Expansion of the Analytical Window for Oil Spill Characterization by Ultrahigh Resolution Mass Spectrometry: Beyond Gas Chromatography

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Results and Discussion

Traditional tools for routine environmental analysis and forensic chemistry of petroleum have relied almost exclusively on gas chromatography–mass spectrometry(GC-MS), although many compounds in crude oil (and its transformation products) are not chromatographically separated or amenable to GC-MS due to low volatility. To enhance current and future studies on the fate, transport, and fingerprinting of the Macondo well oil released from the 2010 Deepwater Horizon disaster, we created an extensive molecular library of the unadulterated petroleum to compare to a tar ball collected on a beach in Louisiana. We apply ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry to identify compositional changes at the molecular level between native and weathered crude oil samples and reveal enrichment in polar compounds inaccessible by GC-based characterization. The outlined approach provides unprecedented detail with the potential to enhance insight into the environmental fate of spilled oil, improved toxicology, molecular modeling of biotic/abiotic weathering, and comprehensive molecular characterization for petroleum-derived releases. Here, we characterize more than 30 000 acidic, basic, and nonpolar unique neutral elemental compositions for the Macondo well crude oil, to provide an archive for future chemical analyses of the environmental consequences of the oil spill.

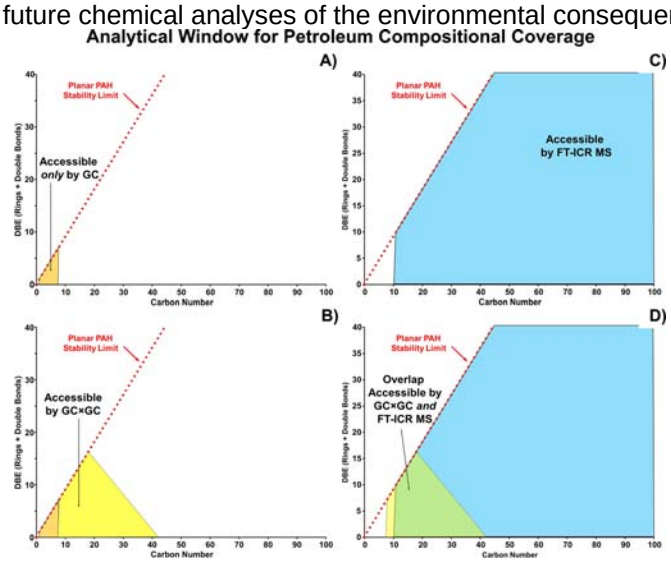

Figure 1 Schematic diagram of the compositional continuum of petroleum (the petroleome) reported as double bond equivalents (DBE, number of rings plus double bonds) versus carbon number. The analytical window accessible only by conventional gas chromatography (GC) is displayed in part a, with the upper boundary limit for all molecules known to exist in petroleum displayed as the PAH planar stability limit, as previously reported. Extension to hybrid analytical techniques (GC × GC) is displayed in Figure 2b. Part c reports the extension to complete compositional coverage of petroleum molecules (up to C_{100}) that have been observed in Macondo petroleum. Part d combines all three techniques in a single image to highlight the need for advanced analytical techniques beyond gas chromatography for oil spill science.

Acknowledgments

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References

[1] McKenna, A.M., *et al*., Environ. Sci. Tech., **47**, 7530-7539 (2013)