# FINAL TECHNICAL SUMMARY
# USGS SIR 2011-5210, BOEM OCS STUDY 2011-016

**STUDY TITLE:** "Fate, Volume and Chemistry of Natural Seeps in the Santa Barbara Channel/Southern Santa Maria Basin"

REPORT TITLE: "Biomarker Chemistry and Flux Quantification Methods for Natural Petroleum Seeps and Produced Oils, Offshore Southern California"

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**BACKGROUND:**

The area off Coal Oil Point, California in the Santa Barbara Channel has long been recognized for the occurrence of prolific offshore natural oil and gas seepage. Early Chumash tribes used tar from local seeps to waterproof the canoes they used to travel from the mainland to nearby ocean islands. The incidence of seepage in the Channel points to the fact that the Channel is also home to large oil and gas reservoirs. In the 1960s when the first oil and gas platforms were placed offshore California, they were often intentionally located on top of known seep areas as a way of locating the reservoir.

The fact, however, that this seepage occurs in the same vicinity as regulated offshore oil and gas production has made it of great interest to resource managers to be able to distinguish between natural seepage and potential anthropogenic oil spills.

**OBJECTIVES**:

The major goal of this study is to build upon the favorable results of a five-year study (Submarine Oil and Gas Seeps of the Southern Offshore Santa Maria Basin, California – Source Markers, Semi-quantification of Seepage Rates, Transport Pathways, and Relation to Oil Residues on the Coastline http://pubs.usgs.gov/of/2009/1225/) that has refined the fingerprinting process to enable differentiation of the highly similar Monterey oils from Outer Continental Shelf (OCS) production and adjacent natural seeps.

Our focus was to evaluate (1) areas of hydrocarbon seepage which are known to occur near OCS platforms not sampled during the previous study; (2) geochemically fingerprint representative oils from the OCS platforms not sampled in the previous study; (3) geochemically fingerprint coastal tar residues associated with unusual coastal oiling events; (4) continue to sample submarine seeps directly to provide refined chemical correlations between offshore active seeps and coastal residues and; (5) measure the rate of natural seepage of individual seeps in collaboration with UC Santa Barbara, and attempt to assess regional natural oil and gas seepage rates.

**DESCRIPTION:**

Oils representing all OCS platforms with the exception of Habitat and Grace (producing gas and condensate) have been included in this updated study. The platforms sampled, east to west are Eureka, Ellen, Edith, Gina, Gail, Gilda, Grace, Hogan, Houchin, Henry, Hillhouse, Platform B, and Platform C. The remaining platform oils previously sampled and analyzed are from Platforms Irene, Hidalgo, Harvest, Hermosa, Heritage, Harmony, Hondo, and Platform A. Two platforms in state waters, Holly and Hilda (Hilda now removed), were included in the first study due to their proximity to natural oil seepage.

For our initial study, biomarker and stable carbon isotope ratios were used to infer the age, lithology, organic matter input, and depositional environment of the source rocks for 388 samples of produced crude oil, seep oil, and tarballs mainly from coastal California. The analysis resulted in a predictive model of oil source families that could be used on unknown samples. The 106 additional samples were inquired by this model resulting in positively identifying all oil samples within known oil families, most tarballs, an about half of the seep samples collected from the seafloor. Seafloor seep samples are composed of viscous, biodegraded hydrocarbon residues. Many of the biomarkers in seep samples are absent due to biodegradation, thus seep oil residues cannot be classified in about 46% of the time. Tarballs, resulting mainly from less biodegraded oil reaching the sea surface, are positively identified by the model about 97 % of the time. We conclude that the original model is robust for determining oil or tarball samples originating from California oil basins.

The results of the original model identify three “tribes” of $^{13}C$-rich oil samples inferred to originate from thermally mature equivalents of the clayey-siliceous,

carbonaceous marl, and lower calcareous-siliceous members of the Monterey Formation. Tribe 1 contains four oil families having geochemical traits of clay-rich marine shale source rock deposited under suboxic conditions with substantial higher-plant input. Tribe 2 contains four oil families with intermediate traits, except for abundant 28,30-bisnorhopane, indicating suboxic to anoxic marine marl source rock with hemipelagic input. Tribe 3 contains five oil families with traits of distal marine carbonate source rock deposited under anoxic conditions with pelagic but little or no higher-plant input. Tribes 1 and 2 occur mainly south of Point Conception in paleogeographic settings where deep burial of the Monterey Formation source rock favored generation from all three members or their equivalents. In this area, oil from the clayey-siliceous and carbonaceous marl members (Tribes 1 and 2) may overwhelm that from the lower calcareous-siliceous member (Tribe 3) because the latter is thinner and less oil-prone than the overlying members. Tribe 3 oil occurs mainly north of Point Conception, where shallow burial caused preferential generation from the underlying lower calcareous-siliceous member or another unit with similar characteristics.

**SIGNIFICANT CONCLUSIONS:**

Platform produced oils are only classified in Tribes 1 and 2, within families 11, 12, 13, 14, 211, 212, 213, and 22. Tribe 1 oils are restricted to the Los Angeles basin, and the eastern Santa Barbara-Ventura basin. Family 13 is the most common produced oil family from this area and the most common produced oil family overall (~40%) analyzed in these studies. The western Santa Barbara-Ventura basin (west of Platform Holly) and the Southern Santa Maria Basin oils are mainly in Tribe 2. Tribe 3 is not represented by any production oil in southern California, and therefore must have sources outside of this area, likely from natural seeps in little-explored basins offshore the central coast of California.

The biomarker parameters used in the chemometric fingerprinting are sometimes sufficient to allow unique discrimination of individual platform oils. However, platform samples and seep samples with oil sources geographically close to each other are too similar to each other, with respect to the biomarker parameters, to definitively differentiate them on that basis alone. In some cases the degree of biogeochemical degradation or weathering that the oils or tars have experienced can be utilized. Unweathered and non-biodegraded oil contain n-alkane hydrocarbons and the isoprenoids pristane and phytane. All of the platform produced oils in our sample set contain these components. In contrast, the seep oils or tars have been exposed to significant biodegradation resulting in the loss of at least the n-alkanes and isoprenoids. Therefore the combination of chemometric fingerprinting and the presence or absence of n-alkanes and isoprenoids help to differentiate anthropogenic production oils versus natural seeps oils and tars.

The differentiation is not always definitive because of the close chemical similarity of some samples and the variability in the biodegradation progression. This is the case near Coal Oil Point, and near Platforms A, B, C, Hillhouse, Henry, Houchin, Hogan (Dos Cuadros Field) and Platform Holly where seep oils produced oils are genetically very similar and cannot be definitively distinguished after a period of a few days of weathering. In contrast, oils from the Point Arguello and Point Pedernales fields (Irene,

Hermosa, Hidalgo, Harvest) can be distinguished on the basis of chemometric fingerprinting alone. In the middle of this spectrum are oils from all the other platforms, where it is expected that oil weathering would take on the order of two weeks to a month to produce tarballs similar to those seen near Point Conception. In this case there is a much greater degree of weathering needed to proceed from produced oil to the biodegraded tar characteristic of tarballs stranded on the beach.

Our studies support the hypothesis that natural oil seepage from sea floor vents are responsible for the majority of tarball accumulation on Southern California beaches. Oil fingerprinting provides the crucial tool to verify of the origin of this deposited oil. While our study results are persuasive, they are not conclusive as they depend on the assertion that beached or floating tarballs, by their inherent characteristics, are very recently deposited. We found that there are three primary areas of seepage currently active in the Santa Barbara Channel: offshore Point Conception, Sacate and Gaviota beaches, and Coal Oil Point. We also found that only a small fraction of tarballs did not correlate with California derived oils and are most likely from unknown ship or land-based discharges into the ocean. Produced oil from offshore platforms can often be ruled out as the origin of tarballs through the fingerprinting process because platform oil is not significantly biodegraded. The ability to distinguish between biodegraded oils diminishes with time, and, under typical conditions, most spilled platform oil could resemble seep oil residues and seep-derived tarballs in about one month. The ability, however, to distinguish between seep-derived oil residues and platform oils within this time span is extremely valuable to regulators responding to an oil spill incident. The four platforms north of Point Conception produce oil that can be fingerprinted on the basis of chemistry alone without the need to consider biodegradation, and can thus be distinguished from known natural oil seeps in and offshore California.

Imaging of seeps has developed significantly during this study with the use of new multi-beam sonar systems. We produced 3-D video visualizations of gas plumes in the water column. The relative intensity of the sonar returns can be quantified, however we are still in need of a controlled calibration experiment to relate intensity to gas and oil volume.

**STUDY RESULTS:**

A total of 106 new samples were collected and analyzed for biomarkers. Twenty eight samples came from seeps (27 submarine, one subareal), 47 oil samples of representative production zones and depths form oil platforms, and 31 random tarballs, mainly deposited in northern California during a storm event in February, 2008. The results show that biomarker fingerprinting predictive model that we have developed work very well with California oils as long as they are not severely biodegraded. Careful chemical inspection of any tarball or oil slick in question can likely be ascribed to a natural seep or anthropogenic spill using our methods.

During this period our protocols were taught, accepted, and used by the State of California, Office of Spill Prevention and Response (OSPR) in their efforts to fingerprint oil spill in and offshore California.

Seep imaging has improved remarkably of the course of this study not only in seafloor mapping with resolution on the order of 0.5 m that pinpoint asphalt mounds, but also the ability to visualize gas bubble plumes in the water column with extreme accuracy.

**STUDY PRODUCTS:**


Bradley, E.S., Leifer, I., and Roberts, D., 2010, Long-term monitoring of a marine geologic hydrocarbon source by a coastal air pollution station in southern California. Atmospheric Environment, vol. 44, no. 38, p. 4973-4981, doi:10.1016/j.atmosenv.2010.08.010.

Dartnell, P., Lorenson, T., and Edwards, B., 2007, Offshore Mapping Captures Tar Seeps in the Santa Barbara Channel, California, Sound Waves, September 2007, available on line at: http://soundwaves.usgs.gov/2007/09/

Draut, A.E., Hart, P.E., Lorenson, T.D., Ryan, H.F., Wong, F.L.,Sliter, R.W., and Conrad, J.E., 2009, Late Pleistocene to Holocene Sedimentation and Hydrocarbon Seeps on the Continental Shelf of a Steep, Tectonically Active Margin, Southern California, USA. Marine Geophysical Researches, vol. 30, no. 3, pp.193-206, doi:10.1007/s11001-009-9076-y.

Leifer, I., and Wilson, K., 2007, The tidal influence on oil and gas emissions from an abandoned oil well: Nearshore Summerland, California, Marine Pollution Bulletin, vol. 54, no. 9, p. 1495-1506.

Leifer, I., Kamerling, M., Luyendyk, B., Wilson, D., Stubbs, C, and Lorenson T.D., 2008, Large-scale spatial and temporal trends in seep emissions in the Coal Oil Point seep field – A seep resistance model to understand geologic and environmental control. IX International Conference on Gas in Marine Sediments, Bremen Germany, 4 p.

Leifer, I., M. Kamerling, B.P. Luyendyk, and Wilson, D., 2010. Geologic control of natural marine methane seep emissions, Coal Oil Point seep field, California. Geo-Marine Letters, vol. 30, no.3-4, p. 331-338, doi:10.1007/s00367-010-0188-9.

Leifer, I., and Culling, D., 2010, Formation of seep bubble plumes in the coal oil point seep field. Geo-Marine Letters, vol. 30, no. p. 3-4, 339-353, doi:10.1007/s00367-010-0187-x.

Lorenson, T.D., Hostettler, F.D., Dougherty, J.A., Rosenbauer, R.J., Peters, K.E., and Dunaway, M., 2006, Overview of Natural Oil Seepage in the Santa Barbara Channel and Southern Santa Maria Basin, Southern California. California and the World Ocean 2006, Book of Abstracts, p. 153-154. [http://resources.ca.gov/ocean/cwo06/PDF/abstracts.pdf, abstract PDF, poster PDF (file size: 5 MB; dimensions: 72 in x 36 in)].

Lorenson, T.D., Hostettler, F.D., Peters, K.E., Dougherty, J.A., Rosenbauer, R.J., and Helix, M., 2007, Natural oil seepage in southern California: Occurrence, sources, and

ecology: in Petrotech 2007 Proceedings, New Delhi, India, CD-ROM. 6 p. [http://www.petrotech2007.com/TechnicalProceedings.asp, PDF (5 MB)].

Lorenson, T.D, Hostettler, F.D., Rosenbauer, R.J., Peters, K.E., Kvenvolden, K.A., Dougherty, J.A., Gutmacher, C.E., Wong, F.L., and Normark, W.R., 2009, Natural offshore seepage and related tarball accumulation on the California coastline; Santa Barbara Channel and the southern Santa Maria Basin; source identification and inventory: U.S. Geological Survey Open-File Report 2009-1225 and MMS report 2009-030, 116 p. and spreadsheets http://pubs.usgs.gov/of/2009/1225/.

Lorenson, T. D., and Wong, F.L., 2010, Natural offshore asphalt seepage and related accumulations in southern California 10th International Meeting on Gas in Marine Sediments, Sept. 2010.

Lorenson, T.D., 2011, Greenhouse Gases Generated from the Biodegradation of Natural Seep Oils Offshore California. Geological Society of America Abstracts with Programs, Vol. 43, No. 5, p. 532.

Lorenson, T.D, Hostettler, F.A., Rosenbauer, R.J., Peters, K.A., Wong, F., Kvenvolden, K.A., and Helix, Mary Elaine, 2010, Natural offshore seepage and related tarball accumulation on the California coastline. Geological Society of America Abstracts with Programs, Vol. 42, No. 5, p. 87.

Peters, K.E Hostettler, F.F., Lorenson, T.D, and Rosenbauer, R.J., 2008, Families of Miocene Monterey crude oil, seep, and tarball samples, Coastal California. American Association of Petroleum Geology Bulletin, vol. 92, p. 1131-1152.

Roberts, D. A., Bradley, E. S., Cheung, R., Leifer, I., Dennison, P. E., and Margolis, J. S., 2010, Mapping methane emissions from a marine geological seep source using imaging spectrometry. Remote Sensing of Environment, vol. 114, no. 3, 592-606. doi:10.1016/j.rse.2009.10.015.

Wong, F, Lorenson, T., Dartnell, P., Day, J., Fong, G., Helix, M.E., Hart, P., Hostettler, F., Kvenvolden, K., Leifer, I., Peters, K., Rosenbauer, B., Conrad, J., 2008, Sources, transportation, and fate of natural oil and gas seeps, Southern California. *in* Helterbrand, W.S., Sieverling, J.B., eds., Proceedings of the U.S. Geological Survey Seventh biennial geographic information science workshop. U.S. Geological Survey Scientific Investigations Report 2008-5074, 19 p. http://pubs.usgs.gov/sir/2008/5074/.