Natural oil seepage in southern California: Occurrence, sources, and ecology

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Abstract

About 650 seep, tarball, and crude oil samples from the California coast were collected and analyzed in order to study possible genetic relationships. A geochemical fingerprint for each sample was determined based on thirty-two biomarker parameters. Samples were categorized using chemometrics (multivariate statistics) applied to source-related biomarker ratios. The distributions of samples in each oil family were mapped, thus revealing information about their origins and seasonal patterns of tar deposition on local beaches. An extensive area of active seeps near Point Conception was located by sidescan imagery and sampled by a remotely operated vehicle (ROV). Biomarker and chemometric analysis indicate that these tar deposits originated from carbonate-rich anoxic Miocene source rock like that in nearby outcrops of Monterey Formation. In this area, about 150,000 barrels of tar up to 5-m thick cover an estimated 5 km^2 of seafloor, creating tar “reefs”. "The older tar “reefs”, or hardened seep features, are actively colonized by sessile invertebrate communities like those found at similar water depths on nearby rocky outcrops."

Introduction

A five-year study of seep, tarball, and crude oil samples in southern California waters and beaches is underway as part of a joint U.S. Geological Survey-U. S. Minerals Management Service (USGS/MMS) program to identify natural and anthropogenic sources. Natural sources for these petroleum hydrocarbons include ubiquitous onshore and offshore shallow oil seeps, especially prominent along the southern California coast. Anthropogenic sources include accidental oil spills from vessels and sunken wrecks, from offshore drilling rigs and pipelines, and from ships involved in the processing and transport of oil.

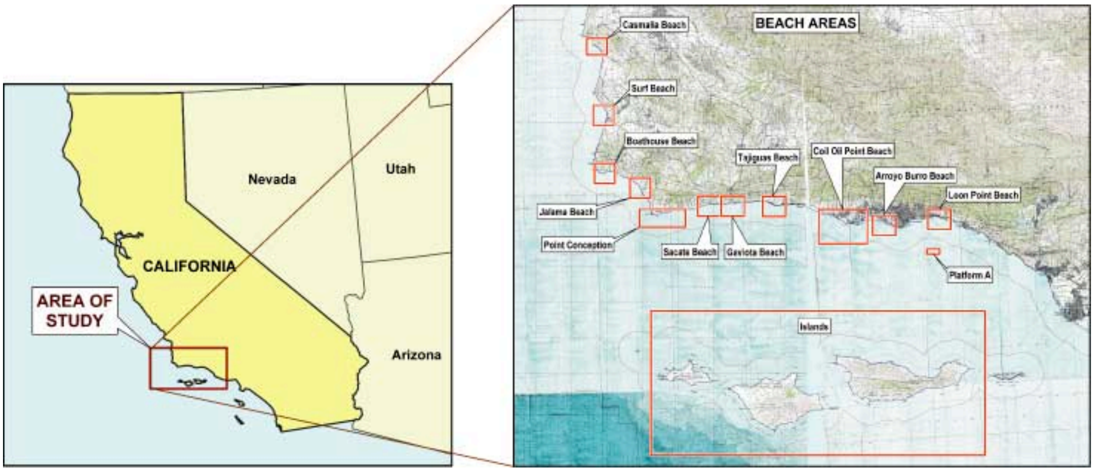

Figure 1. Study area. The main locus of oil and tar seepage occurs in southern California.. The images in Figures 2 to 4 occur within the Point Conception area indicated on the map.

Sample collection

As part of this study, a Remotely Operated Vehicle (ROV) survey was conducted in the Point Conception area where previous studies had noted tar seeps (Vernon and Slater, 1963) and methane water column anomalies (Lorenson et al., 2003). Sidescan imagery (Normark et al., 2003) suggested unusual seafloor features (e.g., Figure 2), and subsequent ROV surveys confirmed vast areas of tar mound accumulation. The tar mounds are typically 10 to 100 m in diameter and in many areas coalesce into extensive tar reefs. The largest of these areas covers an area of about 2 km^2 and is up to 5 m thick. The entire area of seepage covers at least 5 km^2. Closer inspection of the tar mounds shows pronounced viscous extrusion of tar (Figure 3), often producing whip-like extrusions that break off and float to local beaches. Older areas of tar extrusion are heavily colonized by marine invertebrates and resemble reef communites found on submarine rock outcrops (Figure 4). Adjacent sand-covered areas contain fewer invertebrates and fish.

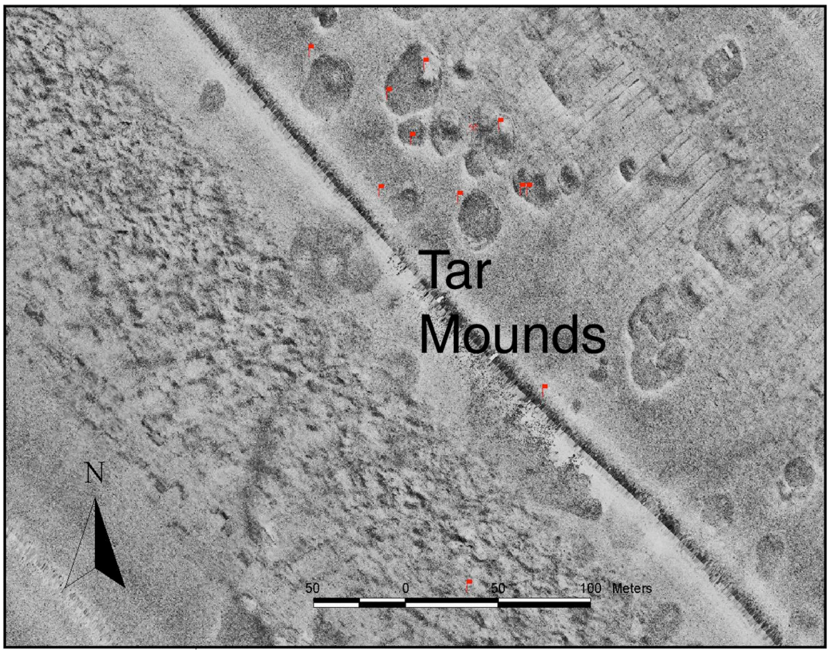

Figure 2. Sidescan image of the seafloor southwest of Point Conception, California shows several tar mounds ranging in diameter from about 10 to 100 m. Tar mounds such as these are confined to the area near Point Conception. They cover at least 5 km^2 and contain about 150,000 barrels of oil. Red flag symbols indicate ROV dive sites.

Figure 3. Remotely operated vehicle (ROV) video image shows a crab near the top of extruding tar on a tar mound like those in Figure 3. Lack of colonizing sessile organisms suggests that this mound is quite young.

Figure 4. Remotely operated vehicle (ROV) video image of a colonized tar mound likely older than than that in Figure 3. This tar “reef” is similar to those in Figures 2 and 3. Sea anemones and other sessile organisms are covering the tar, some of which can be seen in the middle of the photo. Objects in the foreground are part of the ROV.

Biomarker analyses

Seep, tarball, and crude oil samples were analyzed by gas chromatography-mass spectrometry (GC/MS). Oils released into the environment from their source are immediately subjected to weathering and biodegradation. Therefore, only the more refractory constituents of oils can be used for correlation. For example, hopane and sterane biomarkers (Figure 5) are molecular fossils that are ubiquitous in oils, retaining their original chemical signature through extensive biodegradation (Peters et al., 2005a). Some refractory polycyclic aromatic hydrocarbons (PAH) are also useful for correlation. Thirty-two different parameters, plus whole-oil stable carbon isotope values, were utilized. Chemometric analysis of source-related biomarker ratios was used to separate the samples into genetic families. Sample distributions were mapped, giving information on local sources and transport. Other parameters were used to evaluate the extent of biodegradation, and organic matter input, redox conditions, lithology, and age of the source rock for each sample. A prior example of this approach applied to the Channel Islands revealed promising correlations (Hostettler et al., 2004, Kvenvolden and Hostettler, 2004).

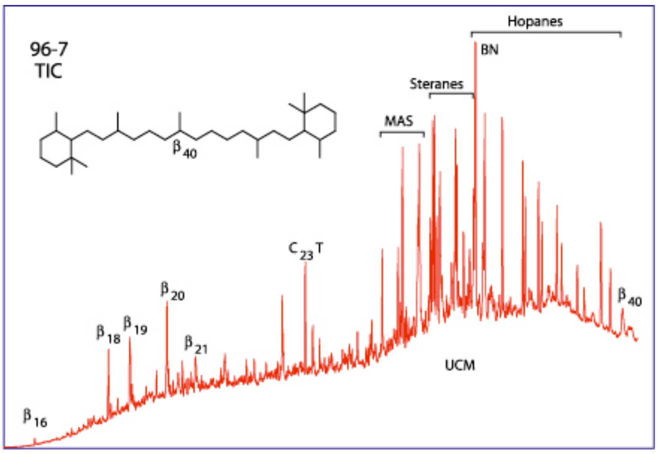

Figure 5. Total ion chromatogram (TIC) of a typical coastal tar residue. Legend: β_{16}, β_{18}, β_{19}, β_{20}, β_{21} = β-carotenoid series; β_{40} = β-carotane; $C_{23}T$ = C_{23}-tricyclic terpane; MAS = monoaromatic steroids; Steranes = C_{26} to C_{29} regular steranes; Hopanes = C_{27} to C_{35} regular hopanes; BN = 28,30-bisnorhopane; UCM = Unresolved Complex Mixture.

Chemometric analysis

Once the biomarker analyses were complete, a 'training set' of 402 samples was selected by omitting severely biodegraded samples. Chemometric analysis of the data included hierarchical cluster analysis (HCA) and principal components analysis (PCA) to establish genetic families. An automated multi-tiered decision tree consisting of multiple K-Nearest Neighbor (KNN) and soft independent modeling of class analogy (SIMCA) models was constructed (Figure 6). The decision tree allows rapid classifications of large numbers of new samples, where confidence limits are assigned to each classification. The data were also used to infer the age, lithology, organic matter input, and depositional environment of the source rock for each sample. The training set results yielded three families consisting of a total of 15 subgroups.

The results confirm that most samples originated from different organofacies of Miocene source rocks, including the Monterey Formation. They comprise three families, each containing groups and sub-groups distinguished by PCA. Samples in Families 1 and 3 have C_{26}/C_{25} tricyclic terpane and C_{31}R/hopane ratios indicating marine shale and marine carbonate source rocks, respectively, while Family 2 has samples with intermediate compositions. Samples in Family 1 have low C_{35}/C_{34} hopane ratios, indicating oxic conditions during source-rock deposition. These samples are enriched in oleanane, a biomarker from angiosperms common in the source rocks for Cretaceous or younger crude oils. Examples of Family 1 samples include produced oil from Platform A (Dos Cuadras Field), nearby seep oils, and tarballs collected from Tajiguas, Goleta, and Gaviota in southern California. Family 3 oil samples have elevated bisnorhopane/hopane and C_{35}/C_{34} hopane ratios, indicating anoxic source-rock deposition. Examples include seep oil and tarball samples from Stinson Beach, Angel Island, Point Reyes, and Drakes Bay in northern California and beaches in northern Santa Barbara County. Because some tarballs found north of San Francisco correlate with samples of produced or seep oils, maps of their locations provide information on transport by ocean currents in and from southern California.

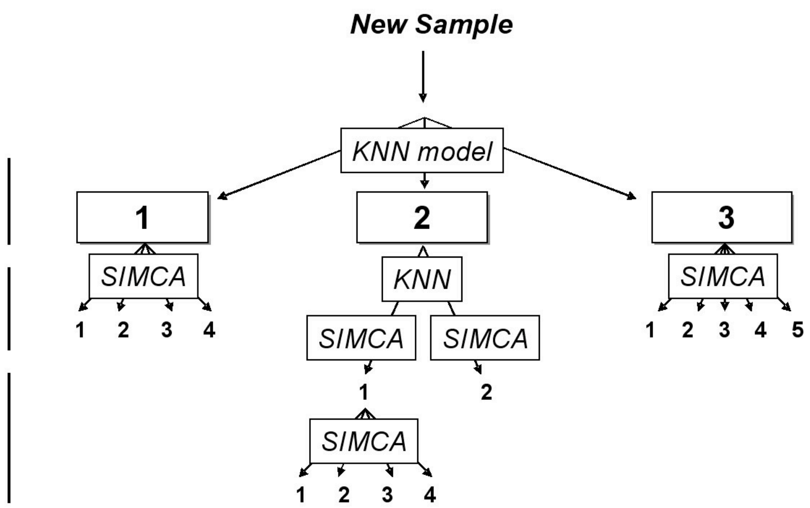

Figure 6. Example of the unique multi-tiered chemometric model constructed that allowed identification of genetically distinct tar groups offshore California, (modified from Peters et al., 2005b). HCA = hierarchical cluster analysis, KNN = K-nearest neighbor, SIMCA = soft independent modeling of class analogy, y/n = acceptable/unacceptable confidence in SIMCA assignment.

Results

The results show that all of the tarball samples can be related to natural seepage from the southern California area. Crude oils from platforms offshore Point Conception are genetically distinct from nearby natural seepage. Offshore seep samples from Coal Oil Point, near Santa Barbara to as far west as offshore Gaviota emit lighter oil that is geochemically distinct from seep samples from near Point Conception. In the area offshore Coal Oil Point and Santa Barbara the results thus far show that platform and seep oil samples are genetically similar, suggesting that the seeps originate from the oil reservoirs sampled by the platforms.

Figure 7 shows an example of interpretation near Coal Oil Point. Abundant hydrocarbon gas is associated with the seeps offshore Coal Oil Point, resulting in numerous gas plumes that reach the sea surface. ROV observations of these sites reveal oil droplets rising from the sediment near steep-walled pits, up to about 2 m deep, often issuing copious amounts of gas. The gas is of thermogenic origin, composed mainly of methane, with several percent higher molecular-weight hydrocarbons. The pits are commonly lined with colonies of the large sea anemone *Metridium giganteum*, in contrast to the adjacent sand-covered bottom. The interior of the pits are often partially lined with tar, which may stabilize the pits and provide a hard substrate for colonization. Fish were also observed to be more abundant near seeps, suggesting that that seep areas serve as reef habitat. at both Coal Oil Point and Point Conception.

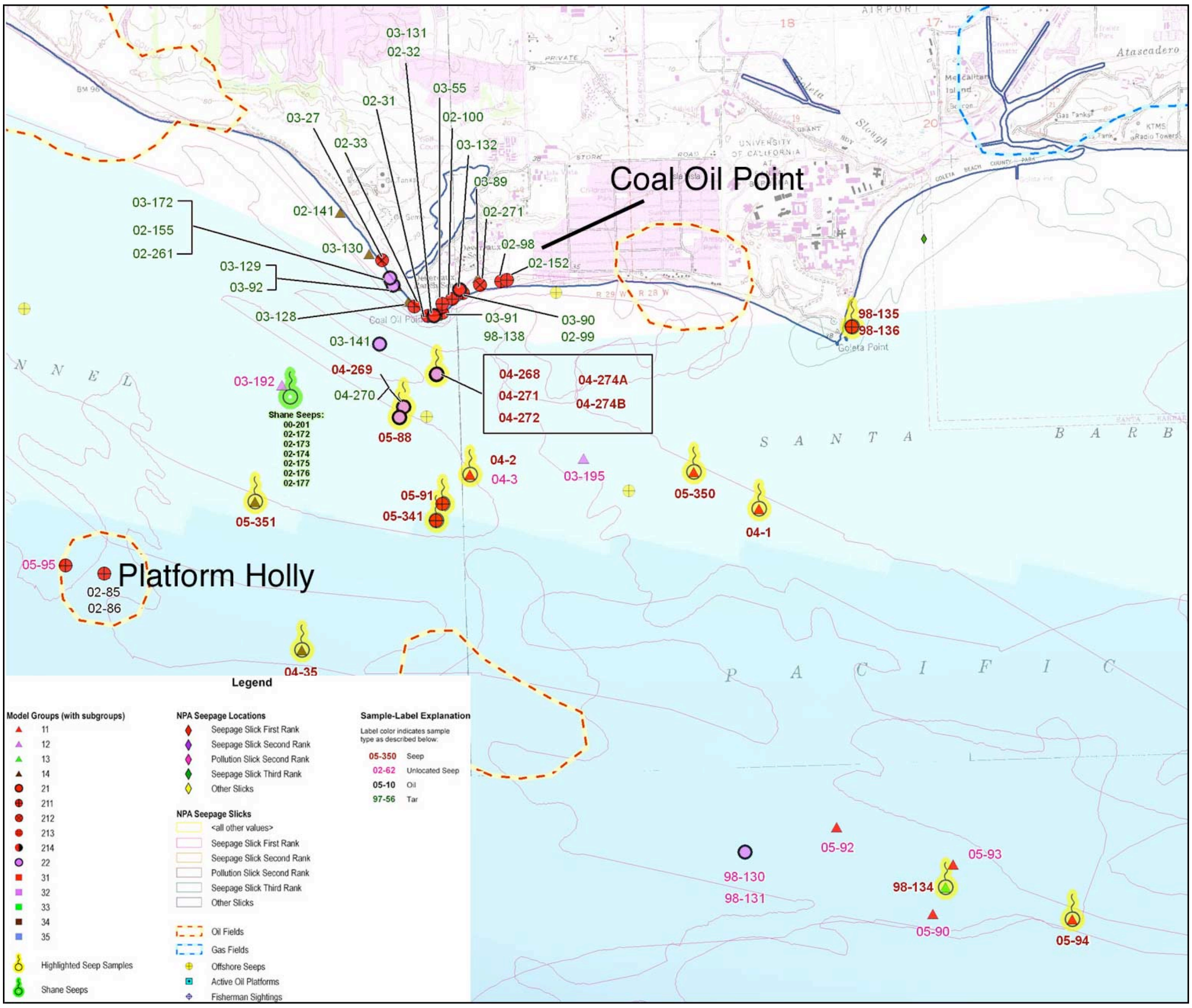

Figure 7. Map of seep, tarball, and production oil samples near Coal Oil Point California and their genetic relationships based on chemometric analyses. Chemometric families are indicated using symbols (legend). Sample numbers are adjacent to each symbol. Natural seep samples are noted by a vertical wavy line. Seep samples without chemometric family symbols, such as “Shane” seep, were too biodegraded for reliable chemometric analysis.

Conclusions

Our results show that tarballs on California beaches can be related to natural sources and that there is extensive natural offshore seepage. The seepage provides hard substrate for sessile organisms that would otherwise not colonize the sand-covered seafloor. Future work will focus on fingerprinting platform-produced oils, monitoring unusual beach tar deposition events, and flux measurements of selected seeps.

Acknowledgements

We thank Grace Fong and Florence Wong for GIS and graphic support. Numerous people at the University of California, Santa Barbara, the County of Santa Barbara Energy Division, and the Monterey Bay Aquarium Research Institute helped in many aspects of this work and they are gratefully acknowledged.

References

Hostettler, F.D., Rosenbauer, R.J., Lorenson, T.D., and Dougherty, J.A., 2004, Geochemical characterization of tarballs on beaches along the California coast. Part I - Shallow seepage impacting the Santa Barbara Channel Islands, Santa Cruz, Santa Rosa and San Miguel: Organic Geochemistry v. 35 p. 725-746.

Kvenvolden, K.A., and Hostettler, F.D., 2004, Geochemistry of coastal tarballs in southern California—A tribute to I.R. Kaplan: In Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan, The Geochemical Society, Publication No. 9, Elsevier, The Netherlands, p. 197-209.

Lorenson, T.D., Dougherty, J.A., Ussler W.III, and Paull, C.K., 2003, Cruise Summary for P-1-02-SC: Acoustic Imaging of Natural Oil and Gas Seeps in Measurement of Dissolved Methane Concentration in Coastal Waters Near Pt. Conception, California OF 03-122 86p. *http://geopubs.wr.usgs.gov/open-file/of03-122/*

Normark, W.R., Fisher, M.A., Gutmacher, C.E., Sliter, R., Hibbler, L., Feingold,B, and Reid, J.A., 2003, Cruise Report for A1-02-SC: Southern California CABRILLO project, Earthquake Hazards Task; USGS OFR 03-110. *http://geopubs.wr.usgs.gov/open-file/of03-110/*

Peters, K.E., C.C. Walters, and J.M. Moldowan, 2005a, The Biomarker Guide. Cambridge University Press, Cambridge, U.K., 1155 p.

Peters K.E., S. Ramos, J.E. Zumberge, and D.L. Gautier, 2005b, Circum-Arctic petroleum systems identified by a new chemometric approach. 22nd International Meeting on Organic Geochemistry (IMOG), Seville, Spain, September 12-16, 2005, Abstract OP3-3, p. 48.

Vernon, J.W., and Slater, R.A., 1963, Submarine tar mounds, Santa Barbara County, California. Bulletin of the American Association of Petroleum Geologists v.47, n. 8:, p. 1624-1627.