Signature Alkane Ratios and Hydrocarbon Emission Estimates for Western Kern County Oilfields

Kelvin Bates[1], Greg Hartt[2], Donald Blake[2]

[1]California Institute of Technology, Pasadena, CA; kelvin@caltech.edu; [2]University of California at Irvine, Irvine, CA

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1. Introduction & Methods

California is the third-largest oil-producing state in the country; in August, production reached 533,000 barrels per day.[1] The state also accounts for 10% of US refining and produces 900 million ft^3 of natural gas per day.[2] This oil and gas infrastructure releases significant amounts of methane and larger hydrocarbons (which have detrimental health effects and lead to ozone formation), in addition to nitrogen oxides, carbon oxides, and other pollutants. Quantifying this pollution is important both for understanding its impacts and for implementation of California's emissions control policies.

Figure 1: Western Kern Co. oilfields

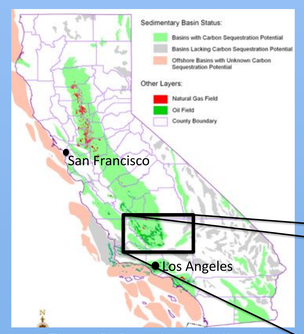


Figure 2: Locations of oil and gas fields in California[4]

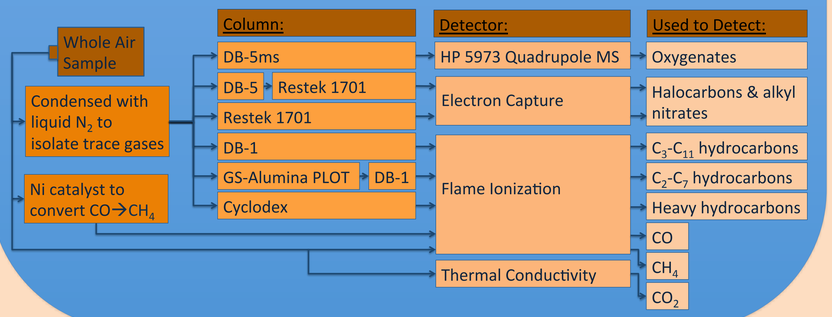
Much of California's oil and gas production is concentrated in western Kern County (black box in *figure 2*), near the towns of McKittrick and Taft, including the Midway-Sunset oil field (the third most productive in the US) and the Elk Hills gas field (California's largest).[3]

Figure 3: Flight paths over Kern Co., June 26 (yellow) and 27 (blue)

For this study, two research flights were conducted over the Kern Co. oilfields in late June (*figure 3*), on which 80 whole air samples were collected (*figure 4*). Additionally, whole air samples at 29 ground sites were collected four times between February and August (*figure 4*). These formed a small part of the NASA Student Airborne Research Program dataset, which consists of over 1000 samples collected on flights every June since 2009. Samples were analyzed in the Blake lab at UCI using a suite of GC columns and detectors (*figure 5*). In all, mixing ratios were measured of 46 hydrocarbons, 8 alkyl nitrates, 23 halocarbons, and 2 sulfur compounds, in addition to CO, CO_2, and CH_4, all with precision near 1%.

Figure 4: Whole air sample collection locations from research flights (blue) and ground samples (June in yellow; February, April, & August in green)

Figure 5: Column and detector specifications for whole air sample analysis



2. Pentane Isomer Ratios

Ratios of alkanes and alkyl nitrates were calculated and analyzed for all 931 sub-boundary-layer whole air samples collected on NASA Student Airborne Research Programs research flights since 2009. The ratio of isopentane to *n*-pentane showed the sharpest separation of trends (the two-lobe pattern seen in *figure 6*), a characteristic that can frequently be used to trace air masses from two distinct types of sources. A map of whole air samples color-coded by isopentane/*n*-pentane ratio (*figure 7*) elucidated the cause of this separation: samples collected near oil and gas infrastructure, including wells, seeps, and refineries, display elevated levels of *n*-pentane relative to isopentane.

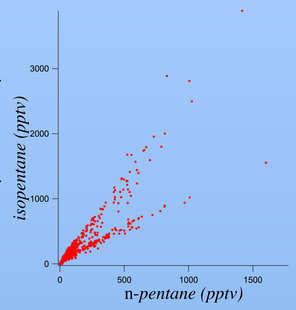


Figure 6: Mixing ratios of n*-pentane and isopentane in whole air samples*

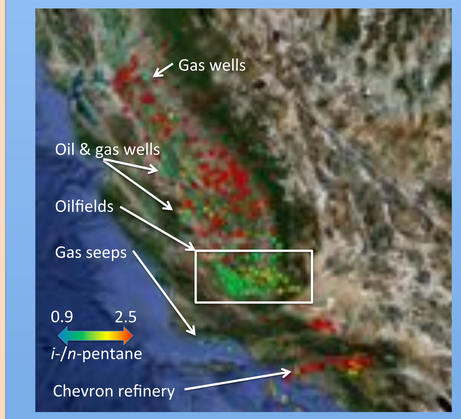


*Figure 7: Locations of whole air samples collected by NASA Student Airborne Research Programs 2009-2012, colored by isopentane/*n*-pentane ratio.*

Figure 8 again shows the ratios of isopentane to *n*-pentane for all 931 samples analyzed, with each sample colored by proximity to particular types of oil and gas infrastructure. With R^2 values in excess of 0.97, samples near fossil fuel infrastructure show an iso-/*n*-pentane ratio of 0.87:1, while those uncorrelated with such infrastructure show a ratio of 2.52:1. Clearly oil and gas production causes relatively greater release of *n*-pentane, likely through evaporation, than more ubiquitous activities such as fossil fuel combustion. By measuring the isopentane/*n*-pentane ratio, one can likely determine whether an air sample contains emissions from oil and gas infrastructure.

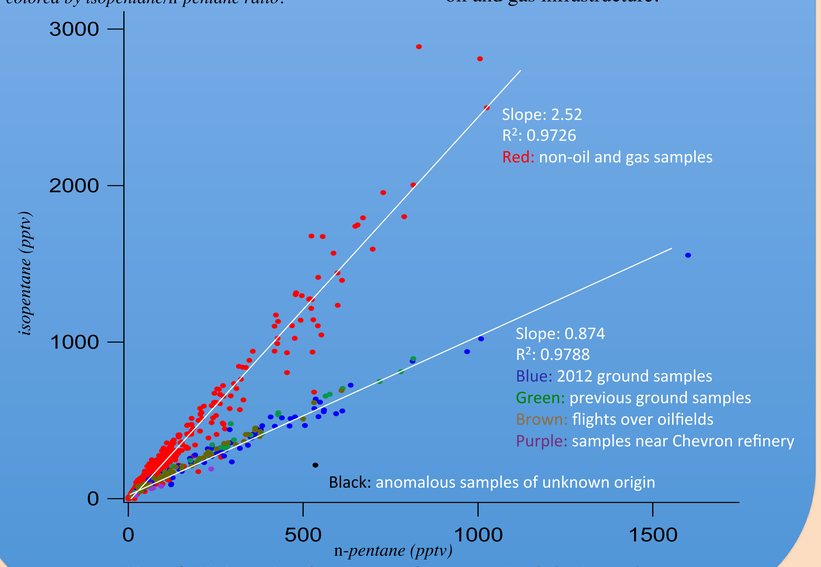


Figure 8: Mixing ratios of n*-pentane and isopentane in whole air samples, colored by the sample's proximity to oil and gas infrastructure*

3. Emissions Estimates

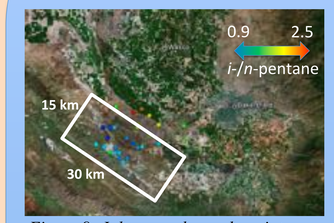


Figure 9: July ground sample points used in box model, with box dimensions and i*-/*n*-pentane ratio included*

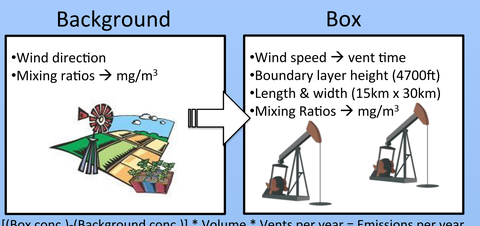
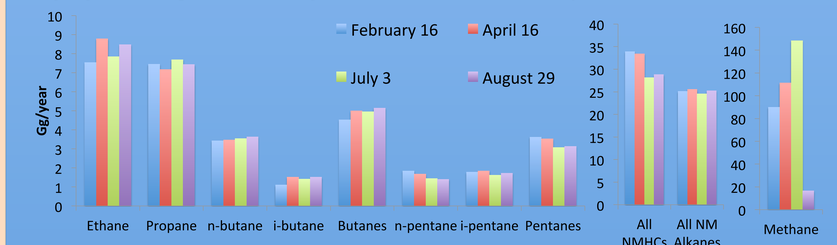


Figure 10: Simple outline of emissions estimate box model

Using the *i*-/*n*-pentane ratio to determine where oil and gas infrastructure emissions originated, a simple box model was constructed to estimate the annual hydrocarbon emissions of the western Kern Co. oilfields (*figures 9 & 10*). The box volume was calculated using boundary layer height estimates from the two research flights; wind speeds and directions were measured during each ground sample session to determine both the time required to vent emissions out of the box and the location of background air entering the box. Then, by subtracting background mixing ratios of hydrocarbons from mixing ratios in the box, and scaling up by the volume and vents per year, total annual emissions within the box were estimated. The procedure was carried out four times, once for each set of ground samples. Results are shown below (*figure 11*).

The four sample sets gave consistent results for non-methane hydrocarbons (NMHCs), suggesting a robust model. These results were similar in magnitude and in alkane ratios to previous studies of oil and gas infrastructure emissions, and represent nearly 2% of California's hydrocarbon emissions on 0.1% of the state's land. Methane estimates showed large variations, likely due to high (and variable) background concentrations of methane in California's Central Valley. Further studies may include extension of the box model with a larger grid of samples or modeling ozone formation from these hydrocarbon emissions.



	February	April	July	August	Average	Std. Dev.	% Relative SD
Methane	80	91	160	17	91.5	55.5	60%
Ethane	7.0	8.4	8.1	8.5	8.16	0.57	7.0%
Propane	7.0	7.6	7.9	7.4	7.43	0.22	2.9%
Butanes	4.5	5.0	5.0	5.1	4.91	0.26	5.4%
Pentanes	3.2	3.3	2.7	3.1	3.34	0.28	8.3%
Non-methane alkanes	25.1	25.6	24.6	25.2	25.1	0.4	4.1%
All C_2+ hydrocarbons	33.9	33.4	28.2	28.8	31.1	3.0	6.9%

Figure 11: Estimates of annual hydrocarbon emissions from a 450 km^2 section of the western Kern Co. oilfields, in Gg/year.

Acknowledgements and sources:

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