Oil Spill Source Identification by Principal Component Analysis of Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectra

Y.E. Corilo (NHMFL, Chemistry); D.C. Podgorski (NHMFL, Chemistry); A.M. McKenna (NHMFL, Chemistry); K.L. Lemkau (Woods Hole Oceanographic Institute, Marine Chemistry); C.M. Reddy (Woods Hole Oceanographic Institute, Marine Chemistry); A.G. Marshall (FSU, NHMFL, Chemistry); R.P. Rodgers (FSU, NHMFL, Chemistry)

Results and Discussion

A fundamental challenge with either acute or chronic oil spills is to identify the source, especially in highly polluted areas, near natural oil seeps, when the source contains more than one petroleum product, or when extensive weathering has occurred. Here, we focus on heavy fuel oil that spilled when 58,000 gallons from two suspected tanks were ruptured on the motor vessel (M/V) *Cosco Busan* when it struck the San Francisco-Oakland Bay Bridge in November 2007. Principal Component Analysis (PCA) applied to thousands of elemental compositions obtained from ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry of neat samples from both tanks correctly identifies the source of environmental contamination caused by the unintended release of heavy fuel oil (HFO). The PCA components were based on double bond equivalents for constituents of heteroatom elemental composition, $C_cH_hN_1S_1$. To determine if the fidelity of our source identification was affected by weathering, field samples were collected at various intervals up to two years after the spill. Members of the NS class persist for almost two years after the spill (see Figure 1). We confidently identify that only one tank was the source of the spilled oil: in fact, a single principal component could account for 98% of the variance. Although identification is unaffected by the presence of higher polarity, petrogenic oxidation products, future studies may require removal of such species by anion exchange chromatography prior to mass spectral analysis due to their preferential ionization by ESI.

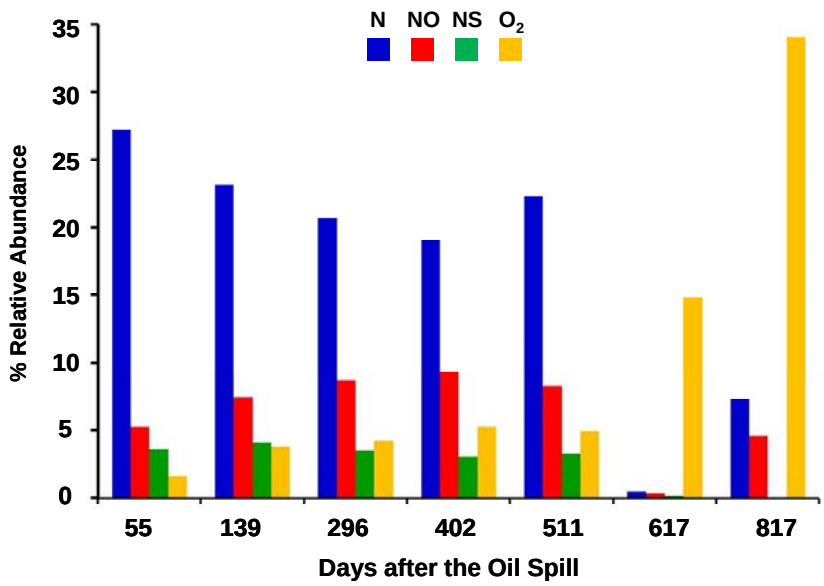

Figure 1. Heteroatom class distribution for components of present at >1% of the total sum of relative abundance from the N, NO, NS and O_2 classes identified by PCA as potential indicators for seven weathered samples collected from the same contaminated site associated with the M/V *Cosco Busan* spill. Note the persistence of the NS class.

Acknowledgments

This work was supported by NSF Division of Materials Research through DMR-06-54118 (AGM), NSF CHE-10-49753 (AMM), NSF OCE-0960841 (CR), EAR-0950670 (CR), BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium (YEC,DCP), and the State of Florida (RPR).

References

[1] Corilo, Y. E., *et al*., Anal. Chem., **85**, 9064-9069 (2013).