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Re: REGULATION 13 CLIMATE POLLUTANTS RULE 5 PETROLEUM REFINERY HYDROGEN PLANTS

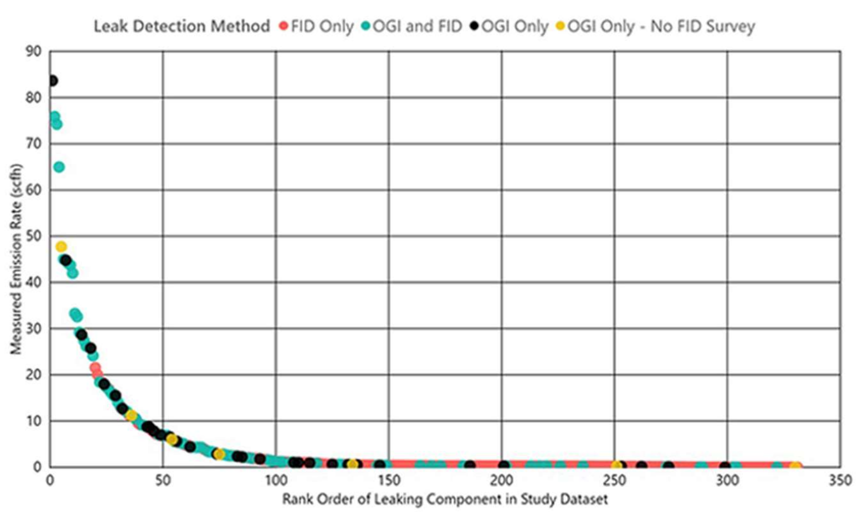
From: Charles Davidson. Hercules CA. [redacted]

This comment on BAAQMD Draft Rule 13-5, refers to the refineries' self-reporting of fugitive methane emissions levels from their Steam Methane Reforming hydrogen plants using the USEPA's Method 18. (1-3) The objective of this comment is two-fold: first, to question the quality of data on fugitive methane emissions from refineries using EPA Methods 18 and 21, and second, to compared them to alternative, superior methods which are currently available.

I.

EPA Method 18 specifies laser-based in-situ optical gas imaging by a technician placing an optical gas imaging (OGI) device within only several feet of the suspected or potential leak and limited to the parts per million sensitivity level. The refineries' current use of EPA Methods 21, primarily using flame ionization detection. (FID), is also limited to the parts per million level of detection and must be used a mere several inches to a few feet away from the suspected individual leak, at most. (2-5)

It was recently reported that larger methane leaks were better detected than small leaks using OGI and small leaks using FID. (5)



"Distribution of equipment leaks detected by OGI and FID-based surveys in this study. The figure shows the emission rate in standard cubic feet per hour (scfh) that was measured with the high-volume sampler for each leak identified by one or both emission detection methods. Leaking components identified only by OGI techniques tended to be higher on the overall distribution of measured equipment leaks in the study while those identified uniquely by FID surveys tended to be lower in emission magnitude."

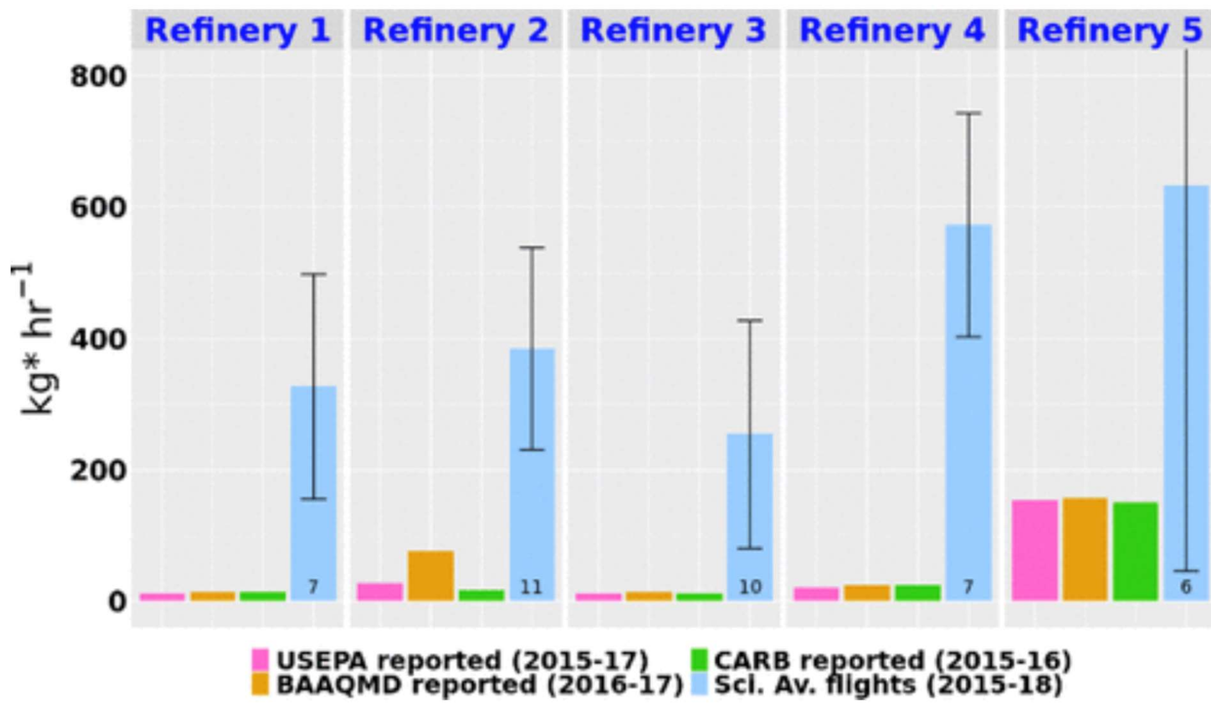
The alternative suggestion ~~being~~ proposed in this comment letter, is for a superior and portable methane detection method, having wide-angle areal methane plume detection capability, when placed at least 100 yards away from the source and having parts per billion (ppb) level sensitivity. Wide-angle plume detection at the ppb level of sensitivity can detect many potential sources of fugitive methane simultaneously. A portable device could then be guided to the actual source of the leak. Why is this important?

II.

There was a recently published airborne survey~~s~~ demonstrating a much higher methane plume detection capability when compared to EPA Method 18 or Method 21, using airborne remote methane detection methods and areal plume modeling. (6)

Using a repeated circular flyover method (spiraling in multiple loops) above refineries, researchers have recently determined that fugitive methane emissions from the five Bay Area refineries were 6-11-times higher than was determined in three previous *non-airborne* in situ flame ionization detector methods performed by the USEPA, CARB and BAAQMD (using Method 21). In measurement at one refinery, the level was 23-fold higher. This airborne (flyover) method used Cavity Ring-Down near-infrared laser Spectroscopy, which avoids this sensitivity limitation of both method 18 and 21, by using an effective pathlength of up to many kilometers. From overhead, it enables methane gas to be monitored in seconds or less and at the parts per billion level. (6)

BAAQMD Rule 13-5 STANDARDS, section 12-5-301, (entitled: Emission Limits for Existing Petroleum Refinery Hydrogen Plants), states that "Effective [five years from the date of adoption], an owner or operator of a petroleum refinery hydrogen plant shall not vent to the atmosphere any emissions containing more than 6.8 kilograms (15 pounds) per day." However, according to the airborne assessment of refinery methane cited above (and shown in the graph below), the lowest daily emissions reported from any refinery (Phillips 66) is 12,000 pounds per day (800-times higher than BAAQMD's proposed venting standard). Therefore, the proposed BAAQMD limit would either be based upon poor measurement standards and methods or otherwise be highly unrealistic. (1,6)



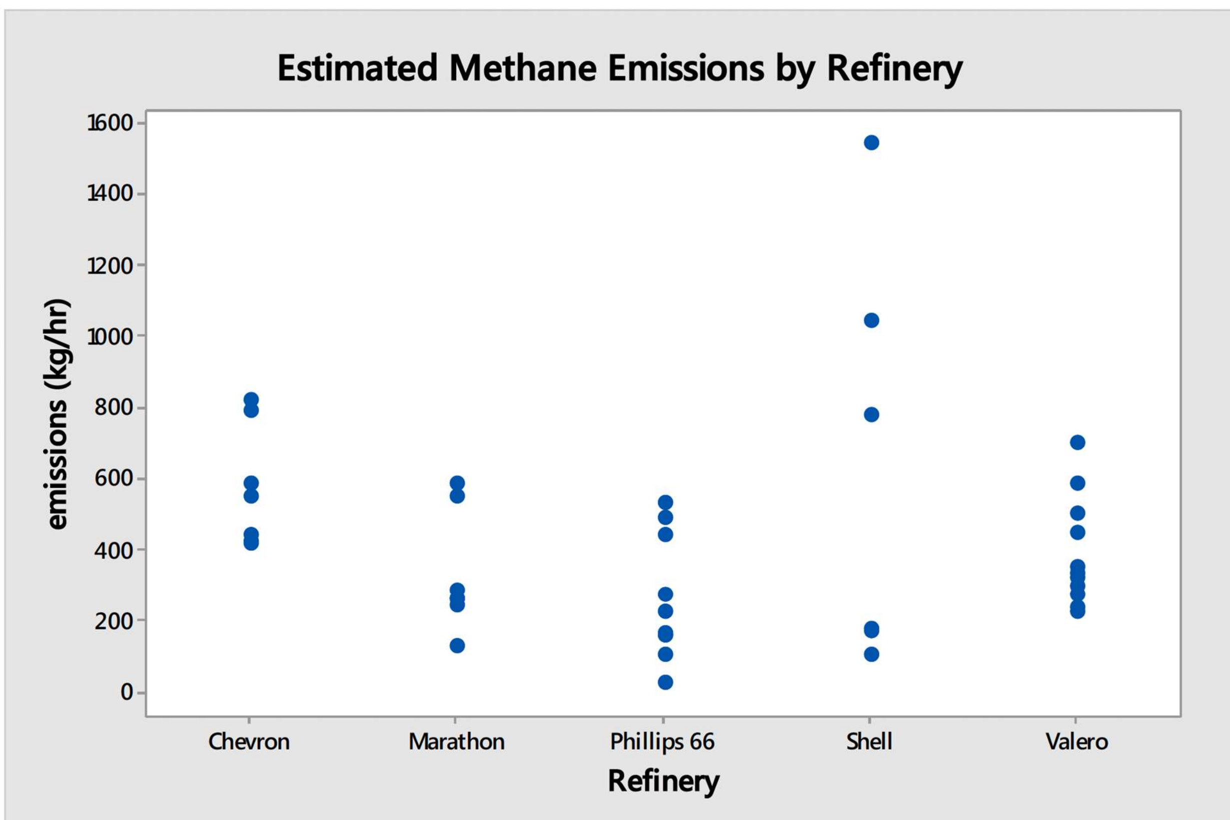


Figure S2. Estimated Methane Emissions by Refinery.

There are two main problems with BAAQMD's assessments of methane releases from Bay Area refineries: one, being the exclusive use of EPA Methods 18 and 21 to base their yearly methane emissions upon and the second, being the entire voluntary nature of the refineries doing their own methane self-reporting in the first place. The following chart is from BAAQMD's own methane database, predicated upon the refineries' self-reporting, which they used to based their emissions violation fines upon (against the refineries). Demonstrating the major gaps in BAAQMD's approach to current and possibly fugitive methane detection, the agency's flawed reporting of zero methane emissions for Chevron, Phillips 66 and Marathon are *diametrically* opposite the assessments of the airborne/flyover study (which, incidentally, has a BAAQMD scientist as the principle investigator). The following chart shows that there must be numerous sources of undetected and/or possibly unreported methane leaks from all of the Bay Area refineries, which would most likely be daily leaks from their hydrogen plants (which use the most natural gas). (7)

Table 1
Hydrogen Plant Methane Emissions from Bay Area Petroleum Refineries

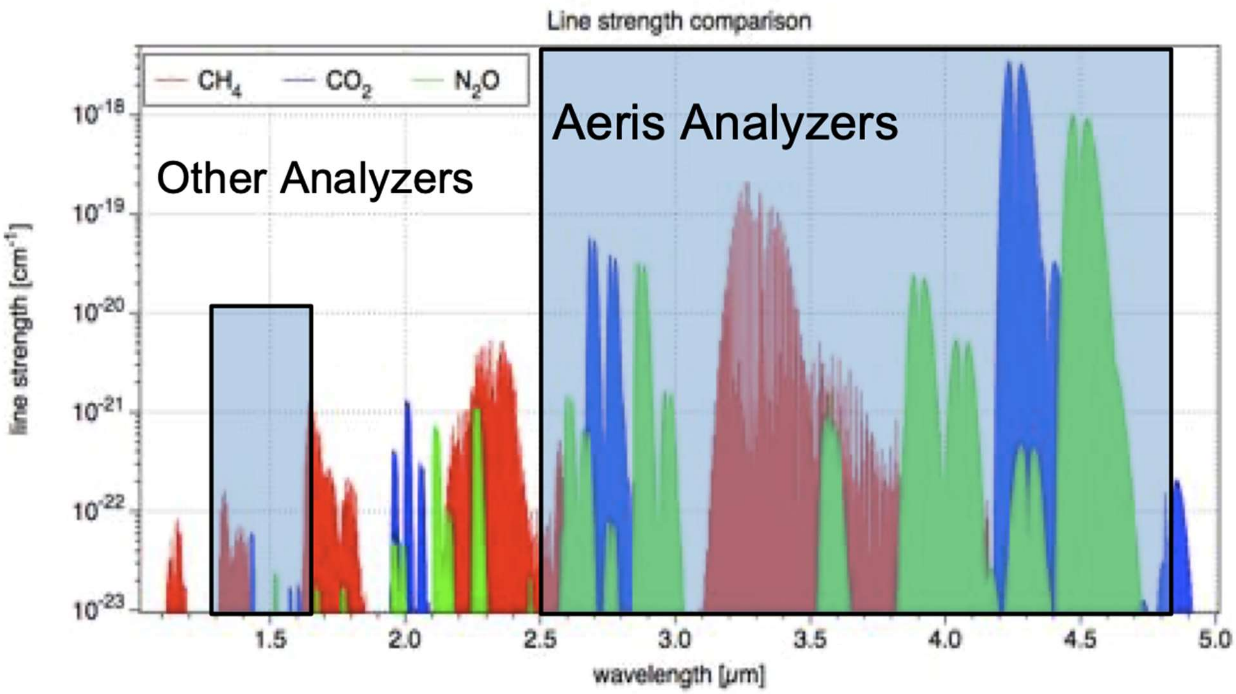
Facility	**2016 Methane Emissions** (metric tons per year)	**2017 Methane Emissions** (metric tons per year)	**2018 Methane Emissions** (metric tons[a] per year)	**Average Annual Emissions for 2016–2018 (metric tons[a] per year)**
Air Liquide [P66] [a]	0	0	0	**0**
Air Products [Marathon] [a]	0	0	0	**0**
Air Products [PBF] [a]	15	4	76	**32**
Chevron Refinery [a]	0	0	0	**0**
Marathon Refinery [a]	0	0	0	**0**
P66 Refinery [a]	0	0	0	**0**
PBF Refinery	907	1,520	589	**1,005**
Valero Refinery	988	2,752	814	**1,518**
TOTALS	**1,911**	**4,276**	**1,479**	**2,555**

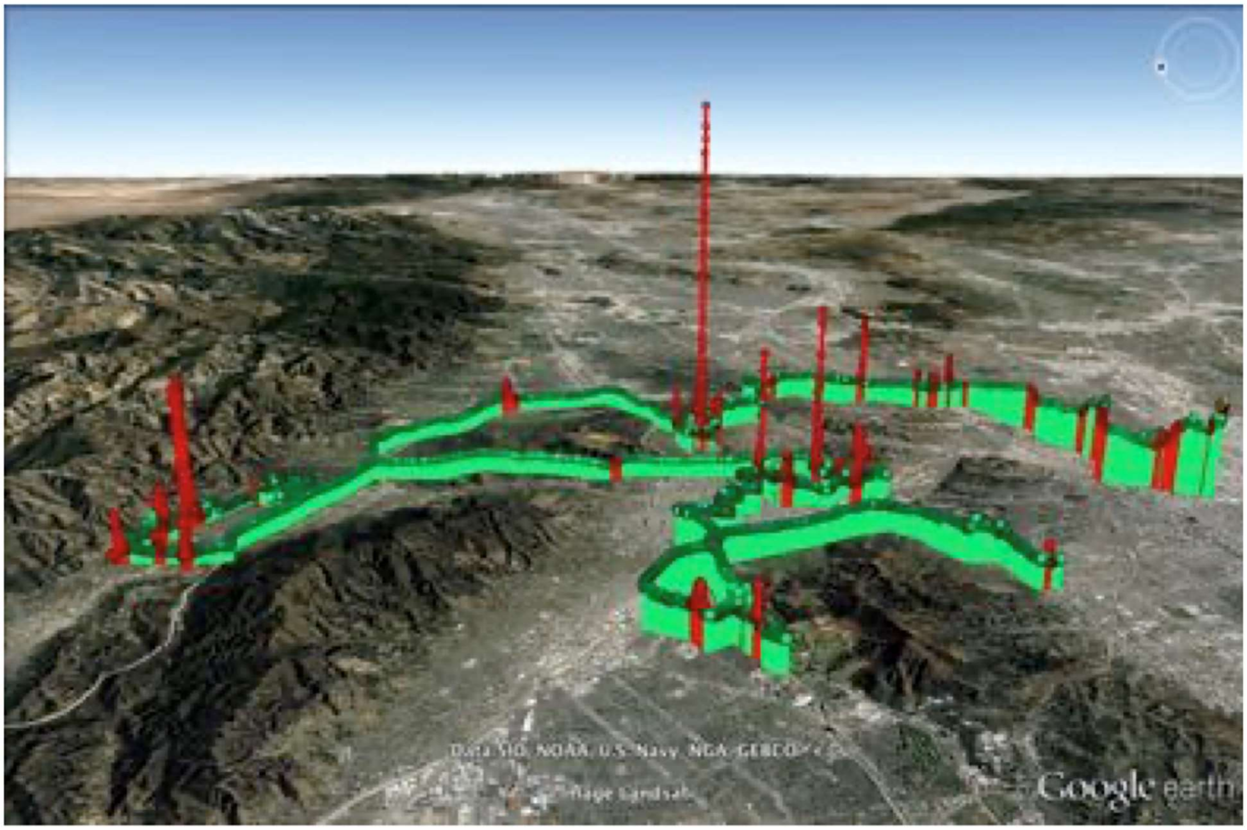
Source: Emissions reported in metric tons per year by hydrogen plant owners/operators in response to Air District hydrogen plant emissions questionnaire.

III.

A highly sensitive alternative to airborne cavity ringdown spectroscopy for areal plume detection, is the recently developed MIRA Pico Mobile LDS Natural Gas Leak Detection System (with GPS capability) from Aeris Technologies, and co-developed with the USEPA and US ARPA-e. The MIRA Pico System employs mid-IR laser spectrometry to distinguish methane from ethane (at the 1 ppb level) and establishes the methane-to-ethane ratio in order to be able to distinguish methane-only landfill or compost methane from ethane-containing fossil fuel-based natural gas, such as from a PG&E pipeline, a refinery SMR or from fugitive wellsite emissions. (8)

It is important to stress that while the MIRA Pico System can detect a methane plume from over 100 yards away at the parts per *billion* level, EPA Methods 21 and 18 are limited to the parts per *million* (ppm) level with the distinct disadvantage that it must be used a mere several inches or several feet away from the suspected individual leak. The 13-foot path length of the MIRA Pico is located within a palm-size mirrored cavity which reflects the beam back and forth through a continuous supply of inhaled methane. Theoretically or potentially, the Mira Pico System can be employed from beyond the refinery fence-line (at least in some cases). The MIRA Platform operates in the mid-IR, where ethane absorption is 6000 times stronger than the near-IR where most competing approaches operate, so clearly identifying natural gas leaks which always contain both methane and ethane.





More than two-dozen natural gas leaks (Red) are identified via simultaneous, correlated ethane and methane detection (i.e., as natural gas leaks) while driving at highway speeds.

The Mira Pico System’s sensitivity, mobility and remote capability, is unprecedented and it should absolutely be part of BAAQMD’s arsenal of methane detection capabilities. The cost is not prohibitive and BAAQMD could helpfully lead the State of California in using this technology for the detection of climate pollutants. The acquisition of the Mira Pico mid-IR methane/ethane detector should be permitted under Rule 13-5 601.3, which is included as “any other method approved by the APCO.” This capability should immediately be investigated by the Air District. Use of the Mira Pico System would be a powerful complement to Method 18, if not eventually supplanting it. The fact that it could potentially be used from on- or off-site by BAAQMD engineers would further increase public confidence in data provided by the refineries and provide enhanced safety for inspectors.

Given the Phillips 66 and Marathon refineries’ planned conversion from petroleum feedstock to biofuels, the refineries’ or third parties’ Steam Methane Reforming Hydrogen Plants will be required to operate at their maximum capacity in order to *deoxygenate* vegetable or animal triglycerides. They will therefore more likely be a potential source of increased fugitive methane emissions and flaring. The Phillips 66 refinery proposes, after the Rodeo Renewal Project’s completion, that their main hydrogen plant (Air Liquide) will be increasing its hydrogen production target by 30%.

Finally, because we are in a climate emergency which must urgently be addressed in the short term, any substitute of carbon dioxide equivalents for methane being proposed (for up to 20% of refinery-wide methane emissions), should be based upon the 20-year/86-fold global warming potential (CO2e) compared to carbon dioxide. Our society simply does not have the luxury of considering the 100-year/28-fold CO2e standard.

Conclusion

The above comments describe the weaknesses of both EPA Methods 18 and 21 for high resolution methane detection, which are not stand-off leak detection methods (i.e., are limited to being placed near leaks) and which cannot detect the much broader or expansive outlines of methane *plumes*. The proposed increases in refinery hydrogen plant capacity (with the two Bay Area renewable diesel projects) combined with the vast increase in fugitive methane plume volumes recently detected (using airborne/flyover methods and compared to previously reported refinery fugitive methane) argues for consideration of more rigorous forms of handheld and ppb-sensitivity methane areal plume detection devices, which are currently available.

REFERENCES:

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2) Frequently Asked Questions (FAQs) for Method 18 (8/24/16) https://www.epa.gov/sites/default/files/2016-08/documents/method18_faq.pdf

3) Detection Limits of Optical Gas Imaging for Natural Gas Leak Detection in Realistic Controlled Conditions August 2020. https://pubs.acs.org/doi/pdf/10.1021/acs.est.0c01285

4) Methane leak detection by tunable laser spectroscopy and mid-infrared imaging. https://opg.optica.org/DirectPDFAccess/F7689017-21F3-4374-BF33B87C28B615CA_450164/ao-60-15-C68.pdf?da=1&id=450164&seq=0&mobile=no

5) Methane leak detection by tunable laser spectroscopy and mid-infrared imaging. [Figure 2] https://opg.optica.org/DirectPDFAccess/611493D5-22C1-43C5-B6E8800CEB0A3F4B_450164/ao-60-15-C68.pdf?da=1&id=450164&seq=0&mobile=no

6) Guha et al. Assessment of Regional Methane Emissions Inventories through Airborne Quantification in the San Francisco Bay Area. https://pubs.acs.org/doi/10.1021/acs.est.0c01212 (2020)

7) [BAAQMD] STAFF REPORT
Proposed New Regulation 13: Climate Pollutants, Rule 5: Industrial Hydrogen Plants and

Proposed Amendments to Regulation 8, Organic Compounds, Rule 2: Miscellaneous Operations [Table 1] https://www.baaqmd.gov/~/media/dotgov/files/rules/reg-13-rule-5-petroleum-refinery-hydrogen-systems/rule-version/documents/20220124_01_sr_1305-pdf.pdf?la=en

8) MIRA Pico Mobile LDS Natural Gas Leak Detection System w/GPS by Aeris Technologies.
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b. https://www.epa.gov/sites/default/files/2017-11/documents/16.scherer.aeris_2017aiw.pdf