



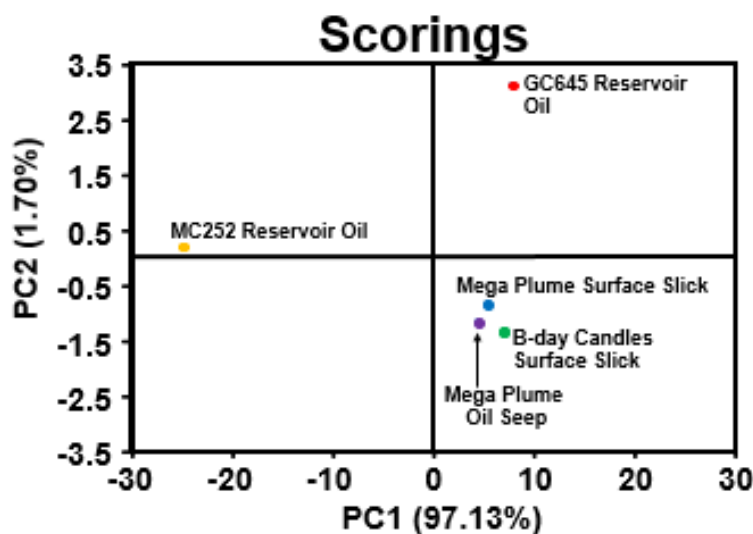
## Linking Natural Oil Seeps from the Gulf of Mexico to Their Origin by use of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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### Results and Discussion

We report chemical characterization of natural oil seeps from the Gulf of Mexico with the NHMFL ICR Program 9.4 T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) and Gas Chromatography/Atmospheric Pressure Chemical Ionization Mass Spectrometry (GC/APCI-MS), to highlight how FT-ICR MS can also be employed as a means to determine petroleum connectivity, in addition to traditional GC/MS techniques. The source of petroleum is the Green Canyon (GC) 600 lease block in Gulf of Mexico. Within GC600, two natural oil seepage zones, Mega Plume and Birthday Candles, continuously release hydrocarbons and develop persistent oil slicks at the sea surface above them.

We chemically trace the petroleum from the surface oil slicks to the Mega Plume seep itself, and further to a petroleum reservoir 5 km away in lease block GC645 (Holstein Reservoir). We establish the connectivity between oil samples and confirm a common geological origin for the oil slicks, oil seep, and reservoir oil. The ratios of seven common petroleum biomarkers detected by GC/APCI-MS display clear similarity between the GC600 and GC645 samples, as well as a distinct difference from another reservoir oil collected ~300 km away (Macondo crude oil from MC252 lease block). FT-ICR MS and principal component analysis (PCA—see Figure 1) demonstrate further similarities between the GC600 and GC645 samples that distinctly differ from MC252. A common geographical origin is postulated for the GC600/GC645 samples, with petroleum migrating from the GC645 reservoir to the oil seeps found in GC600 and up through the water column to the sea surface as an oil slick.



**Fig. 1.** Principal component scoring plot derived from the relative abundances of the hydrocarbon, N1, S1, S2, and O1S1 heteroatom classes. The scorings chart shows a clear separation of the Macondo reservoir oil from all of the other samples along the first principal component, which accounts for 97.13% of the total variance. GC645 reservoir oil is separated from the others along the second principal component axis, which contributes only 1.70% of the total variance.

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### References

[1] Krajewski, L. C., *et al.*, Environ. Sci. Technol., **52**, 1365-1374 (2018).