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The West Falmouth oil spill: A geochemical update after 35 years

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Background

For the past three decades, the West Falmouth oil spill has been intensively studied and been influential in developing the science of oil spill research in the marine environment [1]. This spill occurred when the barge *Florida* went aground near West Falmouth, MA and released between 650 000 and 700 000 L of No. 2 fuel oil into Buzzards Bay on September 16, 1969. Since this spill occurred in close proximity to Woods Hole Oceanographic Institution, it has been the focus of numerous geochemical studies. This nearly 35-yr old data record makes the West Falmouth oil spill ideal for investigating the long-term fate and effects of petroleum hydrocarbons in the environment.

For the past few years, we have begun a major campaign to revisit the Wild Harbor salt marsh, which was the most heavily impacted site from the spill, and to investigate the fate of the spilled oil. One attribute of this effort was to apply new analytical approaches such as ^{13}C, ^{14}C, and comprehensive two-dimensional gas chromatography (GC×GC). Presently, ~25 sediment cores have collected and analyzed with various techniques.

Results

Our efforts have indicated that some areas of the Wild Harbor salt marsh are still contaminated with petroleum residues (as high as 8 mg g^{-1}) and are generally buried 8 to 20 cm below the surface. GC×GC analysis of sediment extracts has provided a highly refined inventory of hydrocarbons that continue to persist and reveals that only the *n*-alkanes have been completely biodegraded. In addition, we do not believe that any microbes are actively respiring petroleum, which is ^{14}C free, as their phospholipids contain only contemporary levels of ^{14}C. However, a 3-D survey has determined that only ~0.001% of the original cargo exists in marsh sediments that were originally the most impacted. These results suggest that a very small fraction of the spilled oil at this site will persist indefinitely in the sedimentary record.

References

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A new procedure to evaluate isotope fractionation in contaminants

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Compound specific isotope analysis (CSIA) is a powerful method to identify sources and *qualitatively* detect *in-situ* transformation of organic pollutants in contaminant hydrology. Recently, the method has also been applied to *quantify* contaminant transformation. The extent of degradation is generally calculated from an observed enrichment of heavy isotopes in the remaining substrate using the Rayleigh equation. A major obstacle to this approach, however, is that measured isotopic enrichment factors ε were often found to vary considerably, whereas in theory they are assumed to describe a constant, characteristic discrimination between heavy and light substrate molecules during reaction. Consequently, large uncertainties are created when such ε-values are taken to calculate *in-situ* contaminant degradation in the field. According to current practice it is difficult to decide whether the variation is random or may be characteristic of different degradation pathways. A major reason is that enrichment factors ε can presently not be compared to bond-specific kinetic isotope effects of which abundant data is available in the (bio)chemical literature. We therefore developed an evaluation procedure that takes into account (a) non-reacting positions within a compound as well as (b) effects of intramolecular isotopic competition so that enrichment factors ε can now be converted into estimates of kinetic isotope effects. Greatly differing carbon isotope fractionation in aerobic 1,2-dichloroethane degradation could thus be attributed to two fundamentally different degradation pathways (oxidation vs. nucleophilic substitution, S_N2) rather than to random variation. Similarly, re-evaluation of literature data on methyl t-butyl ether (MTBE) revealed that aerobic MTBE degradation was initiated by an oxidation reaction, whereas anaerobic degradation occurred most likely in hydrolysis (S_N2). To our knowledge this is the first evidence that has been obtained on anaerobic biodegradation pathways of MTBE.

Quantifying contaminant degradation on grounds of isotope data may therefore be achieved quite confidently, if the "right" enrichment factor ε is chosen. In field situations, however, this insight can only be gained if isotopic data is analyzed for carbon and hydrogen *simultaneously*. The complementary isotopic information from two elements is therefore essential for discovering the degradation pathway, choosing the right enrichment factor and, thus, reliably quantifying *in-situ* contaminant transformation.