

Forensic use of diagnostic biomarker ratios in environmental oil spill geochemistry

by *Marianne Nuzzo and Mischa Gehlen*

Oil spills can have a significant impact on the environment and ecosystem, as e.g. seen in 2019-2020 along the coast of northeast Brazil or after the Deepwater Horizon accident in 2010. But also on a smaller scale oil pollution events cause a range of environmental risks and have to be investigated. The source of oil pollution is not always obvious though as it can be of natural origin, e.g. oil seeps, or anthropogenic, e.g. leaking pipelines or large spills from tankers. Identifying, characterizing and where possible quantifying the source of hydrocarbons is thus an important part of environmental remediation (e.g. Wang *et al.*, 2016).

The use of biomarker data is a long-established tool in petroleum system analysis, but is also widely used in forensic geochemistry to fingerprint petroleum contaminations. Biomarkers are complex molecular fossils derived from once-living organisms which can be measured both in crude oils and in their source rocks, thus representing powerful oil-source correlation tools (e.g. Peters, Walters and Moldowan, 2004). A wealth of biomarker compounds, frequently saturated cyclic triterpane and sterane hydrocarbons, have been shown to be diagnostic of source-rock formation type, age or depositional environment with diagnostic ratios (DRs) being used routinely for oil-source and oil-oil correlations to characterise petroleum systems. Despite being trace components of organic matter/petroleum, biomarker abundances can be measured very precisely and reproducibly by Gas Chromatography-Mass Spectrometry in Selected Ion Monitoring mode (GC/MS-SIM). Consequently, DRs have been shown to be of great use not only for qualitative, but also for quantitative geochemistry in the oil & gas industry (e.g., Peters & Fowler, 2002), and forensic oil spill geochemical studies (Wang *et al.*, 2016). In the latter case, the high precision and reproducibility of the analyses is particularly crucial for the reliable support of legal decisions regarding contamination sources. As the source of crude or processed oils released in the environment is frequently unknown, a defensible identification based on correlation to suspected sources is a critical part of oil spill assessments (Stout *et al.*, 2001). Two major processes complicate the correlation of the spilled oil to its source(s): **weathering** of oil in the environment, and **mixtures** with hydrocarbon compounds from different sources.

Weathering encompasses processes acting at an early stage of the spill, namely spreading, evaporation, dispersion, emulsification and dissolution, as well as longer-term processes such as photo-oxidation, sedimentation and biodegradation, which determine the ultimate fate of the oil (ITOPF Ltd, 2011). Moreover, laboratory studies have shown the terpane and sterane biomarkers to be remarkably resilient to biodegradation in the environment (Foght *et al.*, 1998; Wang *et al.*, 1998), although there is evidence of their degradation under severe weathering conditions (e.g. Chosson *et al.*, 1991). Mixtures of oils from different sources frequently take place in the environment because the oil spilled mixes with background contaminations (e.g. from ships), and sometimes with petroleum from natural seeps (Leifert *et al.*, 2006). Biomarkers represent a powerful forensic geochemistry tool to identify source(s) of oil spills in the environment since they are relatively resistant to weathering, and because accurate GC/MS-SIM concentration measurements support the quantitative fingerprinting of oil spills (Douglas *et al.*, 2016). Importantly, however, forensic biomarker geochemistry requires the use of particularly stringent protocols at all stages, from sample collection (Daling *et al.*, 2016)

to data interpretation, whether based on qualitative or semi-quantitative (e.g. CEN methodology; Kienhuis *et al.*, 2016) or on quantitative methods (Douglas *et al.*, 2016).

Qualitative methods assume that “matching of oil samples is essentially a profiling technique based on the premise that identical oils give identical chromatograms” (ASTM, 1990), which besides introducing considerable subjectivity raises concerns regarding the effects of (i) weathering, (ii) mixing between similar oils (similar crudes, or similar refined petroleum products) and (iii) mixing with background oil contaminations. Semi-quantitative methods rely on the measurement of chromatographic peak heights or areas and these results can be used to match the spilled oil sample to candidate sources using graphical (Figure 1), statistical or numerical analysis tools (Boehm *et al.*, 1997; Dahlmann & Kienhuis, 2016; Mudge, 2016).

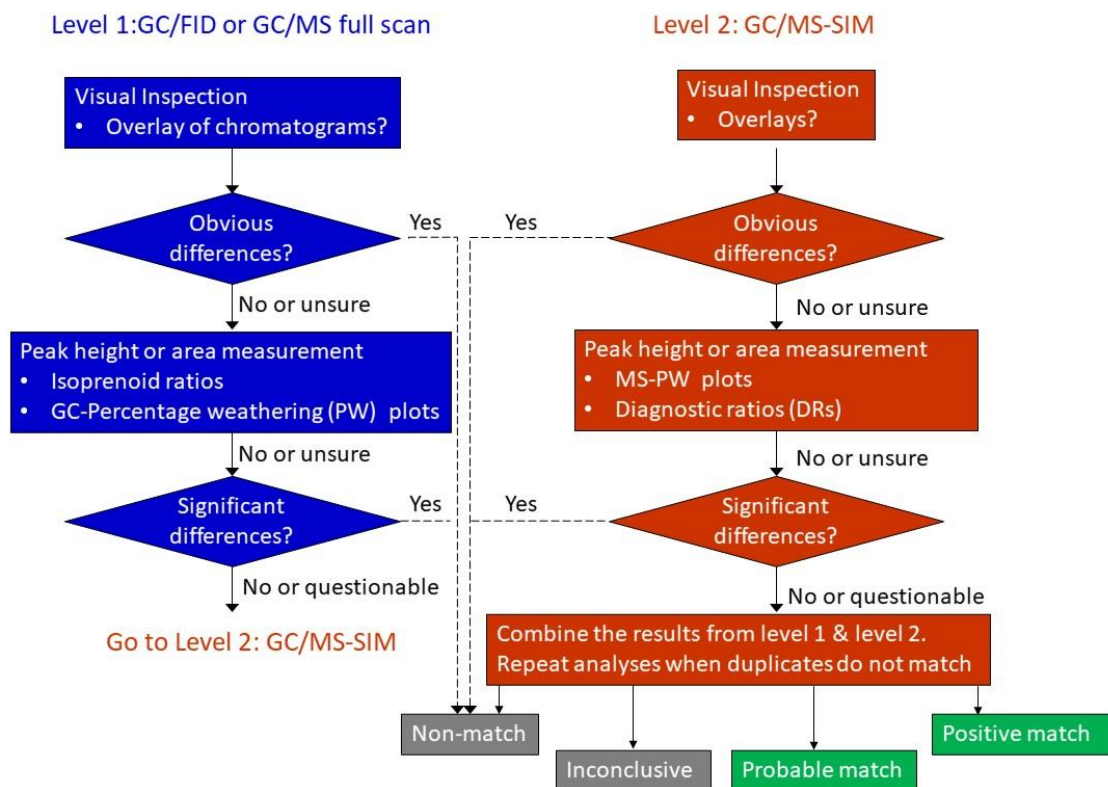


Figure 1: Decision flow-chart adapted from the CEN oil spill identification methodology (after Dahlmann & Kienhuis, 2016)

However, only quantitative data enable the use of DRs to unravel the potentially mixed origins of spilled oil samples in the environment. Hence adequate quantitative data allow to address the issue of spilled petroleum that is comprised of mixtures (Douglas *et al.*, 2016), or that occurs in a highly contaminated urban area or again in a mature oil province. DRs calculated using semi-quantitative data cannot support such interpretations because, unlike concentrations, ratios do not generally mix linearly (Lundegard & Surgi, 2012).

References:

American Society for Testing and materials International (ASTM) (1990). Standard test method for comparison of waterborne petroleum oils by gas chromatography. *ASTM D-3328-90*. ASTM, W. Conshohocken, PA, 7pp.

American Society for Testing and materials International (ASTM) (2000). Oil spill identification by gas chromatography and positive ion electron impact low resolution mass spectrometry. *ASTM D-5739-00*. ASTM, W. Conshohocken, PA, 13pp.

Boehm P. D., Douglas G. S., Burns W. A., Mankiewicz P. J., Page D. S. & Bence A. E. (1997). Application of petroleum hydrocarbon chemical fingerprinting and allocation techniques after the Exxon Valdez oil spill. *Marine Pollution Bulletin* **34(8)**, 599-613.

Chosson P., Lanau, C., Connan J., and Dessort D. (1991). Biodegradation of refractory hydrocarbon biomarkers from petroleum under laboratory conditions. *Nature* **351**, 640-642.

Dahlmann G. & Kienhuis P. G. M. (2016) Development and application of online computerized oil spill identification-COSIWeb. In: Standard Handbook Oil Spill Environmental Forensics. Stout, S. A. & Wang, Z. eds, Second Edition, Elsevier, pp. 729-746.

Daling P. S., von Brukhoeveden A., and Hellstrøm K. C. (2016). Sampling procedures for securing evidence for waterborne oil spill identifications. In: Standard Handbook Oil Spill Environmental Forensics. Stout, S. A. & Wang, Z. eds, Second Edition, Elsevier, pp. 25-60.

Douglas G. S., Stout S. A., Uhler, A. D., McCarthy K. J., Emsbo-Mattingly, D. (2016). Advantages of quantitative chemical fingerprinting in oil spill identification and allocation of mixed hydrocarbon contaminants. In: Standard Handbook Oil Spill Environmental Forensics. Stout, S. A. & Wang, Z. eds, Second Edition, Elsevier, pp. 789-848.

Foght J., Semple K. Gauthier C., Westlake D. W. S., Blenkinsopp S., Sergy G., Wang, Z., and Fingas M. (2008). Development of a standard bacterial consortium for laboratory efficacy testing of commercial freshwater oil spill bioremediation agents. *Environmental Technology* **20**, 839-849.

ITOPF (2011). Fate of marine oil spills. Technical information paper 2, 11pp.

Kienhuis P. G. M., Hansen A. B., Faksness L.-G., Stout S. A., and Dahlmann G. (2016). CEN methodology for oil spill identification. In: Standard Handbook Oil Spill Environmental Forensics. Stout, S. A. & Wang, Z. eds, Second Edition, Elsevier, pp. 685-728.

Leifer I.; Luyendyk B. P.; Broderick K. (2006). Tracking an oil slick from multiple natural sources, Coal Oil Point, California. *Journal of Marine and Petroleum Geology*. **23(5)**, 621–630. doi:10.1016/j.marpetgeo.2006.05.001.

Lundegard P. D. & Surgi R. (2012). Allocation of hydrocarbon mixtures based on chemical ratios. *Environmental Forensics* **13:4**, 293-297.

Mudge S. M. (2016). Statistical analysis of oil spill chemical composition data. In: Standard Handbook Oil Spill Environmental Forensics. Stout, S. A. & Wang, Z. eds, Second Edition, Elsevier, pp. 849-868.

Peters, K. and M. G. Fowler (2002). Applications of petroleum geochemistry to exploration and reservoir management. *Organic Geochemistry* **33**, 5-36.

Peters, K., Walters, C., & Moldowan, J. (2004). *The Biomarker Guide* (2nd ed.). Cambridge: Cambridge University Press.

Stout, S. A., Ulher, A. D. and McCarthy, K. J. (2001). A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environmental Forensics* **2**, 87-98.

Wang, Z., Fingas M., Blenkinsopp S., Sergy G., Landriault M., Sigouin L., Foght J., Semple K. and Westlake D. W. S. (2008). Oil composition changes due to biodegradation and differentiation between these changes to those due to weathering. *Journal of Chromatography A* **809**, 89-107.

Wang, Z., Yang, C., Yang, Z., Brown, C. E., Hollebone, B. P., and Stout, S. A. (2016). Petroleum biomarker fingerprinting for oil spill characterization and source identification. In: Standard Handbook Oil Spill Environmental Forensics. Stout, S. A. & Wang, Z. eds, Second Edition, Elsevier, pp. 131-254.