Why Emission Factors Don't Work at Refineries and What to do about it

By Alex Cuclis

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Abstract

A number of studies in the U.S., Canada and Europe have found that reported emissions of volatile organic compounds (VOCs) at refineries and chemical plants are substantially lower than the measured emissions. In several cases the reported emissions were an order of magnitude or more lower than the measured emissions. One of the main flaws of emissions reporting is that emission factors and other emissions estimating techniques assume equipment is "well-maintained". However, process equipment can have failures due to operator error, faulty design or maintenance that was performed incorrectly or not at all. In order to capture these errors, measurements are required; however, total vapor analyzers (TVAs) or "sniffers" typically used in Leak Detection and Repair (LDAR) programs only measure one point in space. Techniques such as Differential Absorption Light Detection and Ranging (DIAL) and Solar Occultation Flux (SOF) measure the VOC concentrations in a two dimensional vertical plane and calculate VOC flux in pounds per hour. The results determine the total VOC mass released. The National Institute of Science and Technology (NIST) has chosen to develop a DIAL system to measure and verify reductions in greenhouse gases that may be used in off-sets, carbon trading, a carbon tax or other exchange since there are concerns that the emission estimating techniques for greenhouse gases have similar problems. This paper provides a list of studies where measured VOC emissions were found to be substantially higher than reported values and how Sweden is using DIAL and SOF in place of emission factors and emission estimates. Additional information is provided on which parts of the petrochemical facilities are most responsible for low emission estimates and how the U.S. could benefit from the Swedish model as well as some of the obstacles.

Introduction

Several studies performed in the U.S. indicate that the reported values of VOCs from petrochemical facilities are substantially lower than measured values. In 1985, Keith Bauges of the U.S. EPA found that emissions near the Houston petrochemical complex were 5.9 times higher than expected based on reported values.[1] In 2000 at the Texas Air Quality Study (TexAQS) near Houston, the University of Texas (UT) found that emissions were underestimated by a factor of 3-15,[2, 3] whereas a team from the National Oceanic and Atmospheric Administration (NOAA) estimated the error was between one to two orders of magnitude.[4,5] A follow-up study in 2006 (TexAQS 2006 or TexAQS II) found that emissions had dropped by 40% since 2000, but they were still one to two orders of magnitude higher than reported based on the last available inventory.[6]

Similar results have been found in Europe where they have consistently found measured emissions that are several times higher than expected based on EPA/AP-42 estimating techniques. Because of these discrepancies, Sweden has been using either DIAL or SOF surveys as the basis for calculating annual emissions estimates that are entered into their emissions inventories for over two decades despite objections raised by various industry groups.

The concern of underestimated emissions was expressed by EPA employee Brenda Shine in a technical memorandum dated July 27, 2007, with the subject "Potential Low Bias of Reported VOC Emissions from the Petroleum Refining Industry." The memo describes the Swedish approach for determining emissions from refineries as well as the DIAL results indicating measured emissions have been found to be 10 times or more than reported emissions. Shine cited this information, stating that these techniques must be investigated since reported emissions are the basis of U.S. ozone control strategies and abatement of air toxics.[7]

A critical feature of DIAL and SOF measuring techniques is their ability to systematically identify the general location as well as the magnitude of the leaks so that corrective actions can be taken in an efficient manner. The early applications of DIAL at refineries in Sweden has been published by Lennart Frisch, who worked for the local regulatory agency at the time and was the main driving force for getting DIAL as the established method for measuring refinery emissions.[8] Frisch also presented Sweden's experiences with DIAL at a Remote Sensing Workshop in Research Triangle Park hosted by EPA in 2006.[9]

The graphic below by Spectrasyne, one of the DIAL vendors, displays the differences observed between calculated or estimated emissions and measured emissions.

Comparison of Reported Emissions to Emissions Measured by DIAL

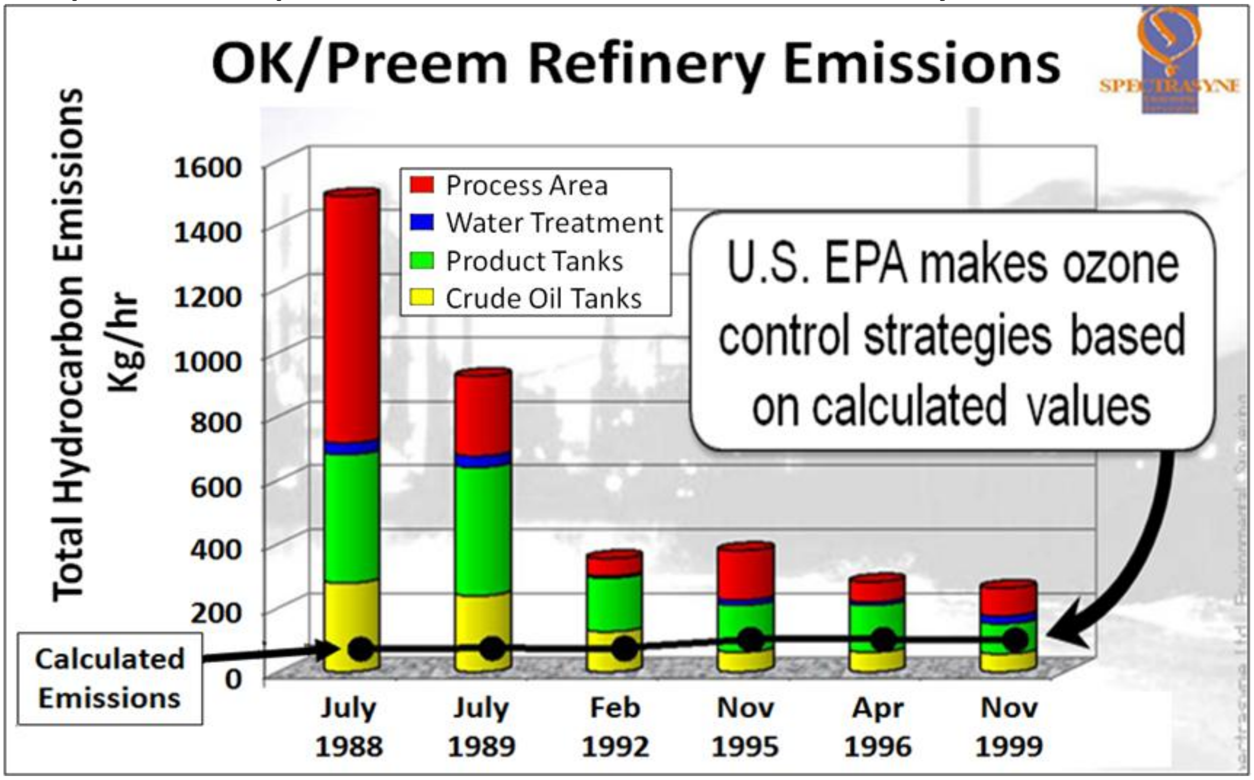

Figure 1. DIAL results at a refinery in Sweden over several years. (used with permission from Jan Moncrieff, Technical Director, Spectrasyne).[10]

Figure 1 illustrates several important issues:

1. At this refinery, measured emissions were initially 20 times higher than reported, but emissions dropped by about 80% over a ten year period.

2. Calculated values, which are based on EPA/AP-42 estimating techniques, did not change much, and actually increased to adjust for increasing capacity, but did not decrease to reflect changes implemented to reduce emissions at the facility.

3. After significant problems have been resolved, the measured emissions change very little, even with changing temperatures. This is an indication that annualization, or taking results from a 2 - 3 week DIAL survey, provides a reasonable estimate of annual emissions. If there were problems accounting for seasonal swings in temperature or extrapolating based on temporal emissions, then there should be much more variation observed in the data.

4. Even after many years of measuring with DIAL, measured emissions are higher than the emissions calculated with AP-42 or other similar methods. This result is consistent with many other studies.

In the late 1980's and early 1990's the Swedish EPA based their hydrocarbon emissions on the calculated results. In 1992 they required all 5 refineries to measure emissions instead of calculating them, without specifying any measuring principle. However, many of the methods selected by Swedish refiners (Open path Fourier Transform Infrared Spectroscopy (FTIR), Differential Optical Absorbance Spectroscopy (DOAS), and others) were incapable of translating concentration or path length measurements to mass flux. As a result in 1995, Swedish authorities required all refiners to report emissions based on DIAL studies performed at least once every 3 years. (Note: Vertical Radial Plume Mapping or VRPM, developed after DIAL and SOF, can be used to measure the mass flux of chemicals on a small scale).

The first DIAL study of hydrocarbons at a refinery was in July 1988. The hydrocarbon emissions measured at the Swedish BP refinery exceeded 1400 kg/h, whereas the expected emission rate based on reported values was less than 100 kg/h. The DIAL measurements led to the discovery of a large and previously unknown leak from a distillation column. After the column was repaired, another DIAL survey was performed in the following year, finding 25% fewer emissions. National Physical Laboratories (NPL) DIAL operator, Rod Robinson, has noted that DIAL studies "often identify emissions not known to the operators. These are usually outside and LDAR programme, and so would likely remain 'unknown.'"[11] This sentiment is also relayed in the DIAL brochure developed by Shell Global Solutions while trying to market their DIAL system. The brochure provides several pages describing why measurement with DIAL is superior to standard estimating methods which can give a "false sense of security" about emissions. It goes on to say, "If you're not measuring, you are guessing."[12]

Canada performed a DIAL study at a refinery in 2005 and found emissions to be 15 times higher than reported, and has not performed another DIAL study since. [13, 14] The Texas Commission on Environmental Quality (TCEQ) with some EPA funding, performed partial studies using DIAL at a U.S. refinery in 2007 and found high emissions at storage tanks and at flares, although not as high as were found in previous DIAL studies.[15] The City of Houston, with EPA funding, performed a DIAL study of a large refinery in 2010, and found very high emissions during a tank-cleaning operation as well as at a wastewater facility.[16]

SOF studies have been performed in the U.S. in 2006,[17] 2009[18] and 2011.[19] "The results from the campaign that was carried out during September 2006 in the Houston area show that the emissions of ethene and propene, obtained by SOF, are on average an order of magnitude larger than what is reported in the 2006 daily emissions inventory (EI)."[20] The 2006 and 2009 studies were focused around the Houston Ship Channel and the Texas City Industrial Complex. A follow-up study in 2011 repeated the measurements in Houston and Texas City, and added measurements at the petrochemical facilities in Port Arthur/Beaumont and Longview, Texas. Figure 2 shows some of the results that were obtained in the Houston Ship Channel.

SOF Measurements of VOCs in the Houston Ship Channel

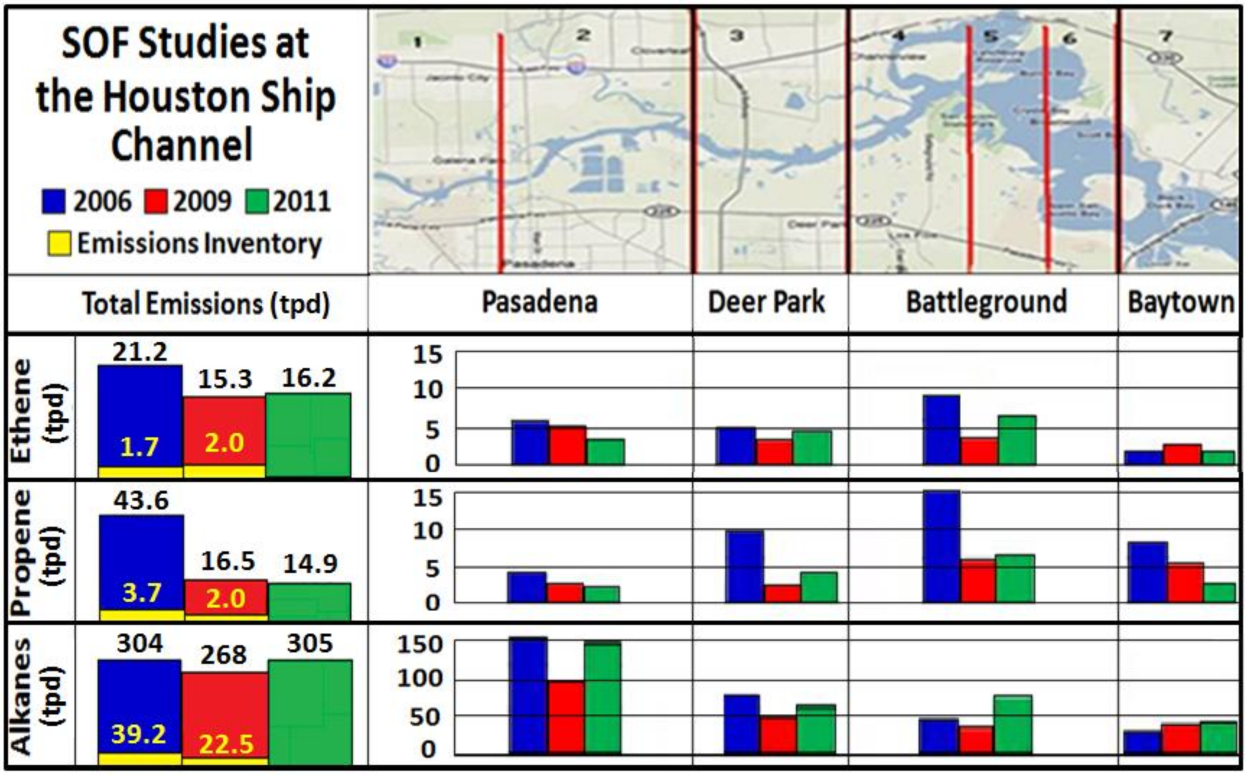

Figure 2. The total ethene, propene and alkanes measured by SOF in 2006, 2009 and 2011 were several times higher than the emissions inventory (in yellow on the left). The emissions were separated into sectors indicated above; however, different wind directions during some measurements likely moved some emissions from one sector to another.[19]

Comparisons between the measured emissions and reported/estimated emissions in the inventory were consistent, leading to the following statement made in the executive summary of the 2011 SOF report:

"A comparison of the 2011 measurements with the 2009 TCEQ inventory… …shows good overall agreement for NOx ((-20)–50)% and SO2 (18–44)%, with the exception for Texas city (260%). However, for the VOCs there are larger discrepancies with (400–1500)% for alkanes, (300–1500)% for ethene and (170–800)% for propene. For the two new areas observed here, Port Arthur/Beaumont and Longview the discrepancies are (300–700)% for ethene, (200–800)% for propene and (900–1500)% for alkanes. Hence, for VOCs it appears to be a persistent difference between inventories and measurements, independent of industrial area or region."[19]

How Sweden Uses DIAL and SOF in Place of Emission Factors and Emission Estimates

When local Swedish environmental authorities saw the results of DIAL measurements at refineries in the late 1980's and early 1990's, they became skeptical of emissions estimating techniques based on EPA's AP-42 results. In 1992 they required all refineries to submit "measured" emissions. By 1995 they required the measured emissions to be obtained using DIAL, citing flaws with other analytical techniques. The DIAL measurements were required every 3 years. In the early 2000's testing began with SOF, a technique developed at Chalmers University in Sweden. By 2005 the Swedish authorities allowed either DIAL or SOF to be used, but also required the measurements to be taken annually. Currently all refiners in Sweden use SOF, because it is much cheaper than DIAL. There are advantages and disadvantages in both DIAL and SOF techniques which will be discussed later.

The DIAL and SOF results are generally gathered during two or three week surveys, however, these measurements frequently get extrapolated to calculate annual emissions. Some have claimed that these extrapolations may not be accurate for the following reasons:

1. DIAL and SOF are "snapshots" of an emissions story that is changing significantly due to the temporal nature of petrochemical emissions and changing winds.
2. Upwind and downwind are not measured simultaneously, so interfering emissions from other sources are possible.
3. The process and emissions are constantly changing, yielding a constantly changing emissions pattern.
4. Petrochemical emissions include emission events which occur during start-ups, shutdowns, or during upset conditions.

These errors cited from taking a snapshot of a variable process and winds would imply that sometimes the snapshots would measure numbers higher than reported and other times the snapshots would measure numbers lower than reported. However, this is not the case. In over 35 studies performed between 1988 and 2008 (as shown in Figure 3), the measured emissions were consistently considerably higher than reported emissions. Never has a comprehensive DIAL or SOF survey of an entire refinery found that emissions are less than expected based on annual estimates.

Refinery VOC Emissions Expressed as a Fraction of Total Throughput

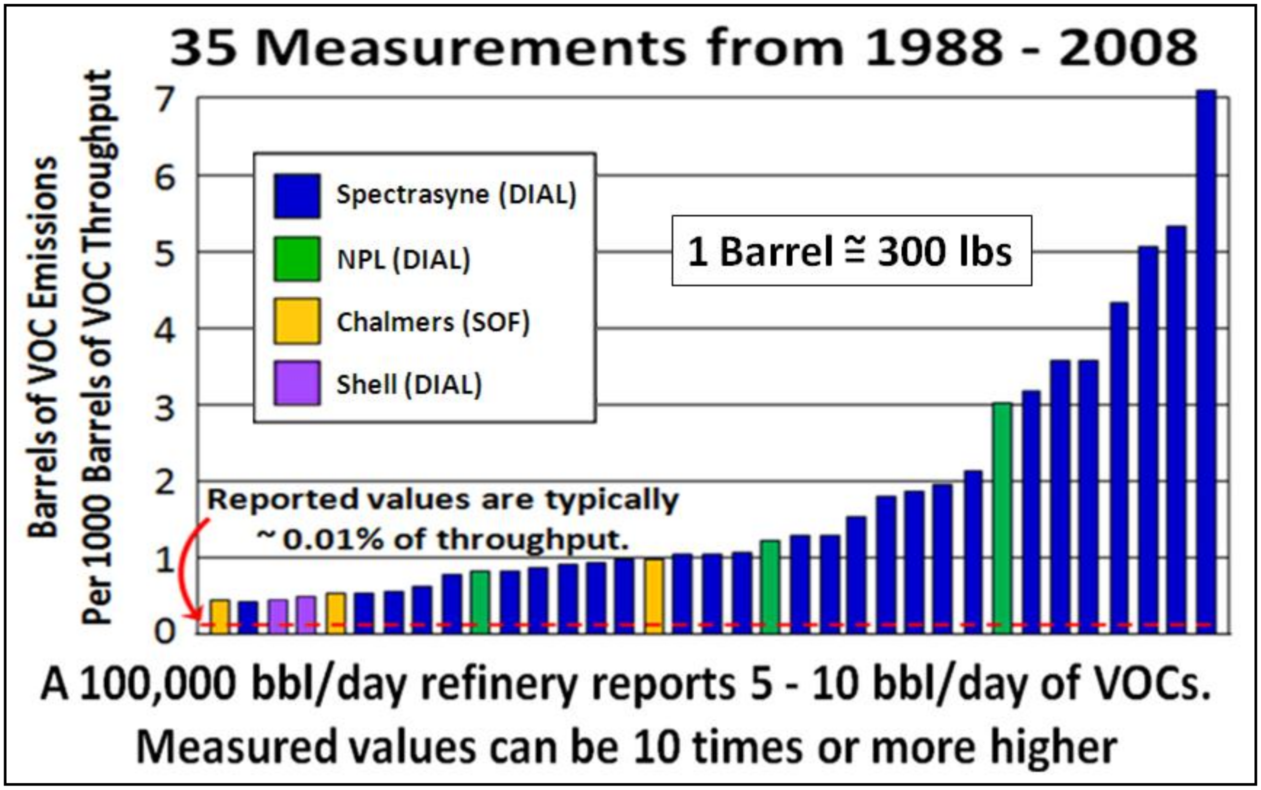

Figure 3. Emissions of volatile organic compounds (VOCs) as a fraction of throughput. Based on data from Jan Moncrieff of Spectrasyne,[10] Rod Robinson of NPL,[11] Johan Mellqvist of Chalmers University[17], Lennart Frisch (formerly with the local environmental regulatory agency in Gotenburg, Sweden)[8] and Allan Chambers, Alberta Research Council.[13, 14] compiled by Alex Cuclis.

There are other arguments that the annual emissions estimates from DIAL and SOF may have a high bias based on the time of day or time of year that most of the samples are taken. For example, some operational activities such as filling and draining a tank may create more emissions, and are likely to occur during the daytime. Also, DIAL and SOF measurements are most often taken in warmer seasons which can lead to a higher bias. Those who have taken these measurements note that measurements taken in February in Sweden, for example, are high and comparable to measurements taken in warmer months. Also, the daytime to nighttime swing in temperatures of a liquid in a tank is very small compared to the swing in ambient temperatures. When the Texas Commission on Environmental Quality (TCEQ) performed a DIAL study in Texas they could not find any significant difference in tank emissions between daytime and nighttime.[15]

Typically when refineries report emissions using standard EPA/AP-42 techniques, the totals come to roughly 0.01-0.02% of throughput (based on an analysis of reported emissions of refineries near Houston in 2004). The reported emissions are the values that the U.S. EPA and many state agencies use to enter into complex air quality models for predicting ozone.

Measured emissions, based on the surveys performed in Figure 3, are more likely to be around 0.1% of throughput, though there is a considerable range. In a 2009 presentation, Robinson on NPL has stated that the average refinery emission rate is closer to 0.2%.[11] The lowest measured numbers are higher than the highest reported numbers. Measured values that are 10 times or more than the reported values are not uncommon and many of those surveys which indicate that emissions are "low" or less than 0.1% of throughput have had the benefit of previous DIAL or SOF surveys which were useful for making corrections about previously unrecognized emissions problems.

All of the above surveys were performed in Europe, with one exception, which was performed in Canada in 2005. Bo Jansson with the Swedish EPA also documented the use of DIAL in "A Swedish background Report for the IPPC Information exchange on Best Available Techniques for the Refining Industry."[21] Jansson continues to advocate measuring techniques over AP-42 approaches to regulatory agencies in other countries.[22]

The Shell Global Solutions DIAL team (which operated from about 1994 – 2002) also found higher than reported emissions from refineries in Europe. In one report focused on tanks, it was noted that "The mean DIAL emission rate for all sites (including the bad tanks) was 4.6 times higher than the corresponding mean API estimate," and "The difference, which is due principally to the few bad tanks, suggests the need to revise the calculations if they are to represent emissions from the average in-service population rather than ideal new installations."[23] P.T. Woods at NPL also reported higher measured emissions from tanks using DIAL, but found the measurements were only a factor of 2.7 times higher than reported emissions.[24]

Annualization of hydrocarbon emission results from DIAL studies at European refineries has been in practice for over two decades. In a report published in 2000 by The European Union Network for the Implementation and Enforcement of Environmental Law (an informal network of the environmental authorities of EU Member States), it is stated that "Remote sensing techniques are applied increasingly and DIAL has become common practise in some of the countries for estimation of the annual VOC emission."[25]

The Shell Sweden annual environmental report for 2008 notes that they have used SOF for several years as the basis for their annual emissions and it includes the chart shown in Figure 4:

VOC Emissions at the Former Shell Refinery in Sweden

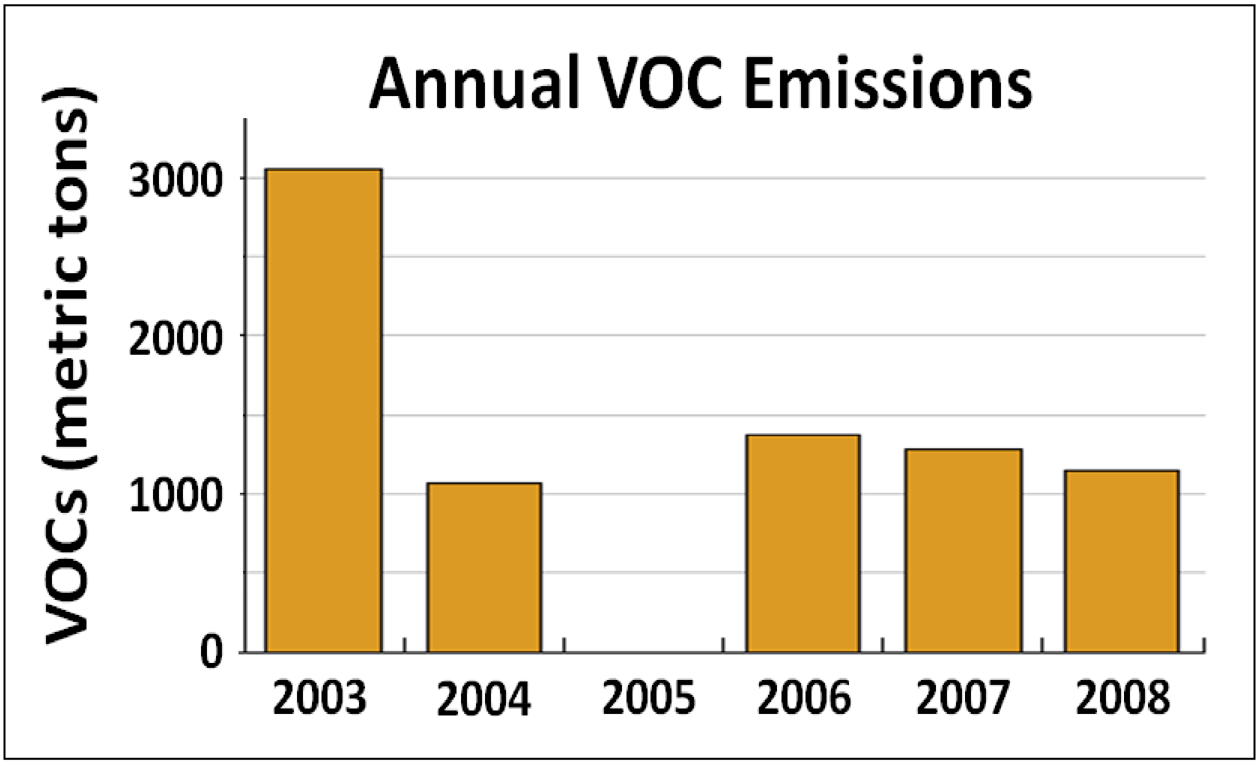

Figure 4. Shell's Swedish Refinery, which has since been sold, has a throughput of about 4 million metric tons. The annual emissions as measured by SOF are 1071 tons per year, or about 0.029% of the annual throughput. This chart was taken from a Shell report to the Swedish environmental agency.[26]

The emission rate of 0.029% of throughput was the lowest reported rate for any refinery that uses SOF or DIAL for measurements at the time. The vendors will be quick to note that this is a very small refinery, about 70,000 barrels/day (larger, more complex refineries routinely have larger leak rates) and it has had the benefit of many DIAL and SOF studies over many years to repair problem areas. This refinery and 4 others in Sweden have been reporting annualized DIAL or SOF emissions to the regulatory authorities since 1995 and, in some cases, as far back as 1988.

In an email exchange with Bo Jansson of the Swedish EPA, notes are referenced to the data shown in Figure 1 of this paper:

"If I understand right the oil industry accept(s) the monitoring techniques (DIAL and SOF) as such but does not accept to extrapolate the two week data to an annual emission. We had that discussion also in Sweden with the refineries. By having the monitoring campaigns at different periods of the year (as you see from the PREEM Gothenburg data) we discovered that summer or winter did not make any important difference in emissions. Also finding that (as you see for the Shell Gothenburg refinery) that emission levels (after having done most improvements at the refinery) are almost on the same level from year to year indicates that Annualization of short term data works quite well."[27]

In 2 review drafts of the EPA's Emission Estimation Protocol for Petroleum Refineries submitted by RTI International in 2009 and 2010, DIAL is mentioned. It must be emphasized that both versions are drafts and are marked specifically, "Do not cite or quote" and should not be considered EPA's position until finalized. These documents have been presented for public comment and a section is quoted here in order to put the comments in context:

"There are other direct measurement methods that have been used to measure emissions from storage tanks even when the emissions from the tank are not vented (i.e., DIAL [Differential Absorption Light Detection and Ranging (LIDAR)] techniques); however, these methods do not provide continuous monitoring and have additional limitations (requiring consistent wind direction, etc.). Therefore, at the present time they are not recommended as primary techniques for emissions estimation. However, they can be used to verify and assess the accuracy and uncertainties associated with tank-specific modeling."[28, 29]

In response, members of the American Petroleum Institute and the National Petrochemical Refiners Association had stronger opposition to DIAL, stating in their written response:

"Because DIAL measurements are typically not long term and have other limitations, there are significant issues with extrapolation of DIAL measurements to estimates of emissions. In addition, since this section of the Protocol acknowledges that 'these methods do not provide continuous monitoring and have additional limitations,' it would not be appropriate to use them to verify and assess other estimating techniques as is suggested. The paragraph in the Protocol is contradictory and needs to be corrected."[30]

Environmental Integrity Project (EIP) also commented on the Emissions Protocol, stating that DIAL should be used more often in the U.S. since it has been successfully used in Europe and Canada. It also cites several incidents where DIAL emissions found that emission rates were several times higher than reported numbers based on annualized calculations.[31]

However, a different section of EPA seems to think annualization on the basis of DIAL results is possible, at least at the Tonawanda Coke facility in New York. In September 2010 they wrote:

"EPA has reviewed the data in this report and has determined that it can be used to estimate TCC's facility-wide annual benzene emission rate for regulatory compliance purposes, notwithstanding CRA's statements in the Executive Summary."[32]

Measured vs. Reported Emissions at Refineries

The U.S. EPA uses reported emissions to build emissions inventories which are used in complex air quality models and become the basis for ozone reduction strategies. Emissions inventories are frequently cited as one of the weakest links in the air quality program design. The U.S. EPA Office of Inspector General has documented the problems with the use of EPA emission factors for developing emission inventories.[33]

The estimates of VOC emissions using these equations have substantial deficiencies due to the limitations of the applicability of the emissions factors. This problem has been noted by several sources. Shell Global Solutions, in a brochure that described the advantages of measuring emissions with DIAL, stated:

"Our experience has shown that the use of emission factors alone can lull you into a false sense of security. Calculations such as those based on component counts and tank roof fittings are fundamentally flawed as they have to assume the typical conditions of the component or fitting… …What calculations do not tell you, is the condition of the components, the effectiveness of maintenance, or about operations that result in emissions… …An important element of ensuring compliance and continuous improvement is verification and 'if you are not measuring you are guessing.'"[12]

There have been several studies in Texas where measured emissions at petrochemical facilities have been several times higher than expected based on reported emissions. Examples are as follows:

1. In an analysis of non methane organic compounds (NMOC) and nitrogen oxides (NOx) data gathered in 1985, Keith Baugues found that, "In Houston, the predicted NMOC levels are always lower than the observed NMOC levels. On average predicted NMOC concentrations in Houston are 5.9 times lower than observed values." However when Baugues included reported emissions from a nearby point source, the value dropped from 5.9 to 4.3. Baugues also suggests that analyses including other point sources that were further away may lower the factor further, and recommended additional studies.[1]

2. Texas Air Quality Study 2000 (TexAQS 2000) – More than 200 scientists participated in this study of the air quality issues in Houston using over $20 million research dollars.[34, 35] One of the primary scientists, David Allen from the University of Texas, reported that when examining measured emissions of ethene and propene near petrochemical facilities, they were 3-10 or 3-15 times higher than expected based on reported values. Researchers from the National Oceanic and Atmospheric Organization (NOAA) claimed that the measured emissions were 10-100 times reported. The final report does not quantify the differences between the inventory and measured values, but notes that while the reported values of nitrogen oxide appear to be in line with the measurements, the reported values of non-methane organic compounds (NMOC) appear to be underestimated.[2]

The Texas Commission on Environmental Quality (TCEQ) noted that "Corroborating field studies (aircraft, monitoring) indicated that reported VOC EIs may be underestimated by 10-100x."[34] In 2002, when TCEQ was developing the State Implementation Plan (SIP) for ozone, they added an additional 200 tons per day of olefins to the inventory, which substantially improved the model results.[35] The changes were justified by TCEQ, "Because of the greater certainty associated with the NOx emissions estimates, TCEQ concluded that industrial emissions of terminal olefins were likely understated in earlier emissions inventories. This conclusion has been reviewed and documented in numerous scientific journals."[36]

3. Texas Air Quality Study 2006 (TexAQS 2006) – A follow-up study to TexAQS 2000 which also involved over $20 million in research funds and over 100 scientists took another look at Houston's air quality. In the final report assembled by contributions from numerous scientists, they claimed that correcting for differences in whether the concentrations of ethene and propene had dropped by 40% since 2000; however, they were still 10-40 times higher than expected based on what was reported in the inventory.[6]

4. The Texas Environmental Research Consortium (TERC) has performed extensive air quality research in Texas. George Beatty, TERC's executive director, asked TERC's Science Advisory Committee, a group of nationally recognized air quality scientists, to develop a strategic plan for 2007-2009. The plan states that "TexAQS (2006) aircraft measurements of pollutant ratios and direct flux measurements using the Solar Occultation Flux (SOF) technique both point to the conclusion that, while VOC emissions in Houston do seem to have decreased between 2000 and 2006, they may still be underestimated by at least an order of magnitude." The report also states that an essential part of improving air quality in the Houston area rests on improving the emissions inventories.[36]

5. Thomas Ryerson, et. al. at NOAA examined the ratio of measured alkene to nitrogen oxide ratios during the TexAQS 2000 campaign, compared them with reported values and found that the alkene emissions were off by a factor between 10 and 100.[4]

6. B.P. Wert, et. al. followed a similar procedure to Ryerson with similar results, finding that VOC emissions roughly 20 times higher than reported.[5]

7. Johan Mellqvist performed a SOF study in the Houston area in 2006 and found VOC emissions roughly an order of magnitude higher than expected when compared to the reported values in the emissions inventory (EI).[37, 38] SOF studies were repeated in the Houston area occurred in 2009 and 2011 with similar results.[18, 19] Note that Mellqvist examined alkanes as well as alkenes. His reports show that, although there is variability in the data, the emissions are consistently several times higher than the inventory levels would indicate.

8. Joost de Gouw, et. al. looked at aircraft measurements of ethene in the Mont Belvieu area near Houston and compared them to the results from the SOF measurements. Although the difference between the measurements was up to 50%, both showed emissions to be multiple times higher than values expected based on the inventory.[39]

9. Additional details regarding the underestimation of emissions from petrochemical facilities can be found in the paper submitted at the National Spring 2009 AIChE Conference in Tampa titled, "Underestimated Emission Inventories."[40]

It is worth noting that shortly after TexAQS 2000, when the environmental regulating agency of Texas was told that the emission inventories may be off by an order of magnitude or more, they hired a consultant to study the problem. One of their conclusions was, "On-site observations reveal that existing EPA emission inventory methods do not reflect local conditions and are not likely to produce accurate emission estimates." The facilities were following the proscribed estimating procedures, but there were problems with those procedures.[41]

SOF Measurements in Texas City

The industrial complex located in Texas City, Texas provides a unique setting for measuring air quality downwind from petrochemical facilities. As can be seen by the map provided in Figure 5, the Texas City Industrial Complex is filled with petrochemical plants and tank storage facilities in an area that is approximately 1 ½ miles by 3 ½ miles. These facilities include 3 refineries and several chemical plants. They are bounded on the west side by Highway 146 and on the east side by Galveston Bay. When wind is flowing from east to west, it passes over the Gulf of Mexico, Galveston Bay and on to the Texas City facilities. When SOF samples are taken along Highway 146, they are rich from the petrochemical facilities' emissions and have relatively small background emissions due to the geography of the bay and the gulf.

Texas City Industrial Complex

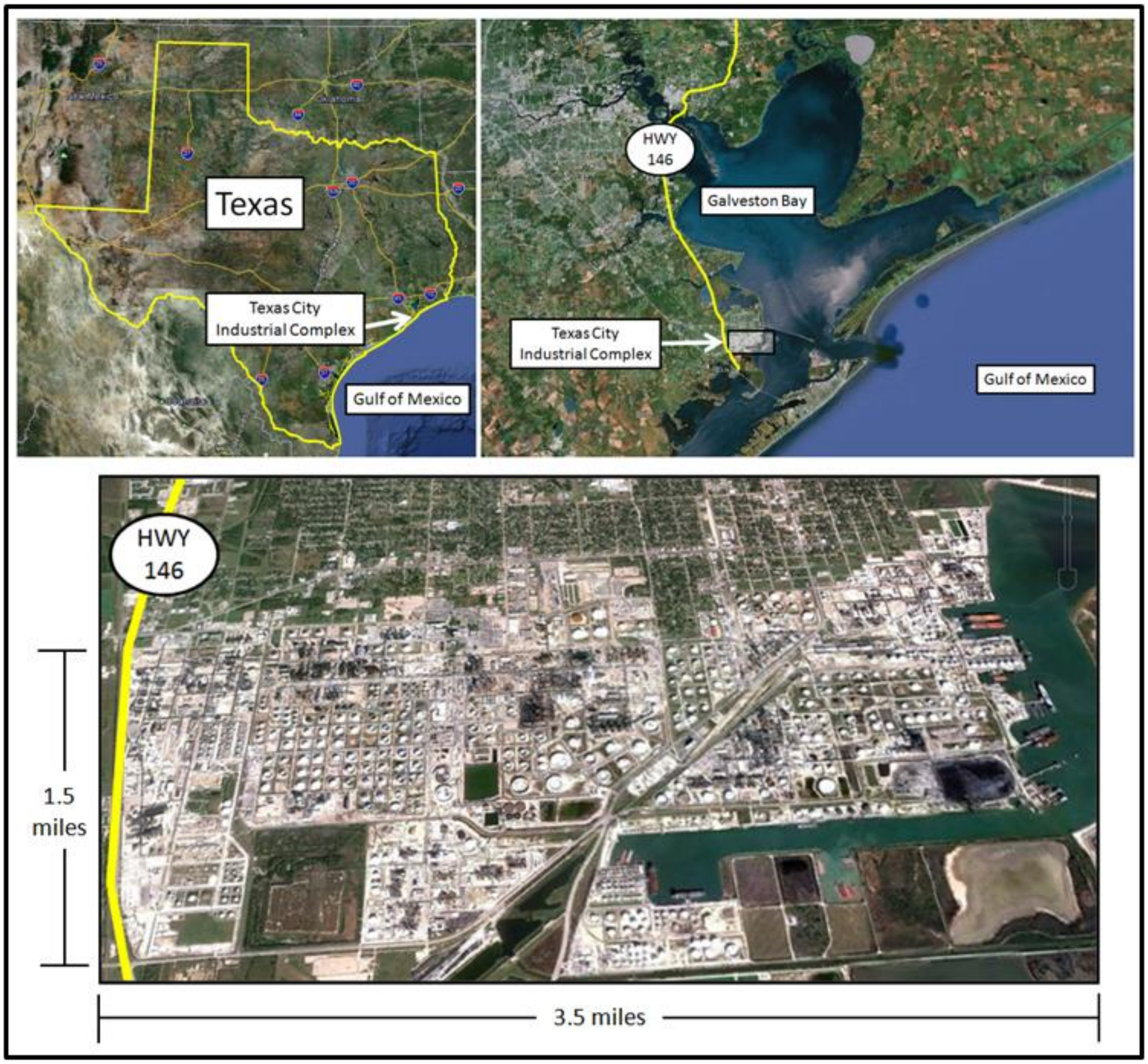

Figure 5. The Texas City Industrial Complex is located south of Houston between Highway 146 and Galveston Bay in Texas City, Texas. Maps taken from Google Earth.

Several SOF measurements were taken in Texas City, Texas in 2006, 2009 and 2011. When the winds were blowing from the east to the west, the SOF van drove multiple times down Highway 146 . A baseline is taken before and after approaching the industrial complex and is subtracted from the total to remove contributions from other sources. Figure 6 has a plot of what the measured alkanes were compared to what is expected on the basis of the 2006 annual inventory.

Emissions Measurements Using SOF at Texas City's Industrial Complex

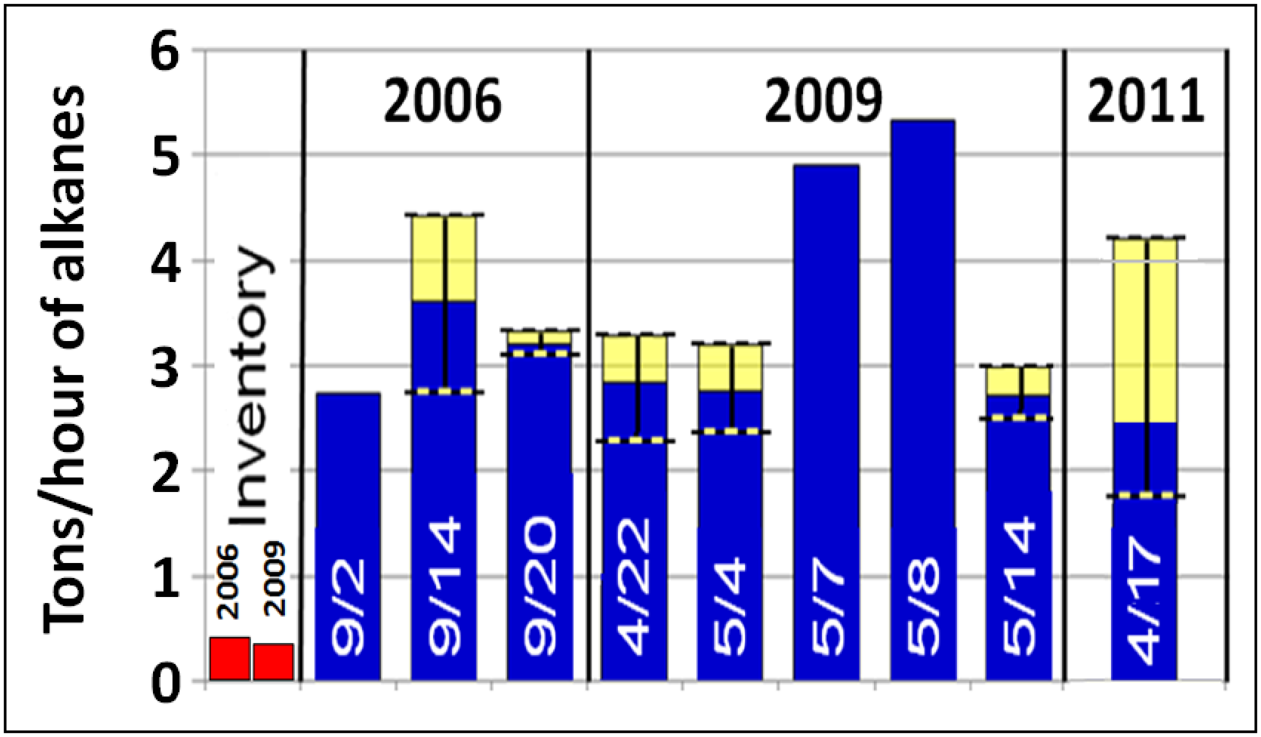

Figure 6. SOF measurements taken in Texas City, Texas in 2006, 2009 and 2011 by Chalmers University, Sweden.[17, 18, 19]

The results show that every time the SOF measurements are taken the alkane emissions are close to 5000 lbs/hr or more, or at least 6 times higher than expected based on the conversion of annually reported emissions to hourly values. Some of the highest values, e.g. May 7 and 8, 2009, were higher than normal due to a flaring event at a refinery; however, repeated passes down Highway 146 provide the same results. The variation in measurement never shows that emissions are lower than the 2006 or the 2009 inventory. These measurements are taken during the day time, in months from March through September, when operations may have more on-going activities which can generate a high bias; however, this does not account for underestimations of a factor of at least 6 or more. This pattern observed with SOF is consistent with other SOF and DIAL results.

DIAL and SOF Technologies

The two technologies that Sweden has used in place of emissions estimates are DIAL and SOF.

DIAL technology was developed in the 1960's and first applied to measure pollutants at petrochemical facilities by National Physical Laboratories in the U.K. DIAL makes use of pulsed lasers which reflect off particles in the air to provide information about pollutant concentration. Typically these lasers are scanned across a vertical plane perpendicular to the wind direction. A two dimensional concentration map is constructed and used in conjunction with the perpendicular wind speed to measure the mass flux of emissions. A depiction of this is provided in the graphic from Spectrasyne, a DIAL vendor, in Figure 7.

How Differential Absorption LIDAR Works

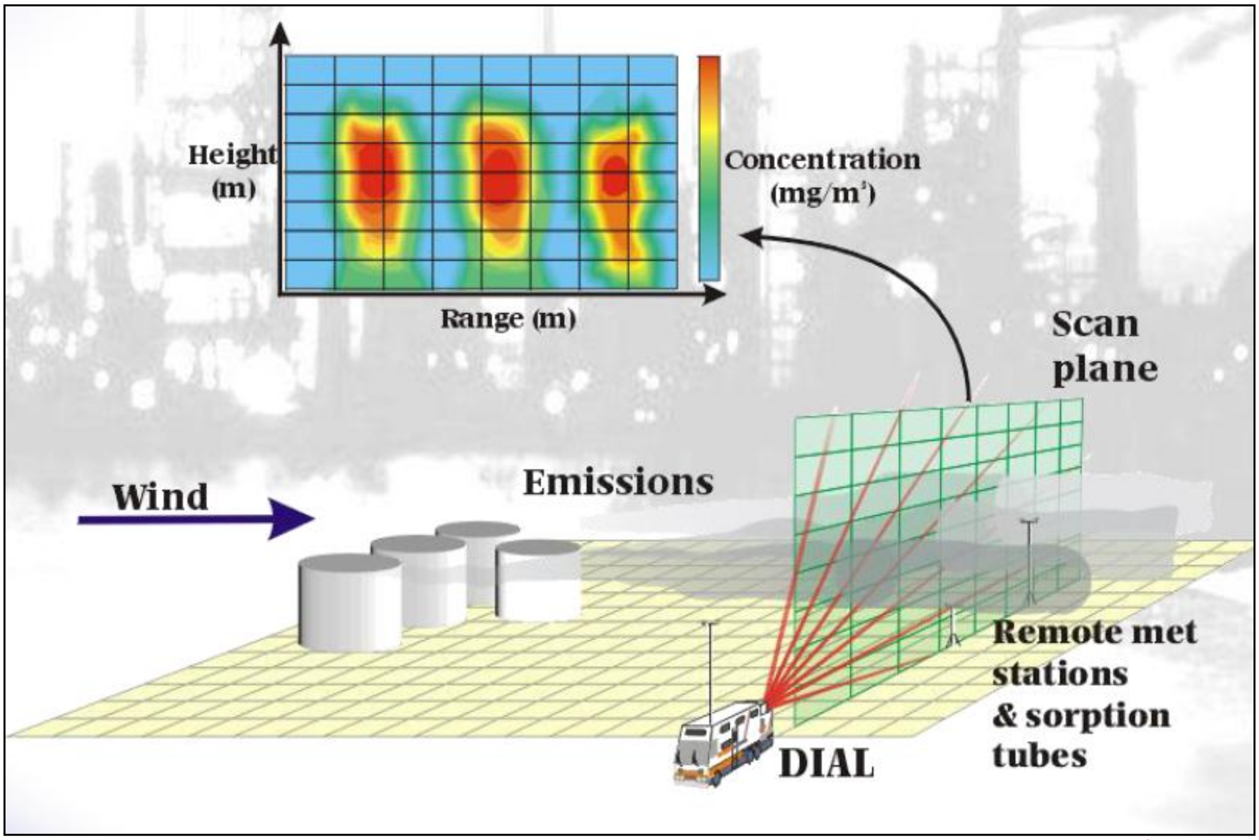

Figure 7. A diagram of a DIAL unit measuring tank emissions, provided by Spectrasyne.[10]

Since all DIAL vendors who take measurements at petrochemical facilities currently are based in the U.K., the cost of the measurement techniques can easily exceed $500,000 for a one-month study. Estimates for the construction of a new DIAL system are typically at least $2-3 million.

SOF technology was developed by Johan Mellqvist at Chalmers University of Technology in Sweden. SOF uses a Fourier Transform Infrared (FTIR) spectrometer mounted in a passenger van. The van has a hole cut in the roof where a solar tracker is mounted designed to always point towards the sun and draw light to the spectrometer. As the van drives past a petrochemical complex on a sunny day, it gathers information about the concentration of chemical species. Readings are also taken before and after approaching the petrochemical facilities to subtract out background signals. When this information is combined with wind direction and speed, it can also be used to calculate the mass flux of pollutants. The cartoon/picture in Figure 8 was provided by Johan Mellqvist.

Illustration of Solar Occultation Flux

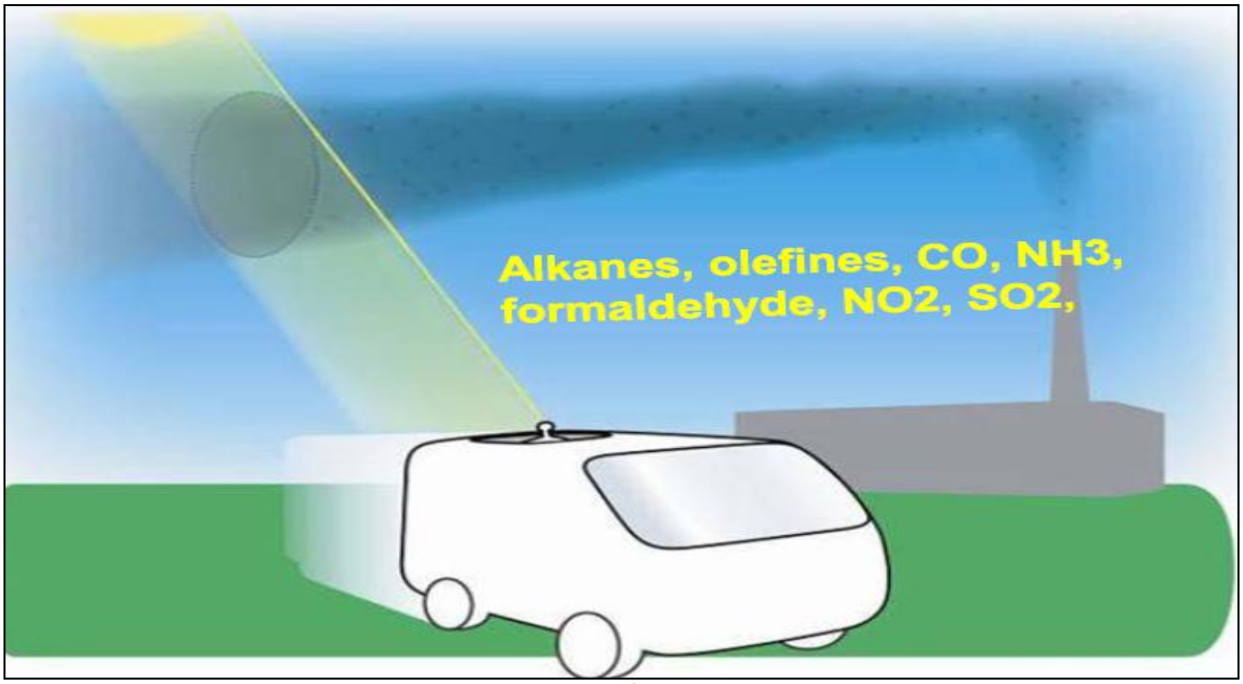

Figure 8. A depiction of the SOF measurement.[42]

The SOF technique requires direct sunlight and cannot measure some compounds like benzene directly. However, the developers use other measurement techniques to address these issues. In this case, the method is currently only available from the developers who are in Sweden. The cost for a one-month study can be less than $200,000. A new SOF unit may be built for $400,000 -$500,000; however, issues relating to purchasing or licensing the SOF technology must be resolved with the developer.

More details regarding the DIAL and SOF technologies and applications can be found in documents by David Picard[43] and Steve Ramsey and Jennifer Keane.[44]

Locating Emissions Inside Refineries

DIAL and SOF were developed not merely to quantify emissions, but also to locate where the emissions problems are inside a refinery. When DIAL and SOF studies are performed, they are set up in specific locations of the refinery. Typically the DIAL studies look at each of the following areas separately: process units, storage tanks, waste water treatment systems, delayed cokers, and flares. SOF is less expensive and easier to set up than DIAL, but it is not possible to take SOF in all the locations that DIAL can go. Both DIAL and SOF studies indicate that about 50% of all VOC emissions come from storage tanks. In fact DIAL vendors have used the ability to detect emissions at tanks to sell their services. They find that a large portion of the emissions come from relatively few tanks. As a result, in order to fix the problem, DIAL will focus on maintenance and repair of a few tanks rather than a large, indiscriminate maintenance program for all tanks. Figure 9 shows where emissions have typically been found inside refineries.

Typical Distribution of a Refinery VOC Emissions Based on DIAL Measurements

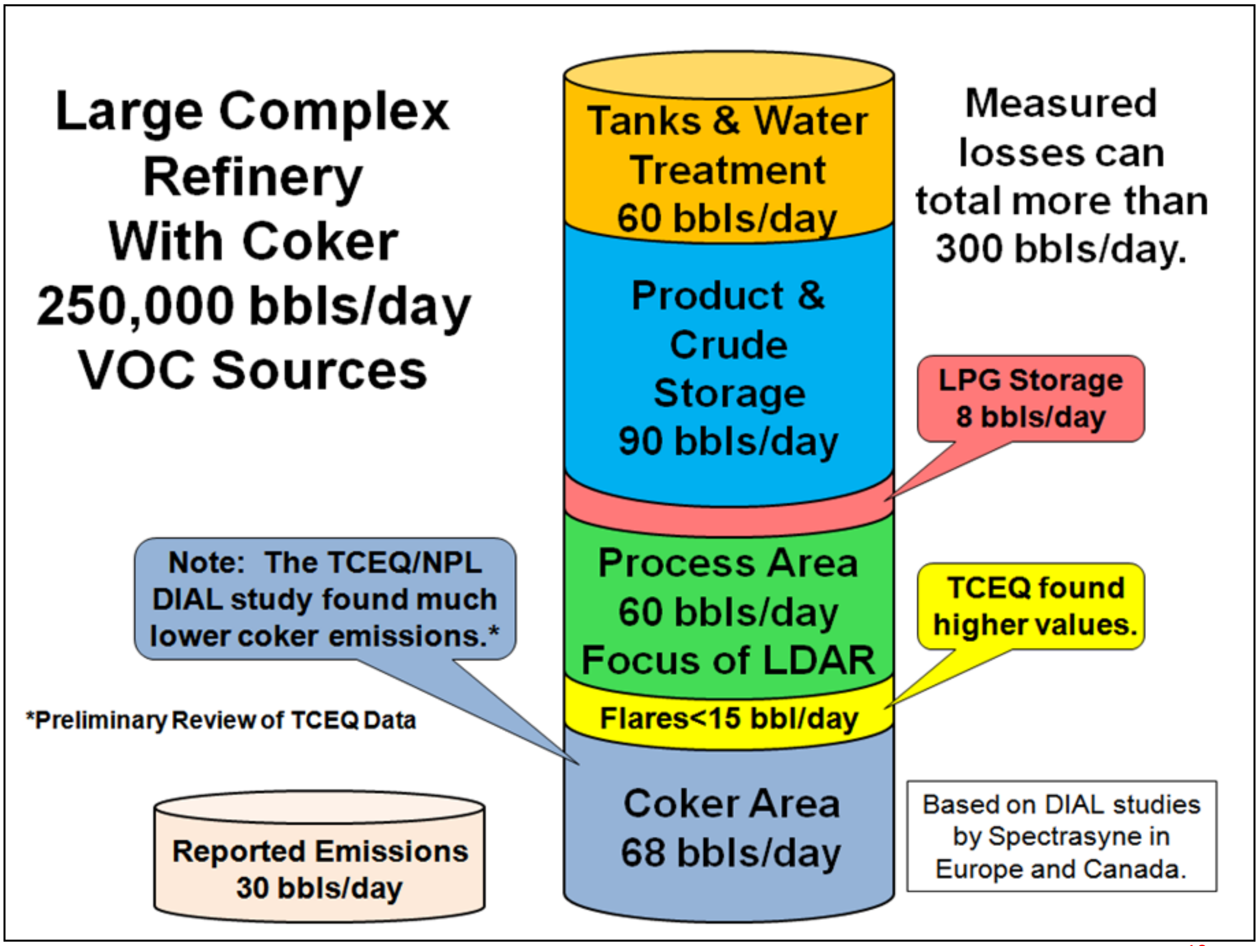

Figure 9. Typical location of emissions from a refinery based on a report from Spectrasyne[10] who has completed over 30 refinery studies and results from a TCEQ/NPL study.[15] Results will vary significantly depending on refinery design. Information compiled and organized in this drawing by Alex Cuclis.[40]

It has become common practice in DIAL and SOF studies to have an IR Camera available, as well, to help locate the exact emission source location. This has been helpful in some cases; however, DIAL and SOF each have detection limits that are 2-3 orders of magnitude more sensitive than the IR Camera. As a result, there are times that the IR Camera does not see emissions identified by DIAL and SOF.

TCEQ is currently working on improving tank emission estimates based on measurements from DIAL taken near tanks in Texas City, Texas. These calculations will be more accurate according to TCEQ because they will eliminate the use of default values for tank parameters among other concerns.[45] However, this process does not address the major concern identified by DIAL and

SOF vendors- the assumption that the tanks are "well-maintained". Emissions can be substantially higher in poorly maintained or damaged tanks.

Verification of DIAL and SOF Results

DIAL is self-calibrating by nature in that it looks at two different wavelengths and subtracts off the wavelength which is not absorbing, providing a continuous zeroing function. This is a major advantage of DIAL. In addition, DIAL vendors typically take a fraction of the light beam while sampling in the field and send it through a cylinder filled with a known concentration of gas so they can automatically correct for other issues such as changes in laser beam intensity. More detail is provided by National Physical Laboratories (NPL) in their report to the Texas Commission on Environmental Quality (TCEQ) for work performed in Texas City, Texas in 2007.[15]

Industry typically does not argue the accuracy of DIAL measurements, but are concerned about extrapolating the results to annual emissions. When Brenda Shine at the EPA performed a review of literature on DIAL in 2007, she wrote the following:

"The general experience reported in the literature from the application of DIAL technology to quantify atmospheric emissions at petroleum refineries has been that, despite some limitations, DIAL is able to accurately quantify the amount of VOC emissions occurring at the time of measurement." [7]

"As noted above, the American Petroleum Institute (API) prepared a letter taking issue with the comparison of the DIAL Canada study and the API estimation methods (AP-42 equations).[46] Additionally, Rob Ferry, API Consultant prepared a critique of the use of the DIAL method for quantifying VOC emissions. Generally, API's objection to the Canadian reports is not that the DIAL measurements are incorrect, but that they were taken over an inadequate time period to allow them to be used for calculating a yearly emission number. Secondly, they note that higher than expected emissions generally occur when there are extraordinary conditions or when emission sources are not properly operated or maintained."[7]

Typically, when a DIAL study is performed in the U.S., comparisons are made between the DIAL results and open path FTIR and/or Differential Optical Absorbance Spectroscopy (DOAS). However, due to concerns about proprietary data and liabilities, access to the instruments while they are inside the facilities has been very limited. In addition, the largest error associated with both DIAL and SOF is generally ascribed to the mass flux values which cannot be obtained with traditional open path techniques. The largest error in mass flux is the wind speeds which can vary in time and altitude; hence, selecting the proper values to calculate flux can be difficult, so measuring the wind speed in or near the measurement plane is important. Finally, collecting data upwind and downwind simultaneously is generally not possible. In order to account for process and other changes, attempts are made to take samples on different days at different times and take an average value. It is also crucial that all the relevant process data is collected during the measurement period.

Open, double-blind cross-comparisons of DIAL and SOF instruments that include released gases as tracers are needed. These kinds of comparisons should occur several times to ensure the measurements maintain their accuracy and to identify improvements over time. However, these kinds of tests are costly and difficult because of concerns about fines, penalties and potential litigation.

There are a number of ways in which the DIAL and SOF techniques have been validated over time in Europe and Canada. One that has already been alluded to in Figure 1 is that DIAL has been used to identify large leaks. When those leaks have been addressed and DIAL is brought back, the measurements indicate that significant problems have been resolved. The same is true for SOF.

A listing of the known studies which have been done in the past to verify DIAL and SOF results is provided below.

1. The Shell DIAL team, led by Harold Walmsley, published a number of studies in the literature regarding their DIAL work. In 1997 Walmsley and Simon O'Connor published a report identifying the factors influencing the sensitivity and accuracy of DIAL.[47] Walmsley and O'Connor's paper published in 1998 "describes the procedures used for measurement, emission rate calculation and data display, and then discusses the factors that affect the accuracy and detection limits of column content and emission rate measurements under practical operating conditions."[48] Walmsley published several other articles about DIAL in scientific journals and at conferences.

2. In November 1993 the European counterpart to the American Petroleum Institute (API), CONCAWE, compared Spectrasyne's DIAL measurements during a barge loading to the measurements obtained by measuring the flow rate of the gasoline being loaded which was equivalent to the volumetric flow rate of the vapors coming out of the barge vent. Samples were also taken of the vent emissions and analyzed for hydrocarbons. DIAL estimated emissions of 390 kg, which was about 12% less than the 435 kg calculated from the vent and gas analysis.[49] CONCAWE mentions DIAL in a 1999 report on best available technologies for refineries. DIAL is recognized as a valid technique, although expensive, and concerns are raised about attempts to extrapolate results for annual averages.[50] In a 2003 report CONCAWE states, "Any attempt by a permitting authority to impose DIAL as BAT would be inappropriate. The record of the TWG meetings will confirm that the debate on this led to the consensus that DIAL is one of the options (not **the** Best Available Technology option) of monitoring VOC."[51]

   In another report published in 2008, CONCAWE describes the details of the DIAL and SOF techniques including discussions about accuracy. Although the report is favorable to both techniques in many regards, CONCAWE states that there is a potential problem with overestimating emissions using DIAL and the accuracy of SOF is +/- 30% - 50%.[52] The DIAL and SOF vendors would disagree, saying they have evidence from verification studies (including the one from CONCAWE in 1993) demonstrating accuracies better than 15-30%. However, the vendors and many air quality modelers, note that even a +/- 50% accuracy is useful when there is evidence that the reported emissions may have a low bias that is off by a factor of 10 (1000%) or more.

3. DIAL was part of the Remote Optical Sensor Evaluation (ROSE) in Europe from August 2001 – July 2004. The purpose of ROSE was described as follows:
   "The primary objectives of ROSE are the determination of "Best Practice" and performance standards, along with a firm theoretical foundation on which to support such statements… …It addresses the problems associated with system and certification approval by inter-comparing five diverse commercially available (remote optical measurement techniques) under both field and laboratory conditions. The measurement techniques included differential optical absorption spectroscopy (DOAS), tunable diode laser spectroscopy (TDLAS), Fourier transform infrared and ultraviolet spectroscopy (FTIR and FTUV), as well as differential optical absorption light detection and ranging spectroscopy (DIAL-LIDAR)."[53]

   The report, "Recommendations for best practise for open path instrumentation," was developed from the review of the results of ROSE. It provides a description of several validations of the Spectrasyne DIAL, indicating that all methods of comparison showed agreement within 15% as well as results from the ROSE comparisons.[54]

4. In Alberta, Canada Allan Chambers has verified DIAL measurements using emissions from a sulfur stack and from a turbine exhaust. Concentrations were measured with in-situ analytical instruments and combined with flow rate to determine the mass flux. Measurements were made of SO2 from the incinerator and of NO from the gas turbine. The observed differences were 11% and 1% respectively.[55]

5. A comparison was obtained of the SOF instrument during the TexAQS II campaign in the Houston area with NOAA aircraft. Both SOF and the NOAA aircraft took ethene samples in Mont Belvieu near the Houston Ship Channel, and both independently found that emissions were roughly an order of magnitude higher than the reported values. However, there were differences of up to a factor of two between the SOF and NOAA readings. This was first described in the Final Rapid Science Synthesis report for TexAQS II[6] and later included as part of a peer reviewed scientific journal.[39]

6. The SOF technique has been tested in Europe using sulfur hexafluoride (SF6) as a tracer gas. Two studies in 2005 showed the SOF measurements were within 10-30% of known amounts of SF6 tracer released.[56, 57] In another study which used a different measurement technique combining flow rate and VOC concentrations, found the SOF measurement differed only 1% (SOF overestimated) in one trial involving bitumen cisterns and by 26% (SOF underestimated) in a separate trial involving storage tanks.[58]

7. NPL performed several tests during the DIAL study in Texas City in 2007. Comparisons were made with an open path Differential Optical Absorbance Spectrometer (DOAS) on

benzene emissions. TCEQ reports that the DIAL measurements were 0.3 - 26 parts per billion (ppb) which matched well with DOAS which obtained a range of 4.9 - 12.7 ppb. In a blind test, standard concentrations of propane, pentane and benzene were placed in gas cells and measured by the NPL DIAL system. The DIAL measurement generally fell within the expected ranges of what the standard values were.[15]

8. In the DIAL study performed at the Tonawanda Coke facility in Tonawanda, ENVIRON found that their open path FTIR measurements of benzene were "generally consistent"[59] with both the EPA DOAS measurements[60] and NPL's DIAL findings.[61]

Although verifications of DIAL have not been published by the National Institute of Science and Technology (NIST), they are currently developing a DIAL system. The NIST DIAL system will focus on improving the measurements of greenhouse gases. [62]

Key Events Related to Underestimated Emissions at Refineries

1978

- NPL and BP begin an IR DIAL development project with the intent of measuring the mass flux rate of hydrocarbon leaks at petrochemical facilities.

1982

- NPL and BP use UV DIAL to measure sulfur dioxide emissions at refineries.

1987

- NPL and BP deploy a jointly funded mobile IR DIAL system.

- BP builds a commercial UV-vis-IR DIAL system.

1985

- EPA Study by Keith Bauges, "On average predicted NMOC concentrations in Houston are 5.9 times lower than observed values."[1]

1988

- BP and NPL begin joint DIAL tests at refineries and chemical plants in Europe.

- A refinery in Sweden finds that emissions are 20 times higher than reported values based on DIAL results. The largest leak was on a distillation column – which had not been previously identified.

1989

- When DIAL returned to the Swedish refinery, after the leak on the distillation column was repaired, emissions were still 15 times higher than the reported values.

1990

- BP starts operating a commercial DIAL system in-house.

1992

- Sweden compels 5 refineries to measure VOCs without specifying a measurement technique.

- NPL and Siemens build an IR DIAL for Shell and British Gas.

- Spectrasyne, consisting of the former BP employees that developed the DIAL system, purchased UV-vis-IR DIAL from BP management.

1993

- NPL finds that tank emissions are on average 2.7 times higher than predicted by AP-42 estimates. Measurements at individual tanks differ from AP-42 estimates by factors ranging from 0.8 to 4.0.[25]

1994

- Shell and British Gas begin using their IR DIAL system in house.

1995

- Sweden requires that DIAL be used at 5 different refineries. The previous requirement to "measure" VOCs led refiners to try using FTIR, DOAS and other methods, none of which provided information that indicated it was an accurate measurement of mass emissions of VOCs that the Swedish regulators desired.

- CONCAWE reports that DIAL measures accurately by taking measurements from a barge. The actual mass flux of VOCs is determined by calculating the known volume being displaced according to the loading flow rate and analyzing the composition of vent samples. DIAL results agree within 12%.[49]

- CONCAWE reports that DIAL can verify emissions estimates from tanks from AP-42. This seems to imply that DIAL is the standard – the tool that can be used to find actual emissions. Concerns have been raised that the tanks used in this study were in near perfect condition, and not indicative of the tanks in the field.[49]

1997

- Chalmers University of Technology in Sweden builds a mobile SOF unit.[63]

2000

- Texas Air Quality Study (TexAQS 2000) results indicate measured emissions of ethene and propene are either 3-10 times or 10-100 times reported.[2, 3, 6]

- Shell DIAL team reports that tank emissions are 4.6 times higher on average than what would be predicted by AP-42. A few tanks are responsible for most of the emissions.[24]

2001

- A Shell brochure, "Industry and Atmosphere: A Ten-Point Guide for Managers", advocates using DIAL over standard techniques (similar to AP-42) for determining VOC emissions. The brochure states that "If you're not measuring, you're just guessing."[12]

2002

- SOF begins testing at Swedish refineries. SOF and DIAL have never been compared side-by-side; however the SOF results obtained were similar to the results found by previous DIAL studies at the same refineries.[63]

- Shell ceases DIAL operation.

2003

- Spectrasyne performs first DIAL study in North America measuring sulfur dioxide, VOCs, methane, benzene and oxides of nitrogen fluxes.[64]

- DIAL presentation at EPA NARSTO conference in Austin. The underestimate emissions identified in TexAQS of an order of magnitude, was very similar to the findings by Europeans using DIAL in petrochemical facilities. Cuclis described how DIAL could be used to systematically identify emission sources from different portions of petrochemical plants, something that was not capable with the aircraft flights or other methods used in Texas at the time.[65]

2005

- Shell sells IR DIAL system to NPL. Shell could not find enough customers to continue their DIAL service.

- Canadian DIAL study at a refinery finds VOCs to be about 15 times higher than reported. This draws attention from U.S. regulators and refiners.[13, 14]

- Sweden to refiners: Pick either DIAL or SOF annually. SOF has been verified as a technique in Sweden. Local regulators require that measurements be taken annually, but the refiners can choose to use either SOF or DIAL. All refiners choose SOF because it is much cheaper. Norway has had a similar policy since the 1990s, but all operators choose DIAL as it gives more detailed information. In Norway, VOCs, methane and benzene measurements are also required.

2006

- EPA Inspector General says that EPA can improve emission factors development and management.[34]

- Texas Air Quality Study II (TexAQS II), as indicated previously, found that emissions of ethene and propene dropped by 40% since 2000, however the measured amounts were still 10 - 40 times higher than expected on the basis of the inventory. Reported NOx from facilities with CEMS appears to be reasonably accurate.[6]

- NPL upgrades the Shell DIAL system. The Shell system had only an IR laser. NPL installed a new IR laser and the capability of swapping out a UV laser into the system.

- API tells EPA the limits of DIAL for VOC estimates. Karin Ritter and Paula Watkins of API states, “The DIAL technology can be a useful tool for measuring short term emissions, but it is inappropriate to extrapolate from such short term emissions to an estimate of annual emissions.” The letter discusses API’s analysis of the results and conclusions from the DIAL study performed in Canada.[46]

- First U.S. SOF study in Houston. Johan Mellqvist finds that emissions are about an order of magnitude higher for alkanes as well as alkenes.[37, 38]

- EPA holds international workshop featuring the IR Camera, DIAL and SOF.[66]

- Shell Canada uses **“**Spectrasyne, a world leader in environmental surveying, to measure our air emissions. Their laser technology, housed in a mobile unit, allows very accurate measurement of concentrations and emissions rates” – finding measured methane emissions matched reported emissions in tar sands applications.[67]

2007

- EPA writes low bias memo based, in part, on DIAL results.[7]

- TCEQ tests DIAL in Texas City. Finds some high emissions from flares, and some, but not all tanks. Coker emissions at BP in Texas City were not as high as those found at the Canadian refinery coker.[15]

- DIAL finds emissions from a U.S. coker. No report is available. Several DIAL studies of delayed cokers have occurred in Europe since the 1990s.

- Environmental Integrity Project (EIP) tells EPA that the Maximum Achievable Control Technology (MACT) is flawed, citing DIAL findings.[68]

2008

- EPA holds second international conference on remote sensing.[69]

- CONCAWE gives a detailed description of DIAL and SOF in a report.[52]

- Mayor of Houston sends EPA a request for correction under the data quality act, based on numerous reports citing underestimated emissions from petrochemical facilities, including DIAL studies.[70]

2009

- EPA responds to the Mayor of Houston, citing the following items:
  a. EPA plans to fund a DIAL study in the Houston area.
  b. EPA had already begun development of a protocol book to include DIAL and other remote sensing techniques.
  c. EPA plans to evaluate the DIAL study in Texas City and other remote sensing studies.
  d. EPA began development of a comprehensive protocol for estimating VOC and air toxic emissions from petrochemical facilities.
  e. EPA is developing an Electronic Reporting Tool (ERT) to improve data quality. [71]

- A bill (House Bill 4581) was proposed by Scott Hochberg, Texas State Representative, District 137, to the Texas House to build a DIAL, but the bill did not get out of committee. Testimony was given by Alex Cuclis of the Houston Advanced Research Center, Russell Nettles of the Texas Commission on Environmental Quality and Matthew Tejada from Galveston-Houston Association for Smog Prevention (GHASP).[72]

- A presentation on DIAL and SOF was given at the NPRA Environmental Conference in Denver, Colorado by ENVIRON and Baker Botts.[42]

- A detailed QAPP was developed for the DIAL study performed at the Shell Deer Park complex.[16]

- The Texas State Implementation Plan (SIP) submitted to EPA includes a discussion about the value and limits of SOF and DIAL. For example they allow for the monitoring of components at elevated sources such as flares, vents and storage tanks. However, "These technologies normally measure a path length average concentration or number of molecules and as such do not provide a specific concentration at any given point. Therefore, results can be difficult to compare with standards or guideline concentrations."[73]

- Second SOF study in the Houston area. Emissions are generally lower than found in the 2006 SOF study, but still 5 - 10 times higher than expected based on the emission inventories.[38]

- Canadian Petroleum Products Institute (CPPI) advises companies not to use DIAL until after results from studies by TCEQ in Texas City and the City of Houston at Shell Deer Park.[74] Canada had already performed the first three DIAL studies in North America on a well test flare in 2003,[64] and oil and gas facility in 2004[55,75] and at an oil refinery in 2005.[13, 14]

2010

- EIP comments on EPA's protocol for estimating refinery emissions, citing DIAL.[32]

- DIAL study at Shell Deer Park. [76]

- BP Consent decree with EPA requires a DIAL study be performed on the environmental biodegradation unit (EBU) by April 1, 2010. No significant emissions were found.[77]

- Tonawanda Coke DIAL study. EPA found high benzene emissions near the Tonawanda facility and required Tonawanda to conduct a DIAL study. The results confirmed that the facility was a significant source of benzene emissions and ordered corrective actions. Details of the exchanges with EPA, Tonawanda, the test results and communications with the surrounding community can be found at this link: http://www.epa.gov/region02/capp/TCC/april2011update.pdf

- EPA performs a critical review of the TCEQ DIAL study.[78]

- Johan Mellqvist, et. al. publish results finding that emissions of ethene and propene are more than 10 times reported values in the Journal of Geophysical Research. [79]

2011

- SOF study is repeated in the Houston area. Emissions are similar to those seen in 2009. High emissions are also observed in test performed in Port Arthur and Longview for the first time.[19]

- EPA completes "EPA Handbook: Optical Remote Sensing for Measurement and Monitoring of Emissions Flux."[80]

- TCEQ uses SOF to measure VOCs in the Houston Ship Channel, Texas City, Beaumont/Port Arthur and Longview. Measured emissions are consistently high, ranging from 3 – 15 times reported values.[20]

- TCEQ uses SOF to quantify emissions from Barnett Shale oil and gas operations in Barnett Shale.[20]

2012

- Alberta, Canada has contracted with the University of Utah to construct a DIAL to measure greenhouse gases.[81]

Finding a Forward Plan in the United States

In the early 1990's in Sweden, when it became clear to local regulators that the VOC emissions from refineries were far greater than they were reporting, they stopped believing in the estimating methods that are based on EPA AP-42 approaches. As mentioned previously, they required that emissions be reported based on measurements in 1992, and in 1995 they required the measurements be taken with DIAL. By the early 2000's the Swedish regulators determined that either DIAL or SOF were acceptable.

The refiners in Sweden were amenable to these changes in large part because the Swedish regulators did not enforce any VOC limits. Instead each time the measurements were performed the regulators reviewed the results with the refiners and discussed what action plan should be put in place to ensure that emissions would be lower during the next scheduled measurement.

There are several barriers to attempting the Swedish approach at refineries in the United States.

1. The permitting system is much more rigorous in the U.S. Even if a new, more accurate means of measuring emissions was universally accepted to be better than the current estimating techniques, the process of revising State Implementation Plan (SIP) permitting and compliance testing would take years.
2. The U.S. regulatory agencies do not have the option of providing an unspecified VOC limit at refineries due to regulatory requirements and the pressures to achieve attainment for ozone in many locations across the U.S.
3. Even if the U.S. regulatory agencies did find a way to give allowances for more VOC emissions during a transitional phase from EPA AP-42 methods to measurements with DIAL and/or SOF, environmental and community groups would potentially sue the agencies, the refiners or both.
4. The refiners are likely to argue that when they obtained their permits and when they have reported their emissions they followed EPA approve estimating techniques. By requiring them to use measurements like DIAL and/or SOF, they are being asked to use a different measuring system from the one that was agreed to when they first estimated their costs to build and operate the refinery. They will argue that higher VOC allowanced must be made in order for this change to measurements to be fair. (Environmental groups will likely provide counter arguments, saying refiners have not kept their facilities "well-maintained", they should always be using the best technologies to perform measurements, and make corrections accordingly, etc.).

For these reasons a different approach may be necessary in the U.S. One proposed scenario, designed with the intent of substantially reducing emissions and improving the accuracy of emissions inventories without creating any fines or penalties for industry, goes like this:

Over 25% of U.S. refining capacity and literally hundreds of chemical plants and storage tank facilities exist on the upper Texas Gulf Coast between Port Arthur and Corpus Christi, Texas (Figure 10). If an independent company operating out of Houston built and operated a licensed SOF van it could be used to quantify mass VOC emissions from more than 200 petrochemical plants and storage tank facilities in a few months. Additionally it could compare those mass VOC emissions with the expected emissions based on reported values and metrological conditions. A deviation report could be developed based on where the largest differences are observed between reported and measured emissions.

Texas Gulf Coast

Figure 10. More than 25% of U.S. refining capacity lies on the Texas Gulf Coast between Port Arthur and Corpus Christi. Map taken from Google Earth.

A regulatory agency could contract the SOF company to produce deviation reports each quarter. After analyzing and verifying the reports, the agency could then contact facilities upwind of the highest emissions and ask them to examine their operations for problems. In those areas in which the deviations persist, the regulatory agency may ask the facilities to consider a contract with the SOF or DIAL company to take measurements inside their property lines. Other monitoring techniques such as UV-DOAS, FTIR, the IR Camera and hand-held toxic vapor analyzers may be used to help isolate the problem.

By taking measurements in an on-going fashion, it will help to alleviate the concerns industry frequently raises regarding the extrapolation of short term measurements for annual emissions estimates. These measurements would also help identify the best performers, who could be recognized by the environmental agency. Finally, over time these measurements may also be used to identify patterns in either type of facilities, process units or even specific equipment that has higher emission rates than are expected based on existing estimating techniques.

This process of measuring emissions will help to identify and reduce the biggest problems and will help establish the actual emission rates that modelers need for input to the complex air quality models. The end result will be lower emissions and better ozone reduction policies, since the accuracy of the models will be improved.

Conclusions

The main points cited in this paper are as follows:

1. Models need to be verified with measurements, and the AP-42 VOC emission estimates perform very poorly compared to measurements at petrochemical facilities.
2. Underestimating VOC emissions impairs the ability of regulatory authorities to identify effective strategies for reducing emissions of air toxic compounds and ozone precursors.
3. Tweaking or otherwise adjusting the calculations or emission factors will only improve the estimates for equipment that is “well-maintained”, but will not solve the problem.
4. The problem of poorly maintained or unmaintained equipment needs to be addressed, as well as other issues such as an operator who accidentally leaves a valve open. Measurements are the only want to identify, locate and resolve these issues.
5. Total vapor analyzers or “sniffers” used as part of leak detection and repair programs help, but they are not used universally around the plant, have limited ability to identify all the potential leaks inside a facility and only measure one point in space. LDAR sniffers lead to the reduction of many emissions, but they do not eliminate them.
6. The IR Camera helps, but does not solve all problems. The response is different for different compounds and the sensitivity is 2-3 orders of magnitude less than techniques such as DIAL and SOF.
7. If you are not measuring you are just guessing. This is a direct quote from a Shell brochure which describes the problems of using techniques like AP-42 for estimating emissions and standard LDAR programs.
8. Fixing VOC emission inventories should not be delayed on the hope of some newer technology. There will always be new technologies. SOF and DIAL have a demonstrated track record of improving the understanding of actual emissions. SOF can be applied economically, and DIAL, although more expensive, can be used for some targeted applications or close in work as needed.
9. Industry will always be concerned about a new monitoring technique because it could lead to more lawsuits, more regulations, more maintenance and in some cases major equipment redesign. These concerns need to be addressed in a thoughtful way.
10. A workgroup made up of various stakeholders from industry, regulatory agencies, the environmental community and scientists to identify the benefits and disincentives for using DIAL and SOF for VOCs and greenhouse gases (GHGs). Consideration should be given to the impacts on permits, ozone reduction models, VOC taxes, the price of carbon, competitive disadvantages, etc.
11. We need to find ways to make refineries greener and more profitable. If the greenest refineries go bankrupt, everyone loses.

Industry representatives rarely comment openly about DIAL and SOF technologies, the findings regarding emissions inventory errors or proposals to fix these problems. Some way must be found for all of these issued to be discussed and argued by industry, regulatory agencies and environmentalists openly.

DIAL was developed and applied for use at refineries during the 1980's when Ronald Reagan was president and MS DOS was the dominate software operating system. DIAL is not new technology. For more than 2 decades it has been applied at facilities in different parts of the world, identifying substantial leaks that the owner operators were not aware of. This technique can identify problem areas in a facility (storage tanks, waste water treatment, flares, process units and others) and help to isolate the location of the leaks. It can help identify whether or not adequate maintenance has been performed and provides an auditing function of emission inventories that is not possible with "sniffers", IR Cameras or other analytical techniques.

SOF was developed in the late 1990's, but has been proven many times in several different countries. In Sweden it has been used annually since 2005 at each of 5 refineries to determine the emission inventories. It is generally much cheaper and easier to employ than DIAL; however, there are measurement trade-offs that must be taken into consideration.

There are substantial challenges to employing DIAL and SOF as the basis for emissions inventories in the U.S., but there are ways to create information about the location of measured emissions and providing opportunities to address them through cooperative efforts with the agencies, industry and community groups.

Ultimately we need to find a way to create a system where the greenest refineries are also the most profitable refineries.

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