin structure prior to decomposition showing the common functional groups. Some fungi can degrade lignin in the presence of other readily degradable substrates (seeping hydrocarbons) as the primary energy source. The newly liberated hydrocarbons are now available for other biological processes or manifest as altered SOM.

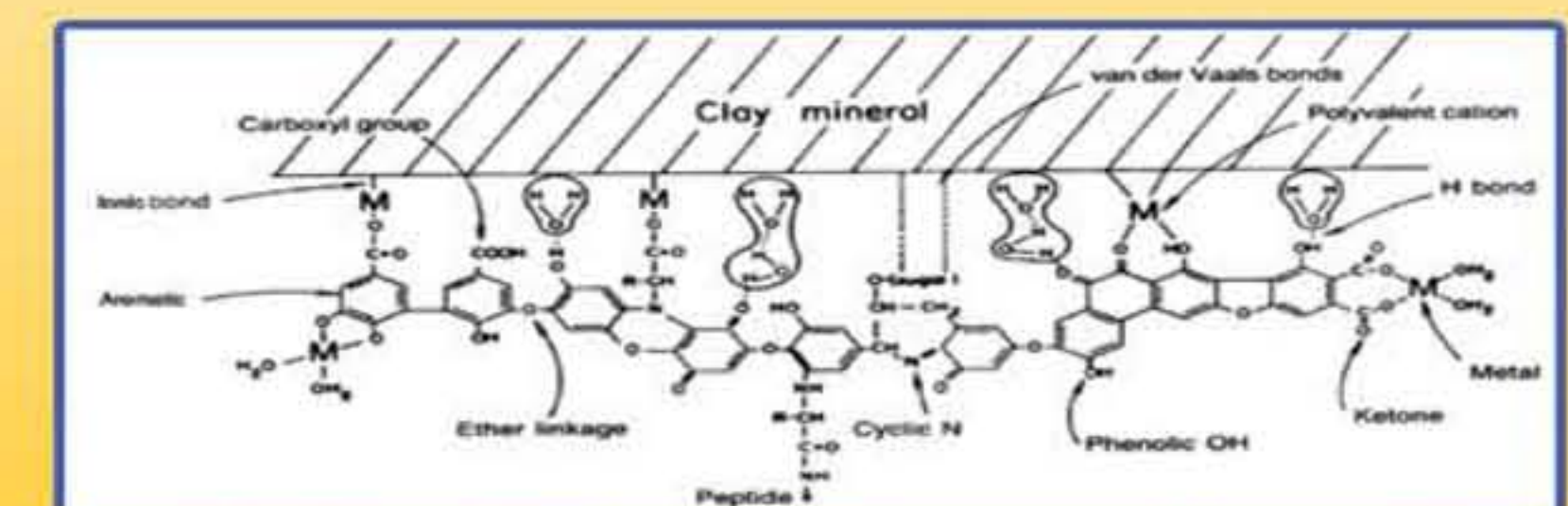
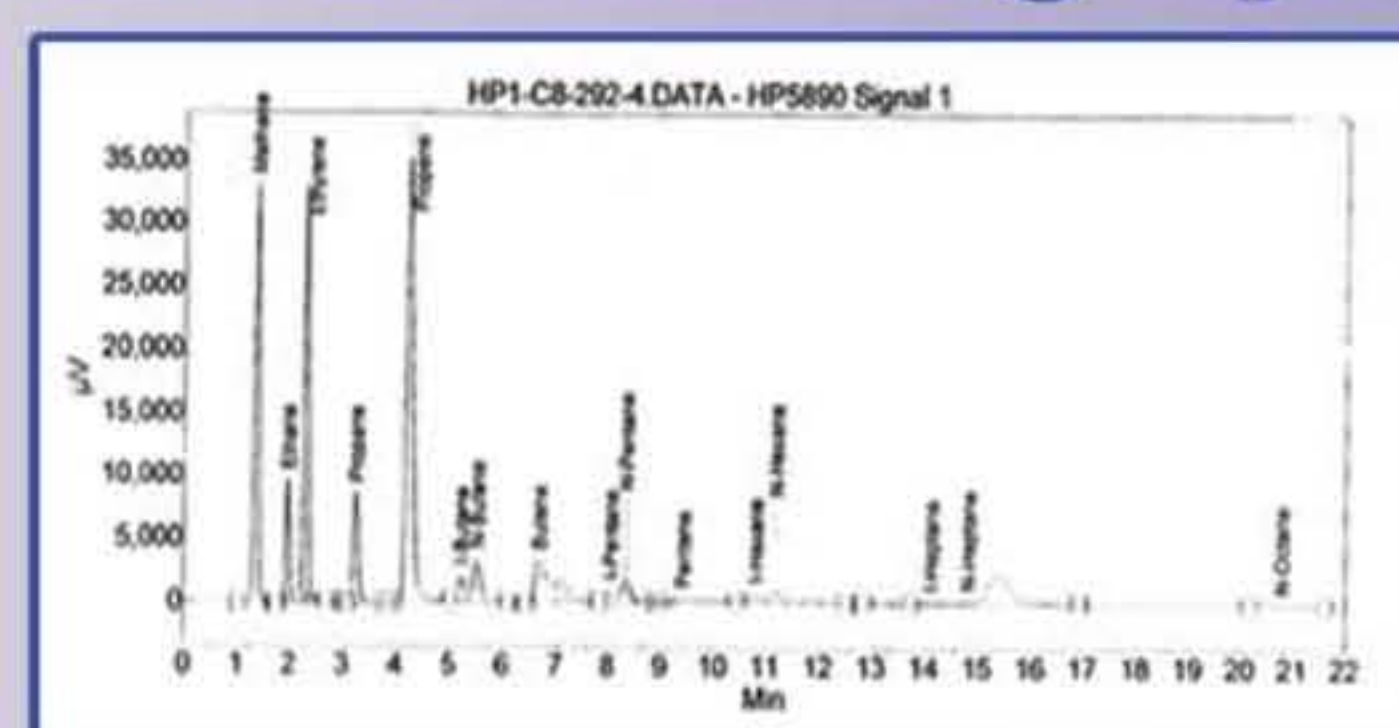


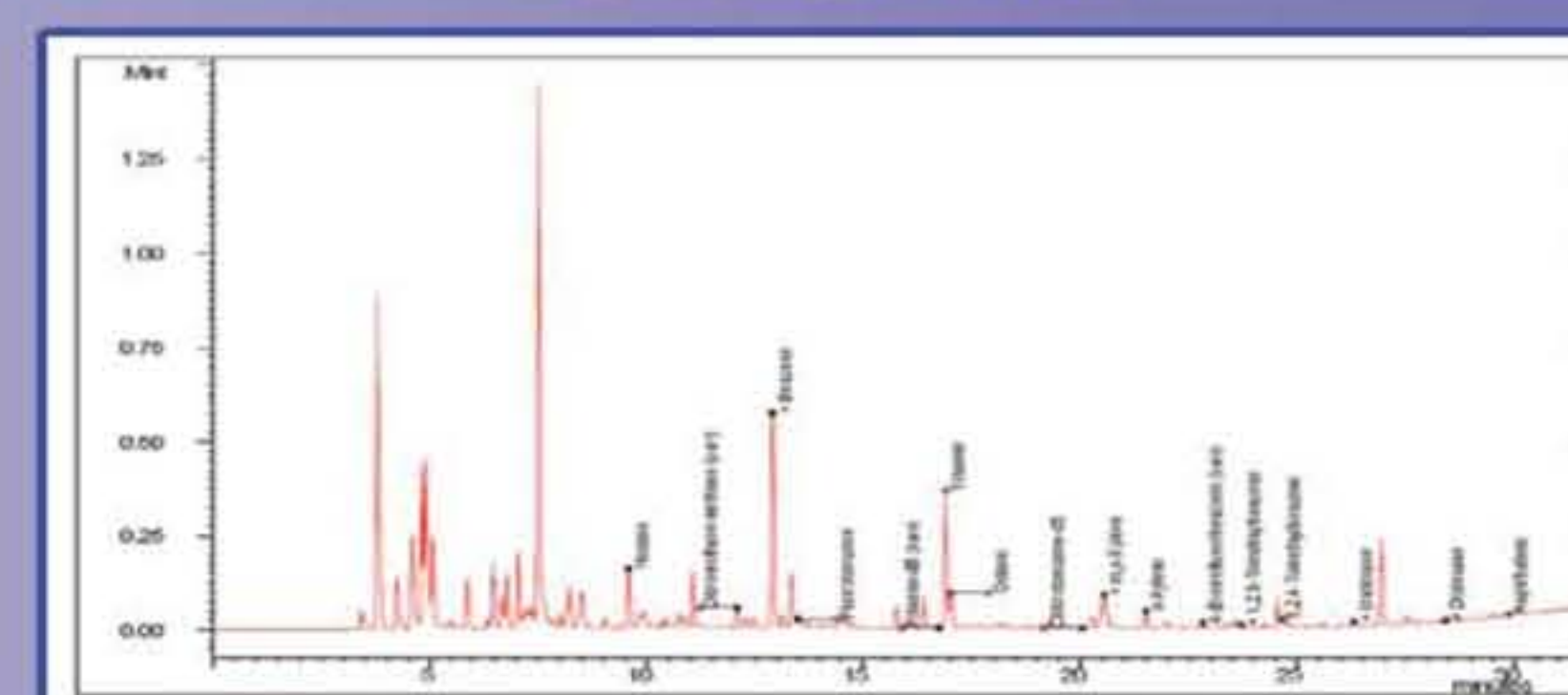
Figure 2. Schematic diagram of a clay-humate complex in soil. Note the large open structure of the molecule which allows the fixing of organic and inorganic compounds.

Sample 1

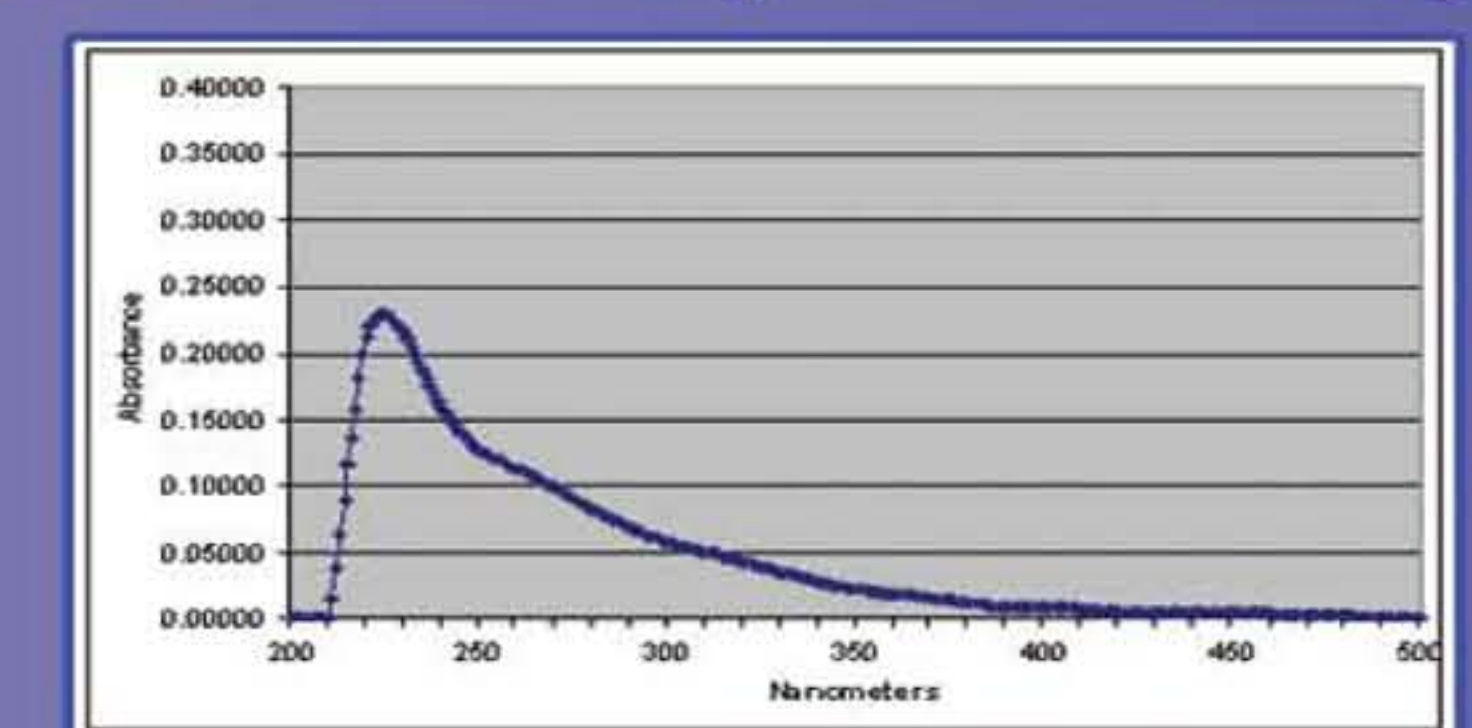
Gas Chromatography



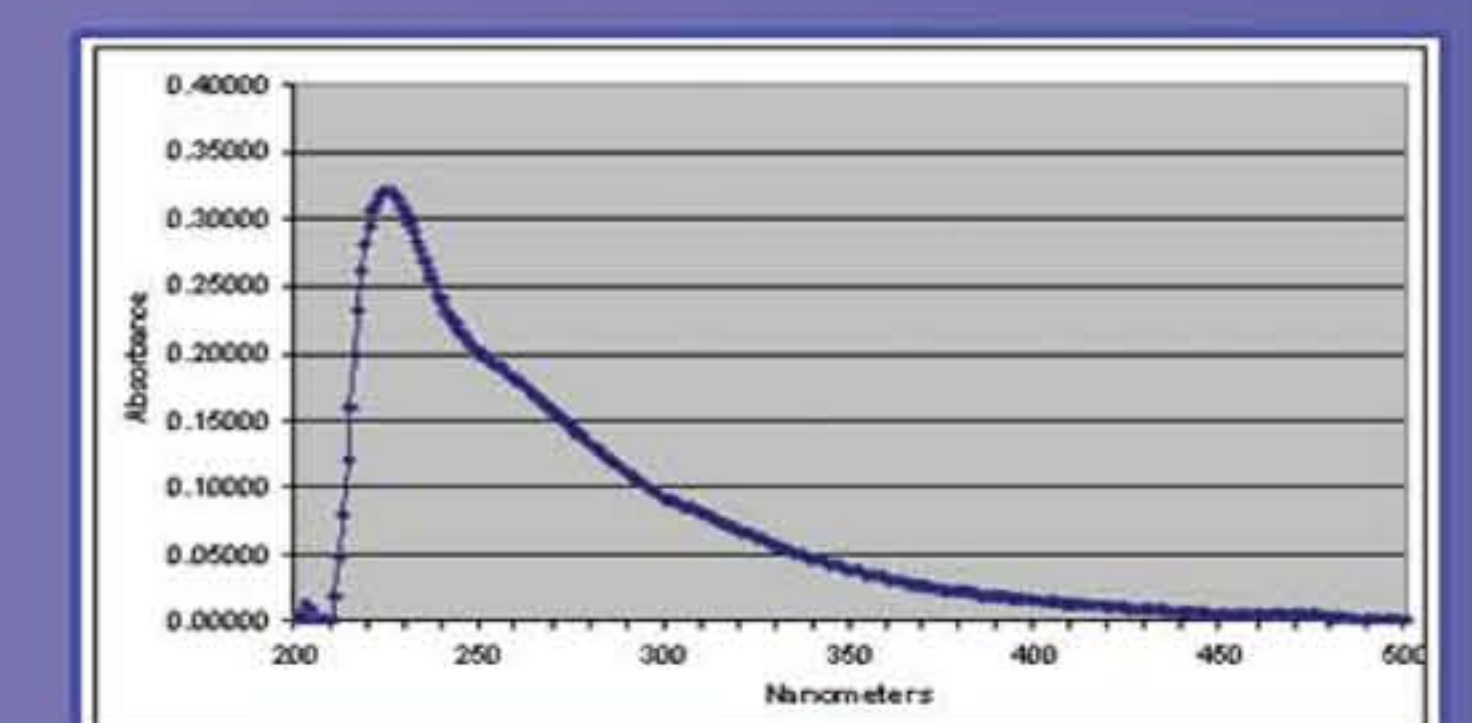
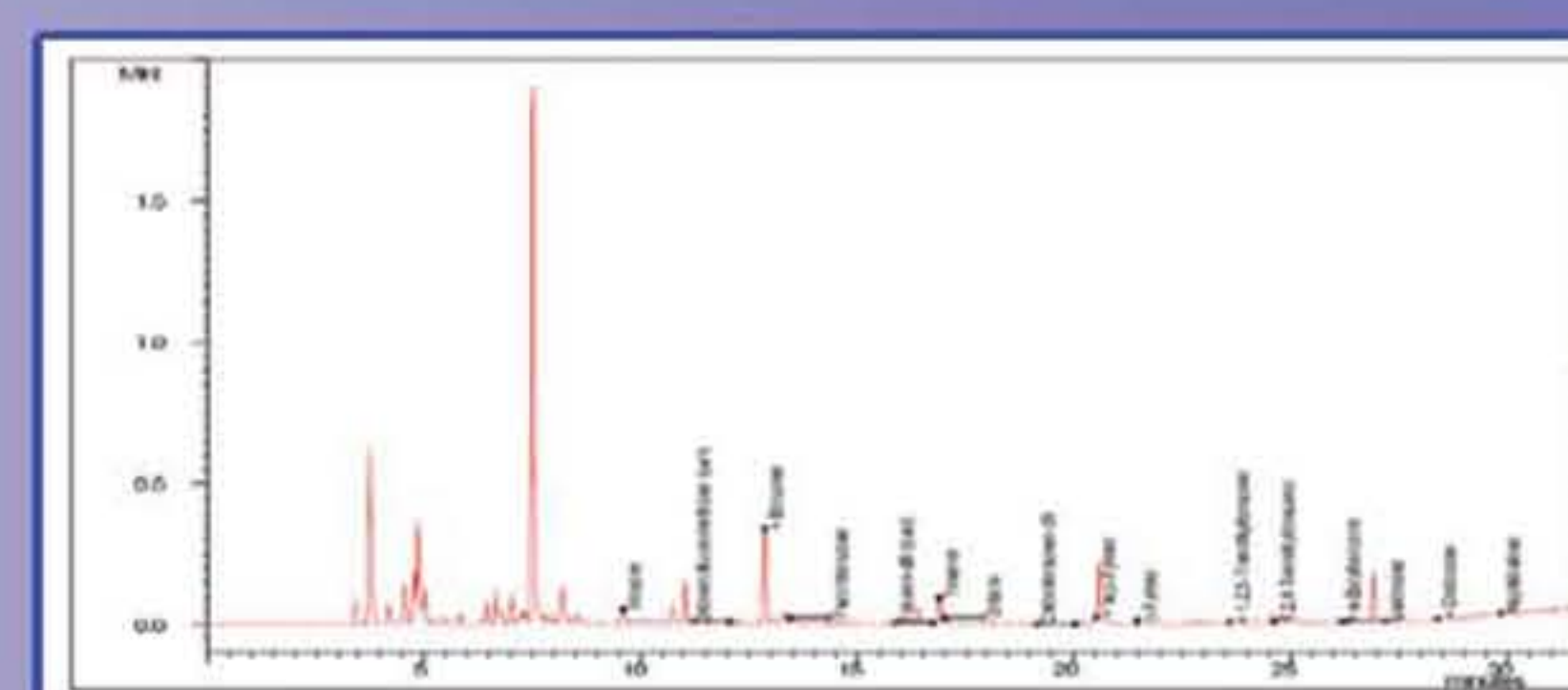
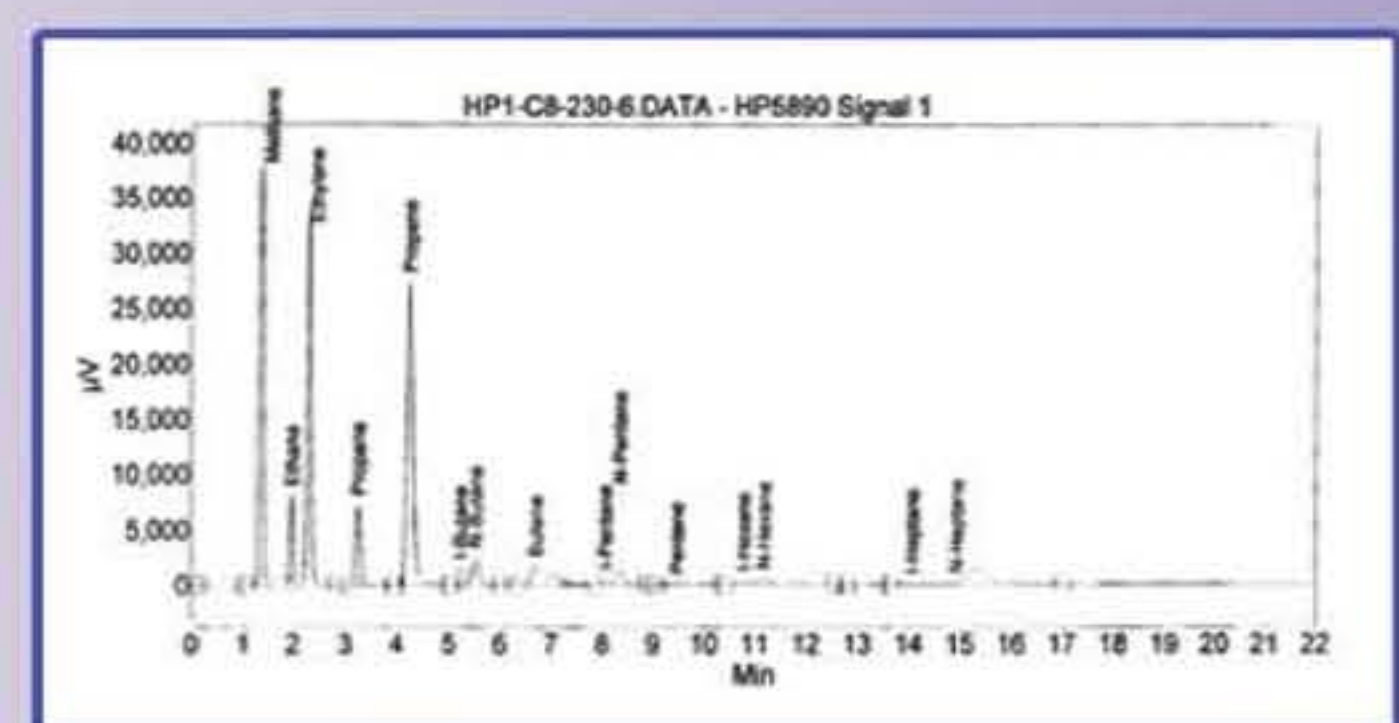
GC / MS



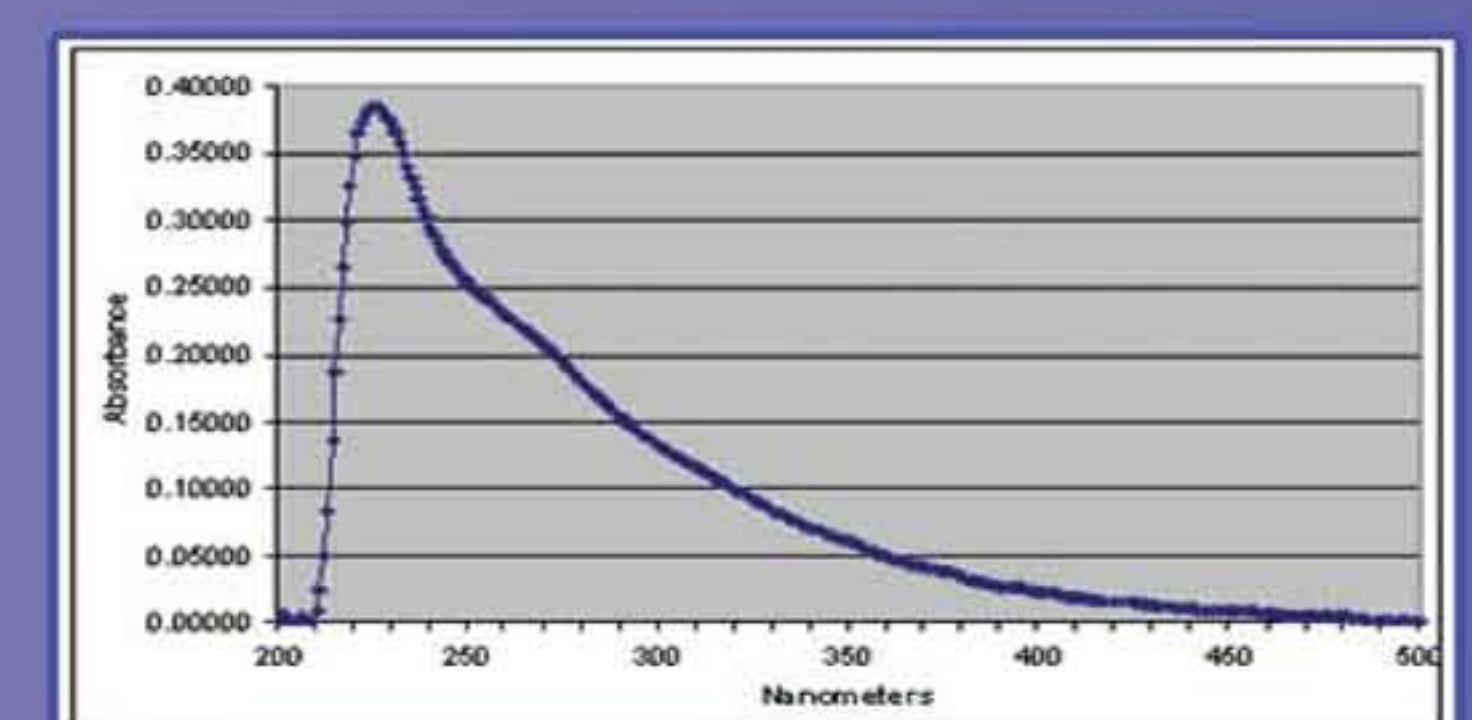
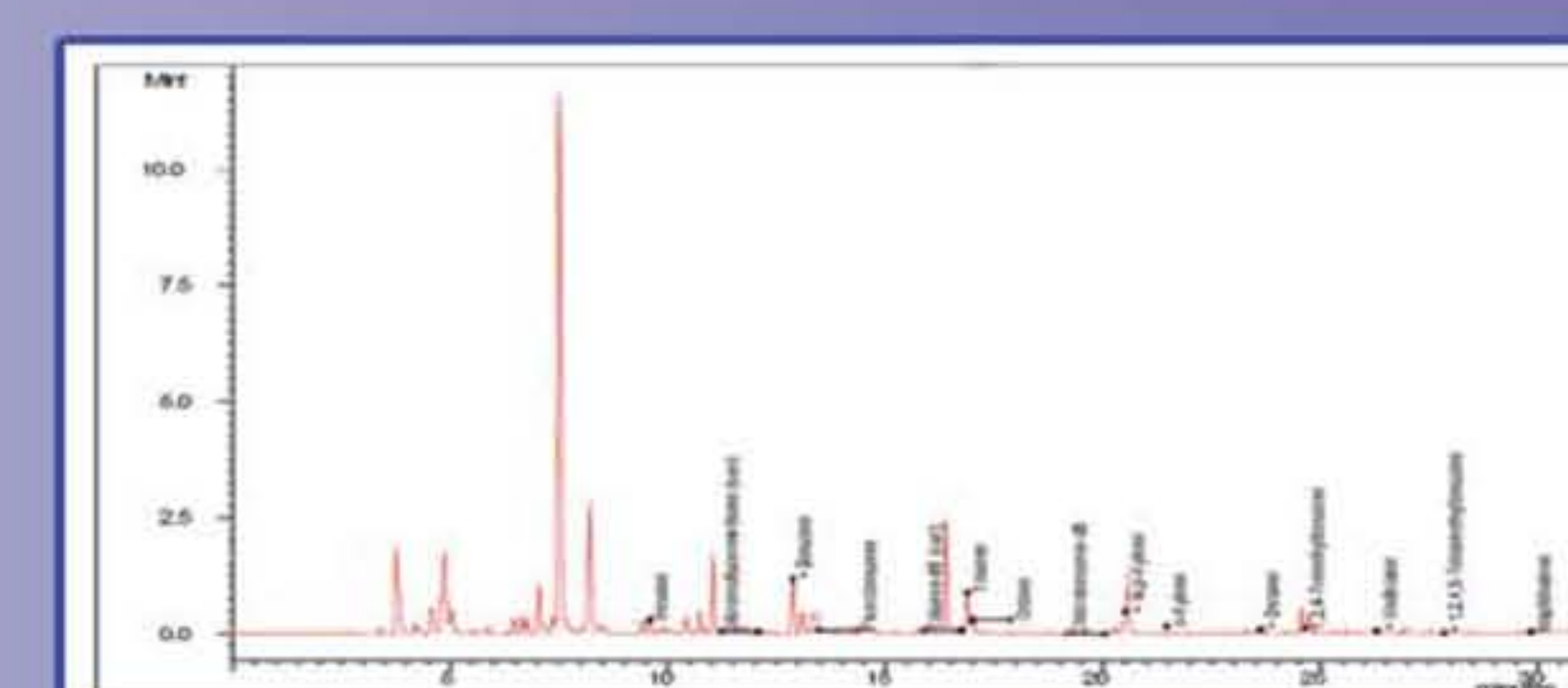
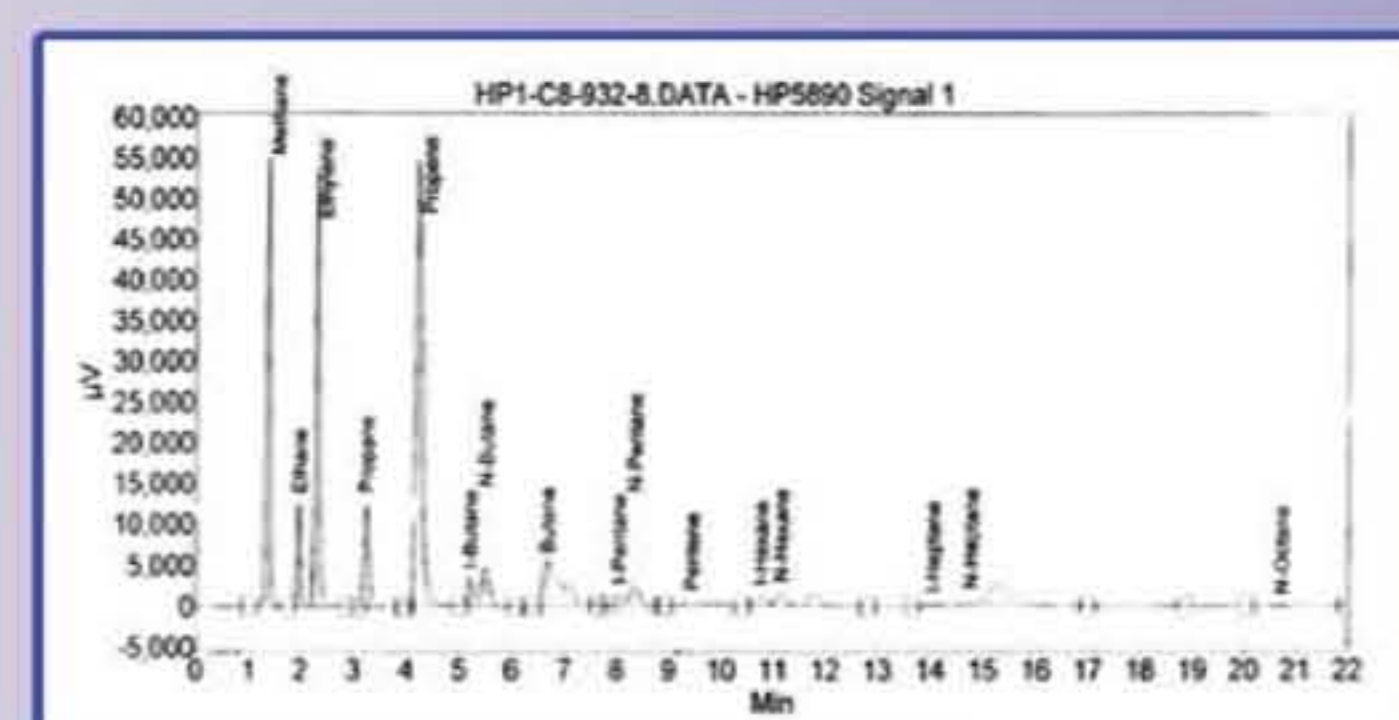
UV - Vis Spectroscopy



Sample 2



Sample 3



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Are the gases being measured at the surface really those escaping from the hydrocarbon reservoir?

By comparing multiple hydrocarbon measurements by different methods, it will be shown that the signature commonly acknowledged as a "direct" hydrocarbon measurement is actually related to the alteration of near surface soil organic matter (SOM).

It is assumed that hydrocarbons seep to the surface, with some escaping into the atmosphere, some being occluded in sediments in gas phase, and some being consumed by soil biota. The occluded gases are termed as being directly related to the hydrocarbon reservoir at depth and are simply waiting in a static environment to be collected and analyzed. Near surface soils are anything but static. Being a significant carbon sink, soil processes help complete the carbon cycle by providing microorganisms with the energy contained in carbon - hydrogen (C-H) bonds. This is the driving force behind nearly all of the nutrient cycling reactions involving organic compounds in soils and sediments. It is proposed that much of the hydrocarbons being measured in near surface soils are related to the incorporation, and subsequent alteration, of near surface SOM by seeping hydrocarbon gases.

Basic Concept

Vertically seeping hydrocarbons react with SOM which alters the SOM within a seep relative to the background SOM. Various biological processes help integrate free reservoir related hydrocarbons into the SOM. Condensation and addition chemical reactions provide the pathways. Any of the soil hydrocarbons can be altered, with primary ones being humic acids, fulvic acids, carbohydrates, and proteins. X-ray analysis, electron microscopy, and viscosity measurements of fulvic acids indicate a relatively open, flexible structure, perforated by voids of varying dimensions. These voids can trap, or fix, organic and inorganic compounds that fit into the voids, provided the charges are complimentary. Many of the phenomena measured in near surface soils to detect seepage anomalies are regulated by the various components of humic and fulvic acids. These include the movement of halogens, fragmentation and integration of aliphatic and aromatic hydrocarbons, pH buffering, oxidation-reduction reactions, cation exchange capacity, carbonate deposition, and the presences and growth of soil flora and fauna.

Data

The data are derived from measurements by various methods. These include loss on ignition, thermal desorption, and hydrocarbon extraction by hot acid, organic solvents, and deionized water. Analysis is by gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC / MS), and ultraviolet - visible light spectroscopy.

Comparisons

Comparisons of UV-Vis absorbance data and conventional GC measurements yield a very high correlation. As the concentration of the hydrocarbon gas homologs increase so does the corresponding intensity of the absorbance. Hydrocarbons analyzed by GC and UV-Vis exhibit linear relationships when compared to adjacent homologs or wavelengths respectively. Therefore, a correlation matrix is a reasonable tool for method comparisons.

The first notable comparison establishes the concentration connection. Conventional hydrocarbon homologs and UV-Vis wavelengths correlate with concentration. High hydrocarbon sample concentrations tend to generate higher correlations while lower hydrocarbon concentrations yield correlations near zero. A comparison of matrices shows that as concentration decreases fewer hydrocarbon homologs correlate with the UV-Vis hydrocarbons (Table 1), while the sample set with the highest concentrations has the greatest correlation with more of the hydrocarbon homologs (Table 3).

Comparison of Concentration by Method Type

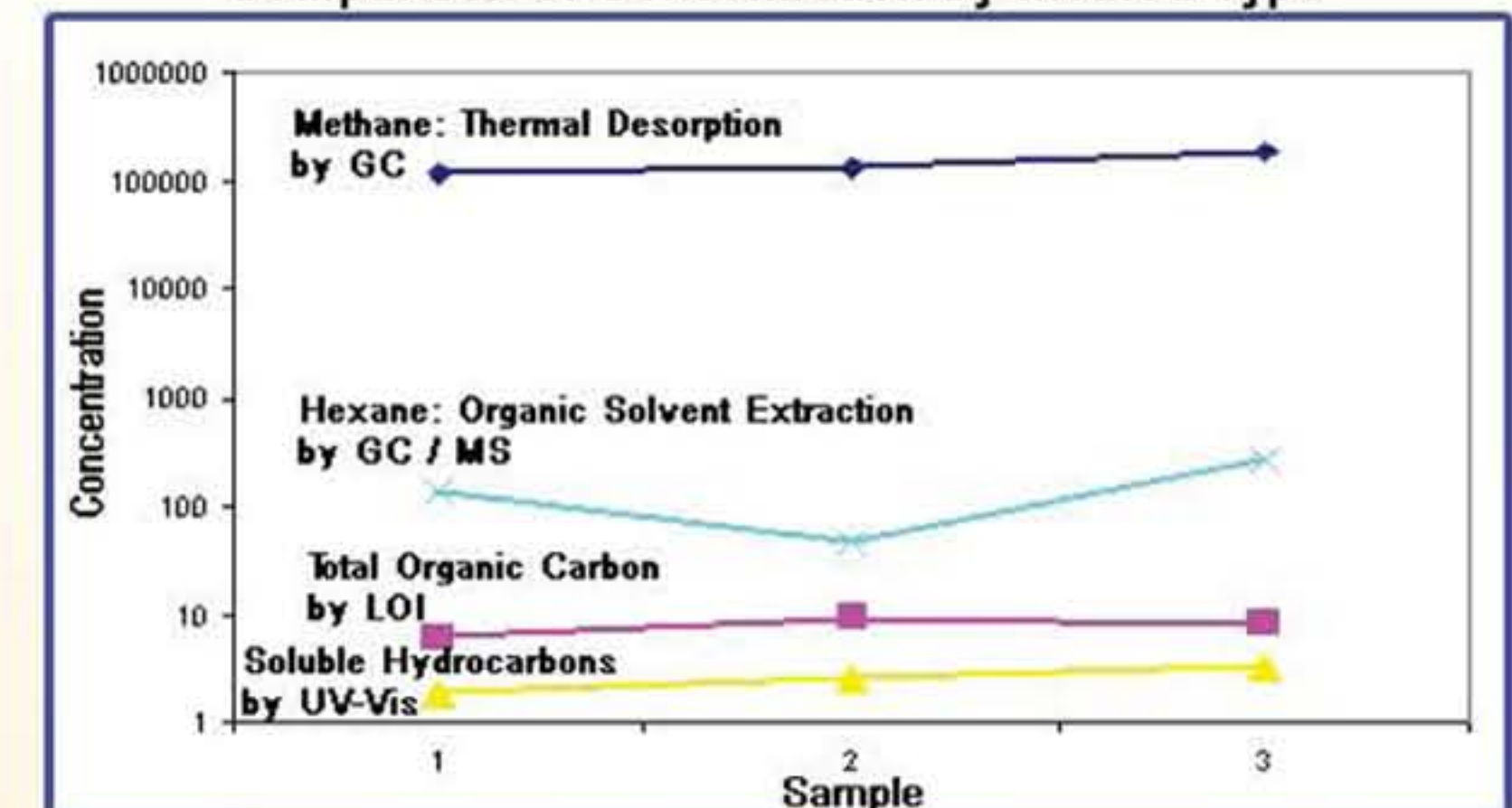


Figure 3. A comparison of four analytical methods and the carbon / hydrocarbon response relative to each. Thermal Desorption and UV-Vis show the greatest correlation. Sample 3 is anomalous when measuring gas phase and solid phase hydrocarbons.

Wavelength (nm)	Methane	Ethane	Propane	i-Butane	N-Butane
NM_260	-0.02829	-0.08658	-0.07352	-0.01173	-0.06049
NM_270	-0.04074	-0.34298	-0.04212	0.19991	-0.04534
NM_280	0.03918	0.68863	-0.03853	-0.55372	0.01037
NM_290	0.13951	0.68917	0.04477	-0.45818	0.08069
NM_300	0.11466	0.60382	0.01699	-0.42884	0.05085
NM_310	0.09903	0.55853	0.00172	-0.41344	0.03393
NM_320	0.09155	0.53134	-0.00595	-0.40011	0.02378
NM_330	0.08444	0.51607	-0.01125	-0.39231	0.01487
NM_340	0.07455	0.49807	-0.01669	-0.38353	0.00649
NM_350	0.05755	0.48183	-0.02850	-0.38015	-0.00909

Hydrocarbon	Mean	Minimum	Maximum
Methane	69	43	100
Ethane	4.6	2.3	8.6
Propane	6.7	3.0	12.9
i-Butane	6.8	1.5	30.1
Butane	2.9	1.5	5.9

Table 1. Correlation Matrix of hydrocarbon homologs and UV-Vis hydrocarbons with low concentrations. Outlined areas indicate higher positive and negative correlations. Ethane and i-butane show some correlation. Hydrocarbon values are in ppm.

Wavelength	Methane	Ethane	Propane	N-Butane	N-Pentane	i-Butane	i-Pentane	Ethylene	Propene	Butene
NM_230	0.90911	0.51907	0.60280	0.54442	0.53279	0.58388	0.40730	0.82495	0.60216	0.49620
NM_240	0.92049	0.54296	0.62505	0.56785	0.55643	0.60653	0.43289	0.84055	0.62442	0.52047
NM_250	0.91786	0.53735	0.61983	0.56225	0.55088	0.60122	0.42607	0.83662	0.61920	0.51477
NM_260	0.91362	0.52843	0.61152	0.55359	0.54204	0.59276	0.41730	0.83110	0.61089	0.50570
NM_270	0.92590	0.55452	0.63578	0.57918	0.56787	0.61747	0.44531	0.84796	0.63517	0.53223
NM_280	0.93689	0.56668	0.66551	0.61065	0.59966	0.64779	0.48002	0.86806	0.66492	0.56497
NM_290	0.94424	0.59713	0.67514	0.62087	0.60998	0.65762	0.49136	0.87443	0.67455	0.57562
NM_300	0.95486	0.62398	0.69276	0.64709	0.63650	0.68278	0.52060	0.89038	0.69919	0.60301
NM_310	0.96023	0.63844	0.71296	0.66119	0.65077	0.69528	0.53643	0.89871	0.71240	0.61778
NM_320	0.96542	0.65311	0.73830	0.67548	0.66523	0.70984	0.55294	0.90697	0.72875	0.63277
NM_330	0.96964	0.66668	0.75933	0.67886	0.66878	0.71326	0.56647	0.90895	0.72899	0.63642
NM_340	0.96796	0.66060	0.73309	0.68277	0.67262	0.71690	0.56080	0.91111	0.73255	0.64044
NM_350	0.96890	0.66342	0.73564	0.68551	0.67540	0.71952	0.56391	0.91265	0.73510	0.64332

Hydrocarbon	Mean	Minimum	Maximum
Methane	145	119	185
Ethane	16	13	20
Ethylene	72	60	95
Propene	14	11	18
Propane	78	55	108
i-Butane	3.5	2.4	4.9
N-Butane	5.5	3.9	7.3
Butene	12.3	6.3	19.1
i-Pentane	1.5	0.8	2.1
N-Pentane	3.2	1.9	4.7

Table 2. Correlation matrix of hydrocarbon homologs and UV-Vis hydrocarbons with moderate concentrations. Outlined areas indicate significant positive correlations. Methane, Propane, i-butane, Ethylene, and Propene show some correlation with UV-Vis wavelengths.

Wavelength	Methane	Ethane	Propane	N-Butane	N-Pentane	i-Butane	i-Pentane	Ethylene	Propene	Butene
NM_230	0.73462	0.89385	0.80497	0.86455	0.49558	0.34798	0.20730	0.69452	0.51680	0.69673
NM_240	0.78547	0.93462	0.88179	0.93002	0.58993	0.44596	0.29171	0.79330	0.64014	0.79148
NM_250	0.79172	0.94253	0.88998	0.93743	0.59651	0.44702	0.28639	0.80894	0.64608	0.80781
NM_260	0.80004	0.93779	0.88186	0.92915	0.56470	0.43135	0.27056	0.79914	0.61899	0.78690
NM_270	0.80294	0.92586	0.87351	0.91730	0.54768	0.42193	0.26395	0.76580	0.58813	0.76119
NM_280	0.80522	0.92483	0.87098	0.91501	0.53979	0.41589	0.25814	0.75776	0.57575	0.75462
NM_290	0.80752	0.92750	0.87049	0.91536	0.53431	0.40997	0.25053	0.75592	0.57195	0.75361
NM_300	0.80925	0.92418	0.86936	0.91242	0.52989	0.40634	0.24880	0.75467	0.57095	0.75112
NM_310	0.80907	0.92149	0.86315	0.90694	0.51607	0.39801	0.23735	0.74253	0.55489	0.74028
NM_320	0.80761	0.92179	0.86344	0.90811	0.51994	0.40005	0.24084	0.74136	0.55209	0.73897
NM_330	0.80890	0.91780	0.86455	0.90701	0.52091	0.40520	0.24531	0.74177	0.55483	0.73675
NM_340	0.80928	0.91598	0.86069	0.90182	0.51137	0.39721	0.23638	0.73791	0.55175	0.73438
NM_350	0.80879	0.91349	0.85846	0.89856	0.50728	0.39449	0.23309	0.73712	0.55184	0.73317

Hydrocarbon	Mean	Minimum	Maximum
Methane	175	54.5	538
Ethane	11.2	3.9	40.5
Ethylene	76.9	45	129
Propane	15.4	4.0	44.7
Propene	130	60	211
i-Butane	10.2	1.4	39.0
N-Butane	8.8	1.7	24.9
Butene	94	32.8	171
i-Pentane	5.1	0.5	21.0
N-Pentane	3.3	1.4	6.4

Table 3. Correlation matrix of hydrocarbon homologs and UV-Vis hydrocarbons in an area of high hydrocarbon concentrations. Outlined areas indicate significant positive correlations. Methane, Ethane, Propane, n-butane, Ethylene, and Butene show correlation with the UV-Vis wavelengths.

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GO TO ABSTRACT

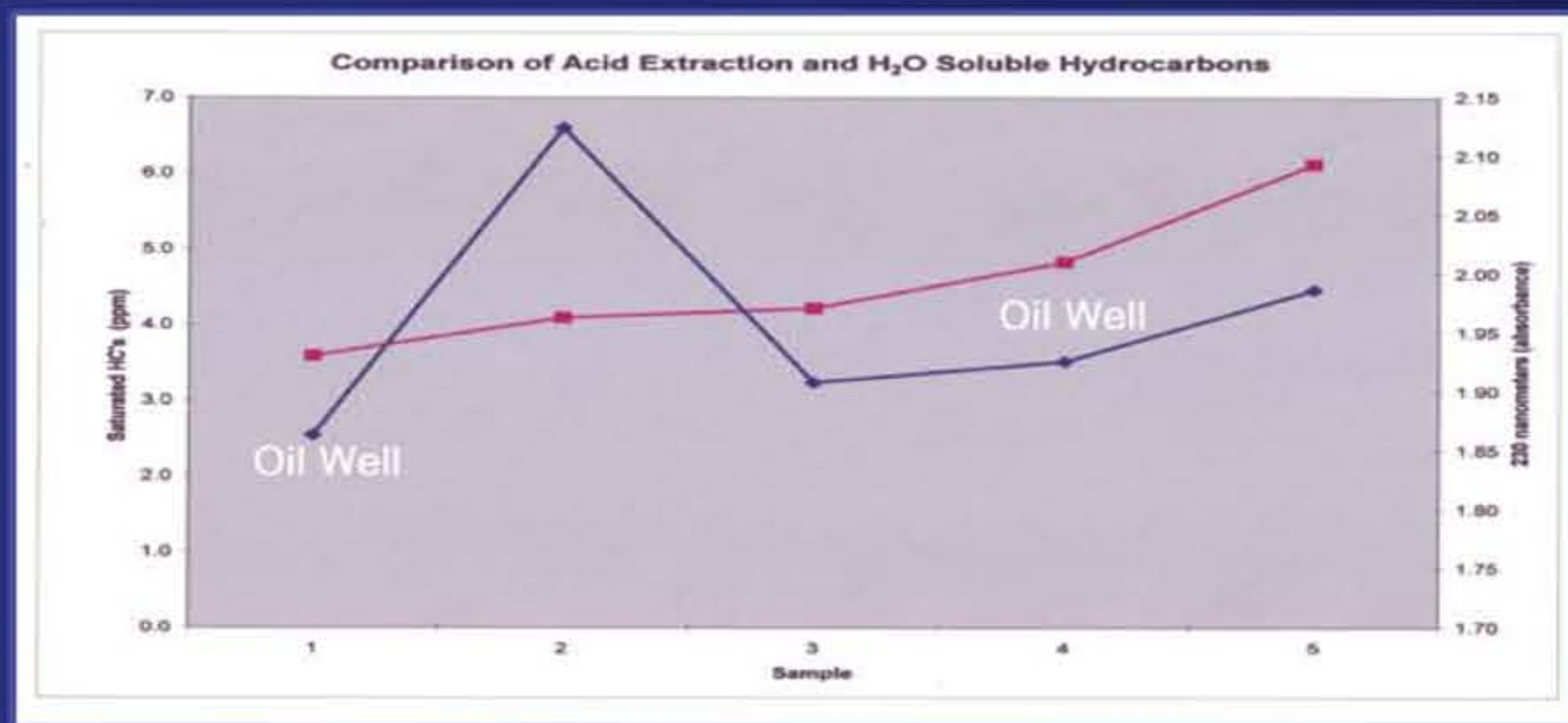


Figure 4. Graph comparing the acid extractable gas phase saturated hydrocarbons and the water soluble hydrocarbons from the solid phase of five soil samples.

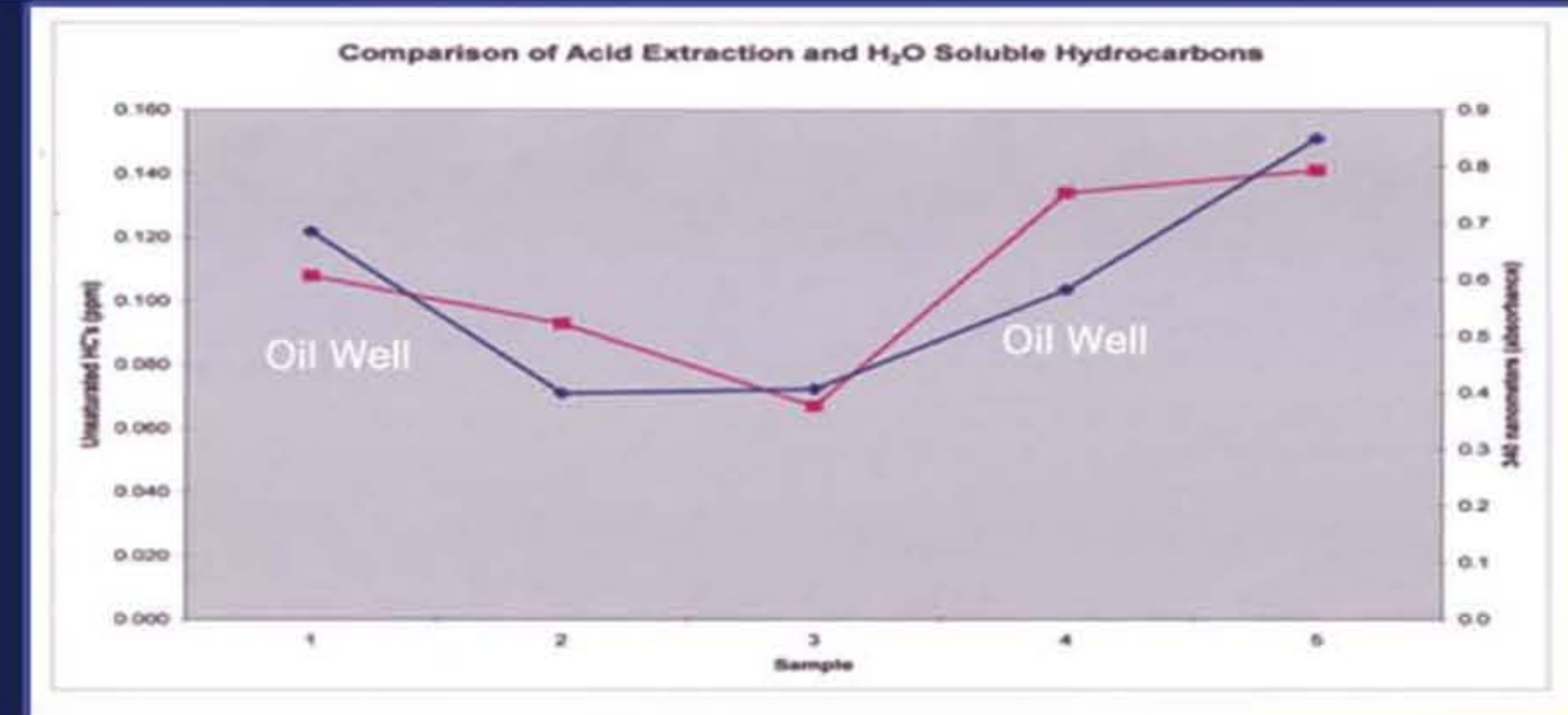


Figure 5. A comparison of unsaturated gas phase hydrocarbons with the 340 nanometer wavelength from the water soluble hydrocarbon fraction of five soil samples.

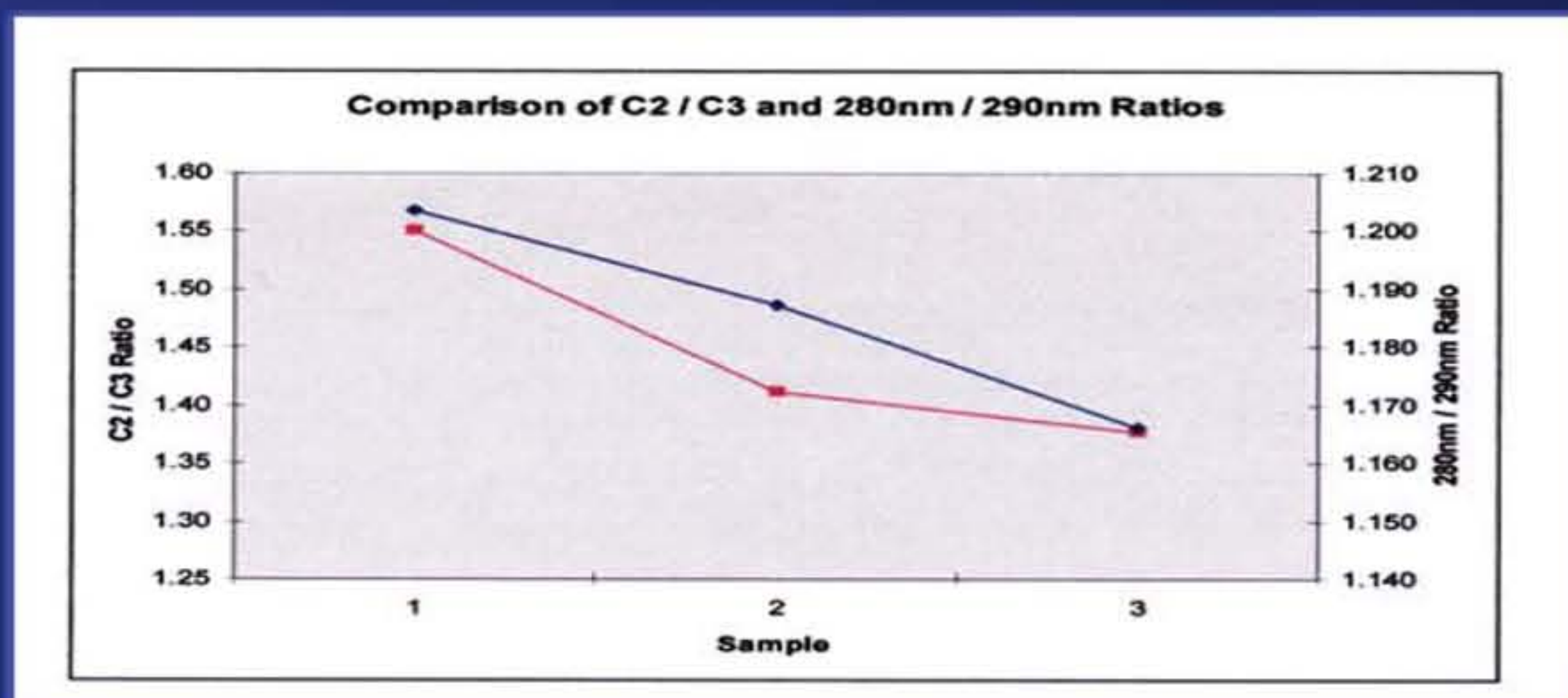


Figure 6. Graph showing the direct relationship of the C_2 / C_3 and 280nm / 290nm ratios. These ratios can be used to characterize a seepage anomaly. For instance, Sample 1 has a higher gas content than Sample 3.

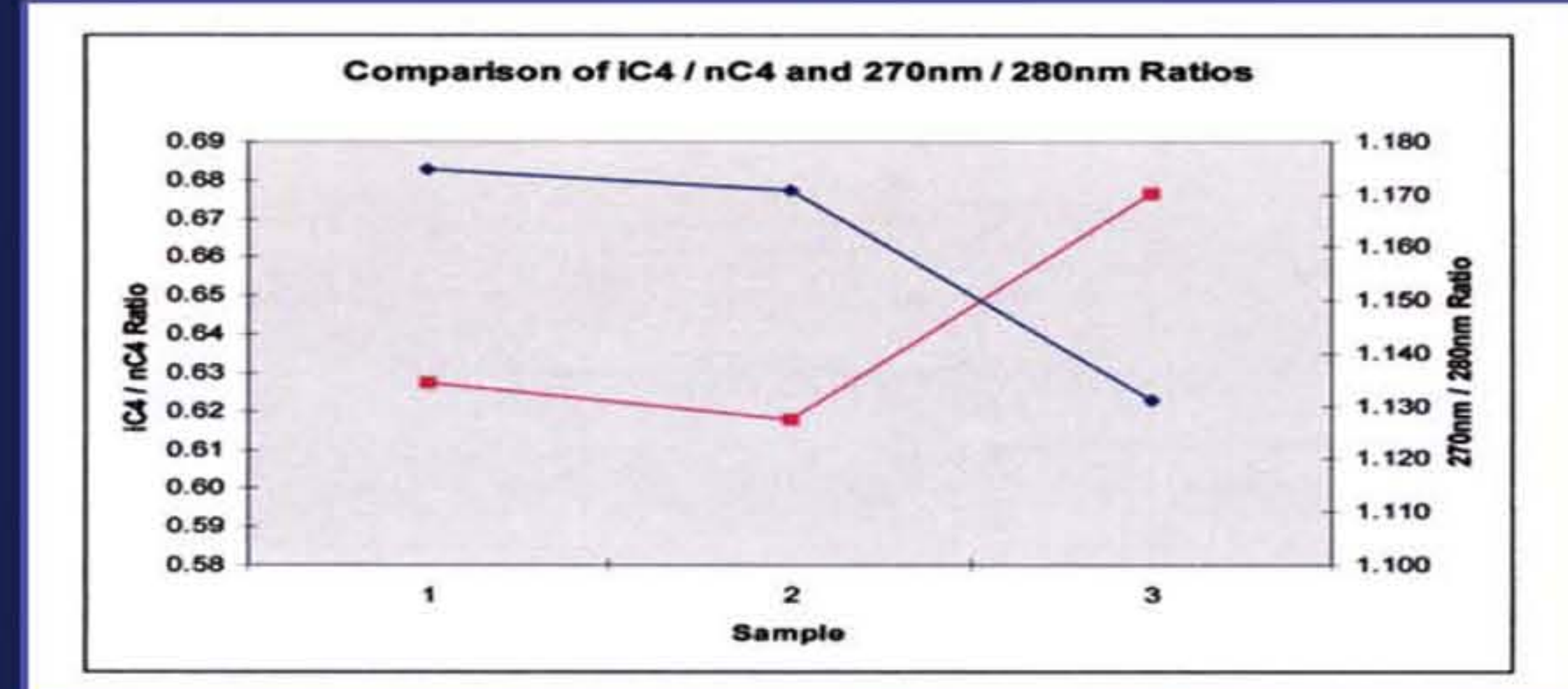


Figure 7. Graph showing the inverse relationship between the iC_4 / nC_4 and 270nm / 280nm ratios. These ratios can be used to determine the maturity of the hydrocarbons associated with the seepage anomaly. The iC_4 / nC_4 values are less than one indicating mature hydrocarbons with Sample 1 being less mature than Sample 3. The 270nm / 280nm ratio shows the same relationship though greater maturity is indicated by increasing values.

Hydrocarbon Characterization Comparison

Gas phase hydrocarbons are often used to characterize seepage anomalies and the reservoirs associated with them. Characterization methods yield an estimate of the type of hydrocarbons that are in place within the reservoir at depth prior to drilling a well. This is accomplished using ratios of the various hydrocarbon homologs.

Correlations between ratios from GC hydrocarbon data and UV-Vis hydrocarbon data exhibit some meaningful correlations. The C_2 / C_3 relationship has been used to estimate GOR and hydrocarbon maturity. Moderate to high correlations suggest that the UV-Vis hydrocarbon data might be used to estimate gas content and degree of hydrocarbon maturity. Correlations show that the C_2 / C_3 ratio is directly proportional to the 280nm / 290nm ratio.

The iC_4 / nC_4 relationship is used to determine hydrocarbon maturity. Values greater than unity indicate immature hydrocarbons while values less than unity are within the oil window. High inverse correlations between iC_4 / nC_4 and the 270nm / 280nm ratio indicate that higher UV-Vis ratio values are equivalent to lower iC_4 / nC_4 ratio values. The matrices verify that the ratios most often represented are C_2 / C_3 and iC_4 / nC_4 .

UV-Vis Ratios	%Methane	$C_2/C_1 \cdot 1000$	C_2/C_3	iC_4/nC_4	C_1/C_2	C_1/C_3	C_1/C_4	C_1/C_5
230/240	0.0889	-0.0277	-0.1722	0.1002	0.0753	0.0197	0.0754	0.0144
240/250	0.1381	-0.1653	0.0917	-0.2100	0.0142	0.1516	0.2586	-0.1361
250/260	-0.1427	-0.0259	0.4030	-0.2580	-0.3008	-0.0467	-0.1144	-0.2582
260/270	-0.0444	-0.1273	0.4486	-0.3319	-0.2513	0.0612	-0.0274	-0.1333
270/280	-0.0421	-0.1456	0.4888	-0.3792	-0.2675	0.0747	0.0102	-0.1763
280/290	0.0198	-0.1704	0.4341	-0.3310	-0.1978	0.1245	0.0611	-0.0926
290/300	-0.0405	0.1578	-0.3574	0.2637	0.1406	-0.1264	-0.0466	0.0008
300/310	-0.0995	0.1023	-0.0960	0.0548	-0.0284	-0.1231	-0.0880	-0.1344
310/320	-0.0238	-0.0129	0.0185	-0.0320	-0.0528	-0.0348	-0.0444	-0.0897
320/330	-0.0591	-0.0417	0.1860	-0.1838	-0.1496	-0.0224	-0.0820	-0.1178
330/340	0.0393	0.0749	-0.2342	0.2141	0.1552	-0.0055	0.0984	0.0471
340/350	0.0491	0.0556	-0.2235	0.1827	0.1409	0.0024	0.1314	-0.0140

Table 4. Correlation matrix of standard hydrocarbon ratios and UV-Vis ratios of wavelengths. Outlined areas indicate significant positive and negative correlations. This comparison is comprised of anomalous hydrocarbon data from the Appalachian's in the Eastern United States.

UV-Vis Ratio	%Methane	$C_2/C_1 \cdot 1000$	C_2/C_3	iC_4/nC_4	C_1/C_2	C_1/C_3	C_1/C_4	C_1/C_5
230/240	-0.3963	0.3549	0.9393	-0.7890	-0.6781	-0.2838	-0.1952	0.0136
240/250	-0.6562	0.6218	0.9991	-0.5653	-0.8691	-0.5613	-0.4835	-0.2904
250/260	-0.7229	0.6913	0.9987	-0.4870	-0.9110	-0.6352	-0.5621	-0.3773
260/270	0.1905	-0.2341	0.5823	-0.9980	-0.1456	0.3063	0.3919	0.5751
270/280	0.0177	-0.0623	0.7142	-0.9721	-0.3146	0.1370	0.2267	0.4248
280/290	-0.3448	0.3025	0.9189	-0.8218	-0.6363	-0.2302	-0.1405	0.0690
290/300	0.2606	-0.3035	0.5223	-1.0000	-0.0740	0.3741	0.4571	0.6325
300/310	0.2454	-0.2884	0.5357	-1.0000	-0.0897	0.3594	0.4430	0.6202
310/320	0.9923	-0.9968	-0.5916	-0.3698	0.8950	1.0000	0.9963	0.9564
320/330	-0.4334	0.3927	0.9526	-0.7632	-0.7076	-0.3227	-0.2350	-0.0272
330/340	-0.3964	0.3549	0.9394	-0.7889	-0.6782	-0.2839	-0.1952	0.0135
340/350	-0.5416	0.5035	0.9829	-0.6774	-0.7895	-0.4373	-0.3535	-0.1507

Table 5. Correlation matrix of standard hydrocarbon ratios and UV-Vis ratios of wavelengths. Outlined areas indicate significant positive and negative correlations. This comparison is of data over a producing field in the Mid-Centiment of the United States.