

# Technical Memorandum

**TO:** EPA Docket No. EPA-HQ-OAR-2003-0146

**FROM:** Brenda Shine, EPA/SPPD

**DATE:** July 27, 2007

**SUBJECT:** Potential Low Bias of Reported VOC Emissions from the Petroleum Refining Industry

## **I. Purpose**

Measurement studies performed in Europe over the past two decades and more recently in Canada, using differential absorption light detection and ranging systems (DIAL), indicate that emissions of VOC from refineries are significantly higher (10 to 20 times) than amounts estimated using standard techniques. This bias is apparently caused by omission or mischaracterization of significant emission sources, and the same quantification issues could exist in this country. Because our emission inventories are currently being used to draw conclusions regarding ozone control strategies and residual risk from air toxics, and because current emission levels from this industry are significant, we are in critical need of a confirming analysis of VOC and air toxic emissions estimates from US petroleum refineries. This document provides the basis for our hypothesis that there is a systematic low bias in reported emissions of VOC and air toxics from petroleum refineries.

## **II. Background**

### **A. DIAL and the European and Canadian Experience**

The most recent experience on a refinery in Canada was conducted for the Alberta Research Council by Spectrasyne Ltd, UK.<sup>1</sup> When the short term DIAL measurements were extrapolated to annual emissions, the annual emission rate of C2+ hydrocarbons (VOC) was 9970 tons per year, 15 times higher than the 670 ton per year estimate the facility had provided in their National Pollutant Release Inventory (NPRI). Similarly, benzene emissions were 18 times higher than the reported NPRI estimates (40.1 TPY versus 2.2 tpy). Major contributors were the coker unit, product tanks, and cooling towers.

DIAL measurement studies have been conducted for a number of years in Europe, with Sweden having the most experience using DIAL to measure refinery emissions. As a result, Sweden has required remote sensing at refineries since the late 1980's and by 1996, all refineries were required to use DIAL measurements every 2-3 years. Initially, measurements indicated emissions of 10 to 20 times the calculated values, but after this long-term experience with the measurements, facilities now experience actual emission levels of 3 to 10 times higher than what estimation methods provide.<sup>2</sup>

July 27, 2007

Page 2

In Britain, the National Physical Laboratory (NPL) developed the source and detection systems for the infrared DIAL in the mid to late 1980s. A joint project with British Petroleum commercialized the system in the late 1980s and spun off Spectrasyne Ltd. to provide the service and equipment. Both entities currently offer measurement capabilities at this time.

In general, the NPL notes that estimated emissions for a facility are lower than DIAL measurements, often due to facilities not including sources in their inventories or from malfunctioning equipment that is not normally monitored. For refineries, the NPL has found that emissions vary from 0.07 weight percent (wt %) to 0.3 wt % of crude throughput, with the average values at about 0.2 wt % of throughput.<sup>3</sup> Similarly, emissions, as a percentage of crude throughput from the Alberta refinery study represented 0.21 wt % of refinery throughput, while fugitive emissions accounted for 0.17 wt % of throughput.<sup>4</sup>

In addition to experience in Britain and Sweden, DIAL measurements on refineries have been conducted in a number of European countries, including Belgium, the Czech Republic, and Germany, and Germany also has formal standards pertaining to the application of DIAL.<sup>5</sup>

## B. Validation of DIAL

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.<sup>6</sup> There have been a number of validation studies conducted by the NPL and other groups. During an NPL verification project, the DIAL measurements for a known methane release were within +/- 10 percent of the actual values. In other experiments, the DIAL measurements were within +/- 12 percent of the actual value of an aliphatic hydrocarbon plume and within +/-15% of a toluene plume. Wind speed measurements, used to calculate flux, were cited as responsible for a significant part of the error.<sup>7</sup> Spectrasyne Ltd also conducted a number of mass emission correlation exercises between DIAL and other measurement techniques, including SF6 tracer gas releases and controlled releases of methane from a point source and a marine tanker vent. In all these exercises, the maximum divergence from the DIAL measurements recorded was 15%.<sup>8</sup> Finally, we note that CONCAWE, the European Oil industry's organization for environment, health, and safety conducted a study to compare DIAL measurements with flux measurements and AP-42 equations. The study showed that DIAL measurements were slightly lower than CONCAWE's flux measurements, and that the AP-42 equations compared well on an hourly basis.<sup>9</sup> The study was cited by the American Petroleum Institute in response to the Alberta Research Council Report addressing storage tank emission estimates as measured by DIAL and the validity of the AP-42 equations. The details of the modeling assumptions were provided for the measurement period; hourly average wind speed was used to estimate emissions for a given hour and these were the results compared. However, the AP-42 equations are set up to calculate yearly emissions using annual average inputs. Similar to the concern voiced by API discussed below regarding the extrapolation of hourly measurements to yearly estimates, this detailed modeling assessment does not necessarily indicate that the annual average inputs to the AP-42 equations yield good annual average estimates as asserted by the API letter.

July 27, 2007

Page 3

### C. Industry's Response

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).<sup>10</sup> 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.

## **III. VOC and Air Toxic Emissions from US Refineries and Bias**

### A. Current US Refinery Estimates and How They Compare to Measured Emissions

The 2002 national emissions inventory (NEI) indicates that there are 128,000 tons per year of VOC reported, and approximately 1000 tons per year of benzene reported emitted from approximately 150 refineries operating in the US. The total crude capacity of these refineries is approximately 16 MM bbls/day; assuming actual throughput is close to capacity, and using a crude specific gravity of .85, the average VOC emission factor is approximately .015 wt % of crude throughput, or about 4 times lower than the lowest emissions factor measured for VOC by the NPL DIAL system and an order of magnitude lower than the average NPL factor and the Alberta Research Council factor of 0.2 wt % VOC. The average benzene emission factor is 0.0001 wt%, approximately one-fifth of the 0.0005 wt % factor measured by the Alberta Research Council.

### B. Omissions and Mischaracterizations

As discussed previously, the general consensus from the Canadian and European studies regarding the reasons for a low bias in reporting of emissions from the industry is related to the omission or mischaracterization of significant emission sources, among them:

- exclusion of upsets, malfunctions, startups, and shutdowns from emissions inventories
- omission of sources that are unexpected or not measured, such as leaks in heat exchanger systems or emissions from process sewers
- exclusion of emission events such as tank roof landings
- improper characterization of input parameters for emission models such as not using actual tank or material properties in the AP-42 tank emission estimation methodologies

In general, our U.S. experience indicates that the same characterization and quantification issues exist at our U.S. refineries, as discussed in greater detail below.

#### 1. Exclusion of Upsets, Malfunctions, Startups, and Shutdowns from Emission Inventories

July 27, 2007

Page 4

Our current National Emissions Inventory does not identify upsets, startups, or shutdowns as emission events, nor is the data specifically requested from the reporters (the states). In trying to understand the order of magnitude of SSM and upsets in relation to routine operations, we reviewed the emission inventory data from the Texas Commission on Environmental Quality (TCEQ) for the 2004 reporting year. This data set contains emissions data for 30 of the approximately 150 U.S. refineries and accounts for over 25% of the US refining capacity. Additionally, the TCEQ inventory identifies emissions from routine events separately from upsets, startups, and shutdowns, so a comparison of reported emissions is possible. In general, the quantity of emissions reported as non-routine is smaller than the routine emissions. For VOC-unclassified contaminant, emissions of upsets and SSM were 5% of the emissions reported from routine events (578 TPY versus 11,032 TPY). However, for some compounds, such as 1,3-butadiene, emissions from SSM and upsets accounted for as much as 20% of the routine emissions (19.8 TPY versus 91 TPY). Additionally, for certain types of emission points, emissions from startups, shutdowns, and malfunctions make up the majority of the emissions. Finally, we should note that this comparison was done between *reported* upsets and SSM events and *reported* routine emissions. This comparison does not consider events such as upsets and SSM events are not properly characterized and reported to begin with.

## 2. Omission of Sources that are Unexpected or Not Measured

A number of emission events that are not measured or expected are in turn not characterized or reported in our inventories. For example, monitoring of cooling tower water return for VOC is required at some refineries because of state permitting and RACT rules, but not required on refineries at the Federal level (eg., by the Petroleum Refinery MACT standard.) Additionally, speciation of the VOC to individual HAP compounds is typically not required. Because there is no requirement to monitor for leaks, there is, in effect, no systematic mechanism for facility owners and operator to identify, quantify, and control emissions in a timely way. Further, there is potential for high emissions of VOC and HAP from such events. For example, in one release report submitted to the National Response Center in 2006, a facility initially reported potential emissions of 700 lbs/day each of benzene, toluene, and xylene from a reformer unit cooling tower, based on sampling of their cooling water return and the expected composition of the process streams that were being cooled. Upon further analysis and speciation of the cooling water, however, the facility submitted a final report indicating that the exchanger had leaked 800 lbs/day of propane and isobutane for approximately 8 days<sup>11</sup>. It is important to note that this facility monitored the tower and this is the reason why the leak was identified and reported. However, many refineries do not conduct routine cooling tower water monitoring. In a sampling of the refining industry to be used to supplement our emissions inventory for the purpose of risk modeling, we surveyed 22 refineries and requested emissions of benzene. Out of the 22 facilities surveyed, only 3 indicated that they have sampled their cooling towers for leaks. The remaining facilities that did report emissions used AP-42 VOC emission factors for cooling towers and an assumed speciation for benzene. Five facilities simply reported 0.

Another area that could be systematically overlooked in the process of quantifying emissions is the delayed coking process. In the measurements conducted at the Alberta Refinery,

July 27, 2007

Page 5

the coker area contributed to over 15% of the site VOC emissions and 26% of the benzene emissions, and measurements were made when the coke from the delayed coking unit was being drilled (after full water quench) and when it was not. Emissions were high when the coke was being drilled.<sup>12</sup> We note that currently, U.S refiners do not report any fugitive emissions of VOC or benzene from the delayed coking cutting/drilling/coke recovery process.

Similar concerns may be warranted regarding the wastewater treatment emission estimates. A recent Bay Area (BA) AQMD study evaluated collection system emissions for five Bay Area refineries<sup>13</sup>. Utilizing extensive sampling, flow measurements, and detailed TOXCHEM+ modeling, the study showed that 4 of the 5 refineries underestimated the VOC emissions from their wastewater collection system. Two refinery estimates were within a factor of two of the BA AQMD estimate (one higher and one lower), but one refinery had underestimated its emissions by a factor of 40 and another refinery underestimated its emissions by a factor of 1,400. In reviewing the emission estimates reported by the residual risk survey respondents for wastewater collection and treatment systems, we also note surprisingly low estimates for several refineries.

### 3. Exclusion of Emission Events Such as Tank Landings

Floating roofs are an effective method of controlling VOC emissions from storage tanks because they prevent direct contact of the stored liquid with ambient air and limit the creation of a saturated vapor in the headspace of the tank. However, if the liquid level in the tank is lowered to below the surface of the floating roof support legs, the roof will land on its legs, creating a saturated vapor space and limiting the control efficiency of the floating roof. Until recently, there had not been a generally accepted method available to estimate air emissions during the period when a floating roof was landed. TCEQ estimates that underreported landing loss emissions in the Houston-Galveston area alone totaled over 7000 tons of VOC in 2003.<sup>14</sup> EPA recently updated AP-42 to include API methodology for calculating roof landing losses. However, as with cooling tower leak monitoring, there does not appear to be a systematic mechanism on the Federal level for facility owners to identify, quantify, and control these events, although TCEQ has proposed rulemaking to limit the circumstances under which tank landings occur and has issued guidelines for reporting of these events in their inventories.

### 4. Improper Characterization of Parameters in Estimation Methodologies

All of the refinery measurements indicate that storage tanks are a major source of VOC emissions. In the Alberta refinery measurement study, emissions of VOC were 30 times higher and emissions of benzene were 100 times higher than emissions calculated using AP-42 equations. The AP-42 equations require a number of inputs about the tank and material characteristics and storage conditions. Mischaracterization of these inputs could lead to erroneous results and API points out that when the DIAL measurements indicate unexpectedly high emissions, it is either because conditions are on the high side of the range expected (eg., temperature, wind speed, or liquid level), or that conditions may be outside the scope of the method. These conditions include loading of non-stabilized crudes, or maintenance conditions, such as seal failures on floating roof tanks.<sup>15</sup> We agree that both of these concerns are potential

July 27, 2007

Page 6

sources of uncertainty, and that they could explain why the DIAL studies were higher than actual. However, while these uncertainties could explain differences on the order of two or three, it is difficult to explain differences on the order of 30 to 100. Given the magnitude of the difference, either emissions are zero most of the time (when events are not on the high side) or the annual emissions estimates are too low. No direct information is available on the actual condition of the tanks to assess if they were properly modeled. Further, there are numerous examples of tank maintenance issues that, if not characterized properly, would lead to erroneous results. For example, on March 11, 2003, the South Coast Air Quality Management District (SC AQMD) filed suit against BP West Coast Products, LLC. Most of the allegations accuse the company of failing to properly inspect and maintain 26 storage tanks equipped with floating roofs, as required under SC AQMD Rule 463. SC AQMD inspections revealed that more than 80 percent of the tanks had numerous leaks, gaps, torn seals, and other defects that caused excess emissions.<sup>16</sup>

### C. General Indicators of Low Emission Reporting Bias

Evidence regarding the underestimation of VOC emissions has been reported in the past. Of note is the Texas Air Quality Study-2000, where ambient concentrations of highly reactive VOC were found to be 10 to 1000 times higher than were reported in the Texas emission inventory for that year, and the NARSTO Emission Inventory Assessment which necessitated that reported VOC emissions be multiplied six fold before models and ambient measurements correlated. Finally, EPA's Office of Inspector General, in a March 22, 2006 report specifically recognized that the problem of under reporting of VOC emissions from the refining sector and concurred with the Agency shifting towards more direct, continuous monitoring and measurement of emissions from all major sources.

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<sup>1</sup> Alberta Research Council Inc. "Refinery Demonstration of Optical Technologies for Measurement of Fugitive Emissions and for Leak Detection" Prepared for Environment Canada. March 26, 2006.

<sup>2</sup> Executive Summary from Workshop entitled: "VOC Fugitive Losses: New Monitors, Emission Losses, and Potential Policy Gaps"

<sup>3</sup> USEPA. NPL Presentation, Appendix Item C-12. (revised)

<sup>4</sup> Alberta Research Council. Email correspondence from Allan Chambers to Roy Huntley, EPA, 11/01/06.

<sup>5</sup> Clearstone Engineering Ltd., Technical Report: A Review of Experiences Using DIAL Technology to Quantify Atmospheric Emissions at Petroleum Refineries. Prepared for Environment Canada. August 10, 2006.

<sup>6</sup> Clearstone Engineering Ltd.

<sup>7</sup> USEPA, p.10.

<sup>8</sup> Alberta Research Council, Appendix A, p.2.

<sup>9</sup> CONCAWE. VOC emissions from external floating roof tanks; comparison of remote measurements by laser with calculation methods. January 1995. Available at:

[http://www.concawe.org/DocShareNoFrame/docs/4/FDBIMDBCBLFOEJGCKIPLJPJJVEVC7191P3PDBK9DW3GK/CEnet/docs/DLS/Rpt\\_95-52-2004-01744-01-E.pdf](http://www.concawe.org/DocShareNoFrame/docs/4/FDBIMDBCBLFOEJGCKIPLJPJJVEVC7191P3PDBK9DW3GK/CEnet/docs/DLS/Rpt_95-52-2004-01744-01-E.pdf)

<sup>10</sup> Letter from Paula Watkins, API, to Mike Ciolek, U.S. EPA. August 9, 2006.

<sup>11</sup> NRC Incident Report 801202, Jun 19, 2006; TCEQ Incident Final Report 77203

<sup>12</sup> USEPA, page 5.

July 27, 2007

Page 7

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<sup>13</sup> Breen, D. 2004. *Proposed Revision of Regulation 8, Rule 8: Wastewater Collection Systems*. Staff Report. Prepared for Bay Area Air Quality Management District, San Francisco, CA. March 17, 2004.

<sup>14</sup> TCEQ Docket No. 2006-1804-RUL. Memorandum on Commission Approval for Proposed Rulemaking

<sup>15</sup> API, page 4.

<sup>16</sup> Whetzel, C, 2003. “South Coast Air District Seeks \$319 For Violations at Los Angeles Area Refinery.” The Bureau of National Affairs, Inc., Washington D.C