Monitoring and Laboratory Division
Vapor Recovery and Fuel Transfer Branch
Vapor Recovery Regulatory Development Section

Project Number VR 11-11

Report No. VR-OP-G1

Overpressure Study

Technical Support Document: Gasoline Sampling and Analysis to Investigate the Effect of Reid Vapor Pressure on Vapor Recovery System Overpressure (VR-OP-G1)

December 1, 2017

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I. Executive Summary

The California Air Resources Board (CARB) staff is investigating how positive pressure in the ullage space of underground storage tanks (UST) can affect the performance of gasoline vapor recovery systems. On several occasions in 2013 and 2014, in Station Diagnostics (ISD) ullage space pressure data was collected from approximately 400 gasoline dispensing facilities (GDF). This data indicates that the frequency of ISD overpressure alarms increases dramatically in winter months when the volatility of gasoline is not limited by CARB regulations.

To investigate the influence of winter fuel volatility, CARB personnel periodically sampled gasoline from GDFs located in both Northern and Southern California. These samples were collected and analyzed for Reid Vapor Pressure (RVP) per CARB adopted test procedures. Analysis of RVP data and ISD system overpressure alarm history shows that there is a strong correlation between the volatility of gasoline and the frequency of overpressure alarms triggered by the ISD system.

II. Introduction and Background

The RVP of stored gasoline is a measure of the gasoline volatility. The more volatile the fuel the more gasoline will evaporate into a volume of unsaturated air before equilibrium is reached and evaporation subsides. The higher the volatility of the fuel, the more vapor volume it takes to saturate a given volume of air resulting in higher evaporation rates and higher UST pressures. CARB regulations limit gasoline RVP to a nominal value of 7 pounds per square inch gauge (psig) during summer months[1]. Figure 1 shows a map with the geographic regions and the corresponding dates during which the CARB RVP regulation applies to gasoline sold at GDFs. The fuel shipped from gasoline producers (refineries) and importers must comply with the RVP limit one month earlier then the dates shown on the map. All California refineries are located in either Region A (Southern California) or Region C (Bay Area and Central Valley). Furthermore, no fuel pipelines cross the Tehachapi Mountain Range that separates the two regions. As a result, almost all gasoline delivered to Southern California GDFs after March 1 and to Northern California GDFs after April 1 meets the RVP 7 requirement. During winter months gasoline RVP varies on a biweekly schedule between 7 and 15 psig and is regulated by the applicable ASTM fuel specification[2]. ASTM includes different specifications for four geographic regions in California, but in fact, there are only two different fuels produced. These fuels meet the specification of the two geographic regions (Los Angeles and Bay Area) where the State's largest oil refineries are located.

While the RVP can vary from 7 to 15 psig over the course of a year, the true vapor pressure is a function of RVP and is affected by fuel temperature. Data from two Sacramento area GDFs showed the TVP ranged between 3.3 to 4.8 psi during summer months (April to October) and 3.5 to 6.9 psi during winter months (November to March).

Figures 2 and 3 show plots of RVP, TVP, and fuel temperature versus the date for samples collected between October 2009 and February 2011 for a moderate and high throughput GDFs[1] in the Sacramento area. These graphs showed that RVP and TVP trends are not dependent on throughput. As expected, the average TVP tracks RVP except that it is more sensitive to temperature.

II. Methodology

RVP samples were collected on a weekly schedule from late October through mid-April in Southern California and from late October through mid-May in Northern California. Samples were collected for regular grade and premium grade gasolines. Fuel sampling was conducted by staff of the CARB Enforcement Division following the procedures referenced in Title 13 of the California Code of Regulations[3]. Samples were analyzed by CARB Emissions Compliance Automotive Regulations and Science Division staff following CARB Standard Operating Procedure MV-FUEL-125 [4]

RVP samples were collected and analyzed for nine different GDFs in the Sacramento Valley Air Basin. Six GDFs were sampled from October 2009 to May 2015. During the summer of 2010 these GDFs were also monitored on a monthly basis during June, July, August and September when CARB regulations limit the RVP of gasoline. A seventh GDF was added to this group in January 2011. Two of the Northern California GDFs were only sampled from October 2009 through April 2010. During the winter of 2012-2013 fuel sampling was only conducted at Northern California GDFs from February 21 to April 3.

Seven GDFs in Southern California were also sampled for various periods. One in the San Diego Air Basin was sampled from October 2009 to April 2015. During the summer of 2010 this GDF was also monitored on a monthly basis during June, July, August and September when CARB regulations limit the RVP of gasoline. One GDF in South Coast Air Basin was sampled from October 2009 to April 2010. Three additional GDFs in the San Diego Air Basin and two additional GDFs in the South Coast Air Basin were sampled from October 2013 to April 2015.

[1] ISD is not required on low throughput GDFs.

III. Results

All data have been entered into a spreadsheet and are available in Appendix 1. For illustrative purpose, Figures 4 and 5 show the regular grade gasoline RVP data for GDFs sampled in Northern and Southern California, respectively. The data show how RVP increases beginning on November 1 and peaks in mid-January before decreasing back to RVP 7 soon after the refineries begin shipping summer fuel on March 1 in Southern California and on April 1 in Northern California. (Note: The data for the two Northern California GDFs that were only sampled from October 2009 to April 2010 are not shown in the graph.)

Figure 1 - RVP Control Regions and Dates

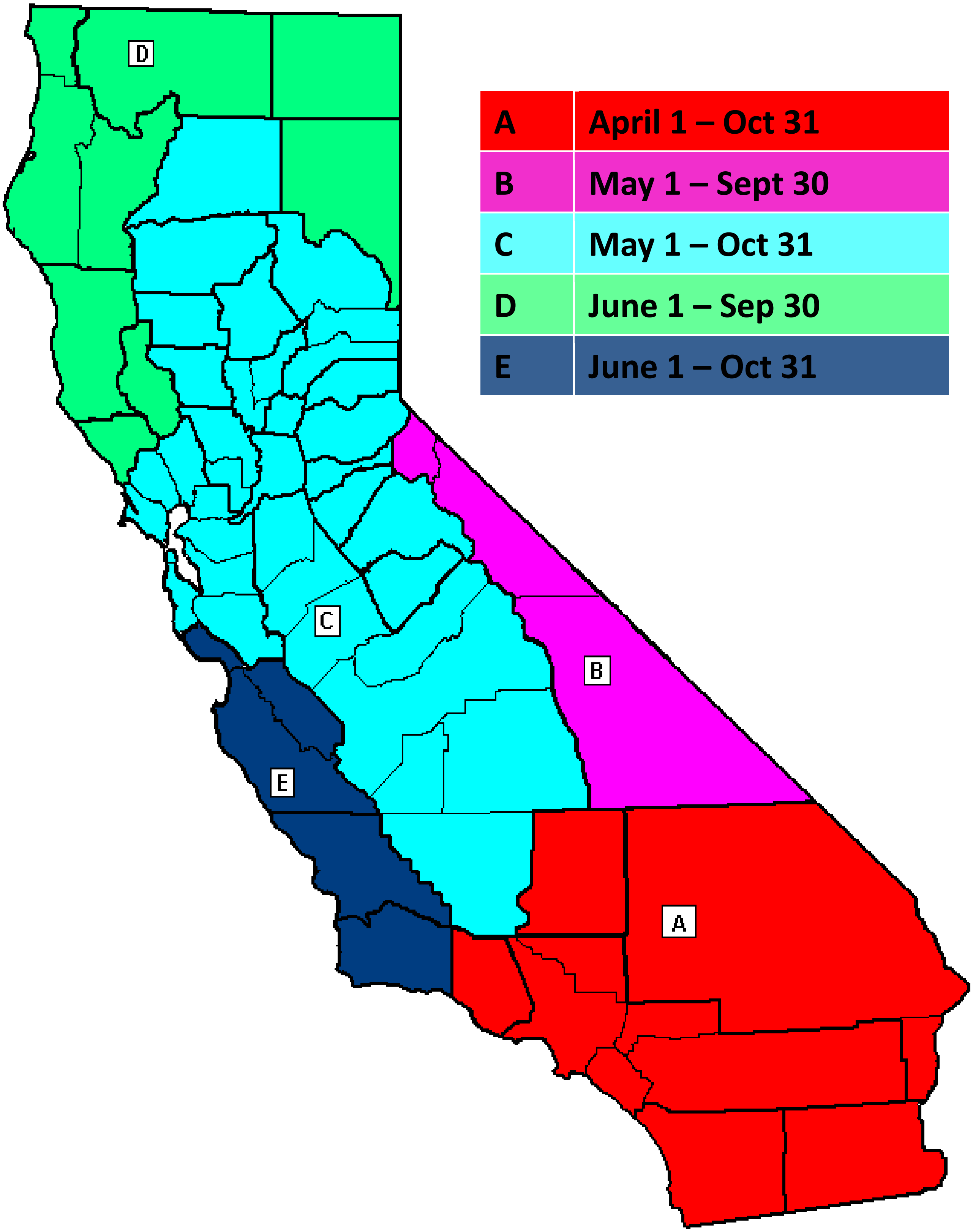
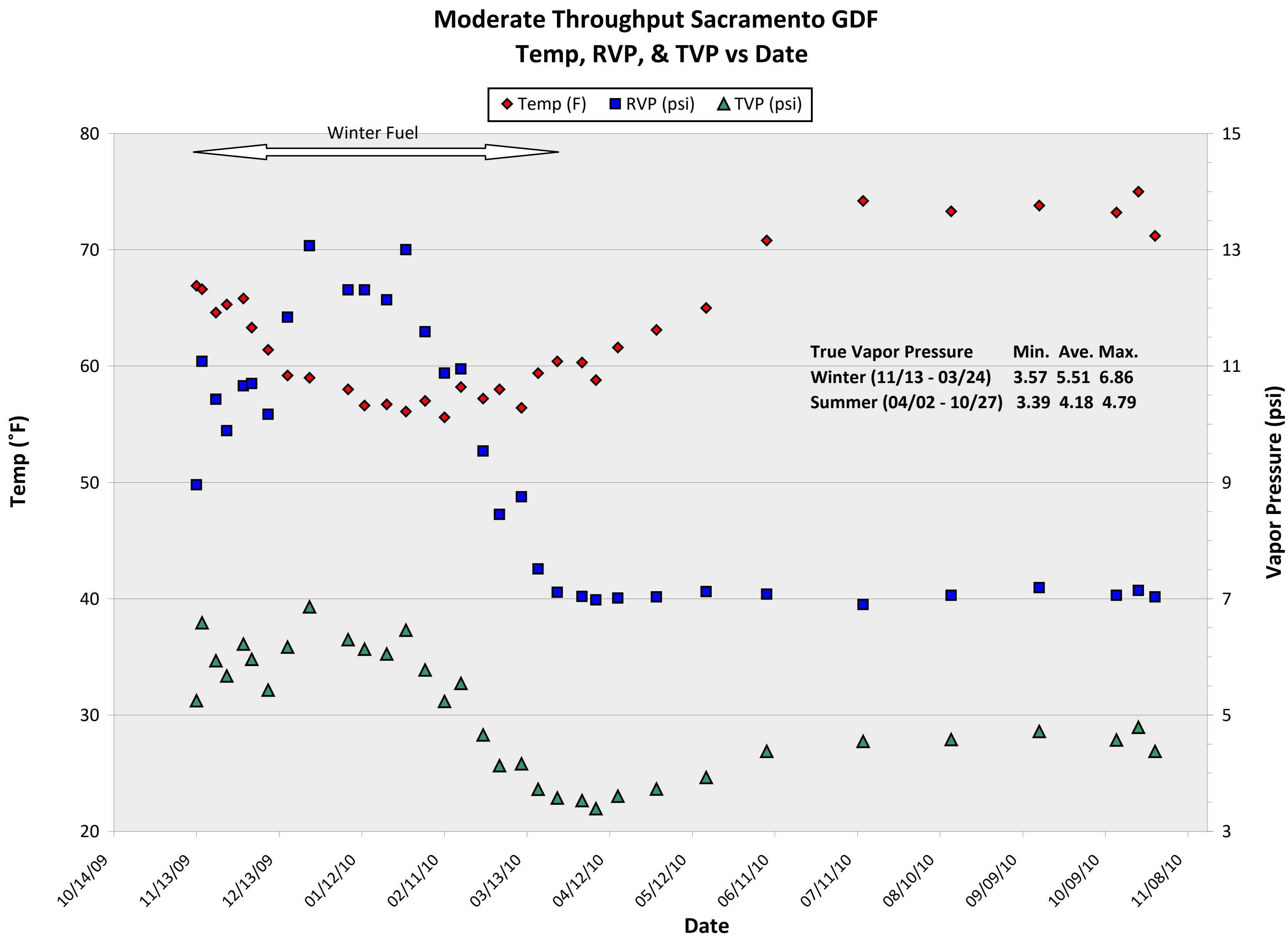


Figure 2


Moderate Throughput Sacramento GDF
Temp, RVP, & TVP vs Date
Temp (F)
RVP (psi)
TVP (psi)
Winter Fuel
True Vapor Pressure Min. Ave. Max.
Winter (11/13 - 03/24) 3.57 5.51 6.86
Summer (04/02 - 10/27) 3.39 4.18 4.79
Temp (˚F)
Vapor Pressure (psi)
Date
80
70
60
50
40
30
20
15
13
11
9
7
5
3
10/14/09
11/13/09
12/13/09
01/12/10
02/11/10
03/13/10
04/12/10
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06/11/10
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09/09/10
10/09/10
11/08/10

Figure 3

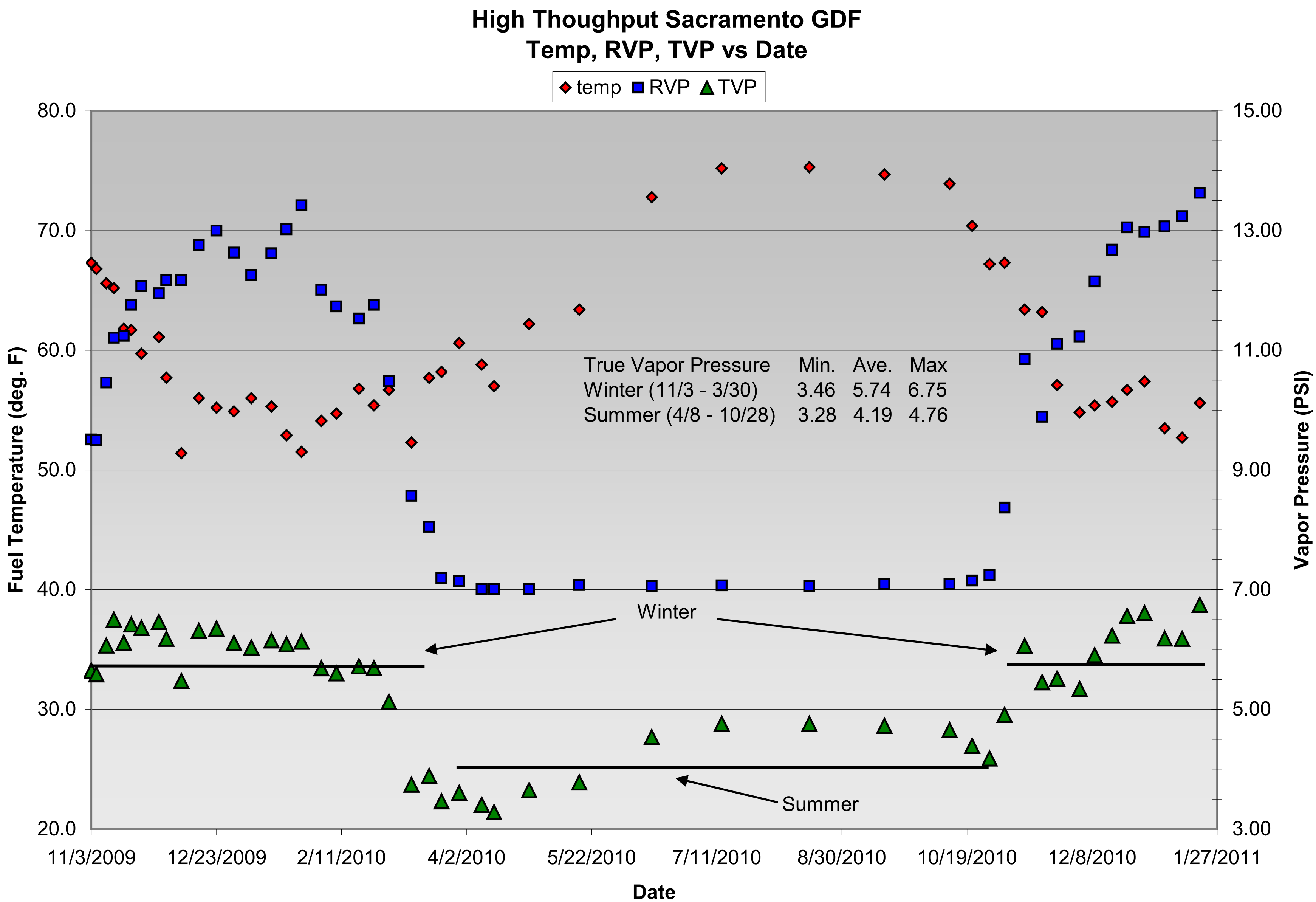
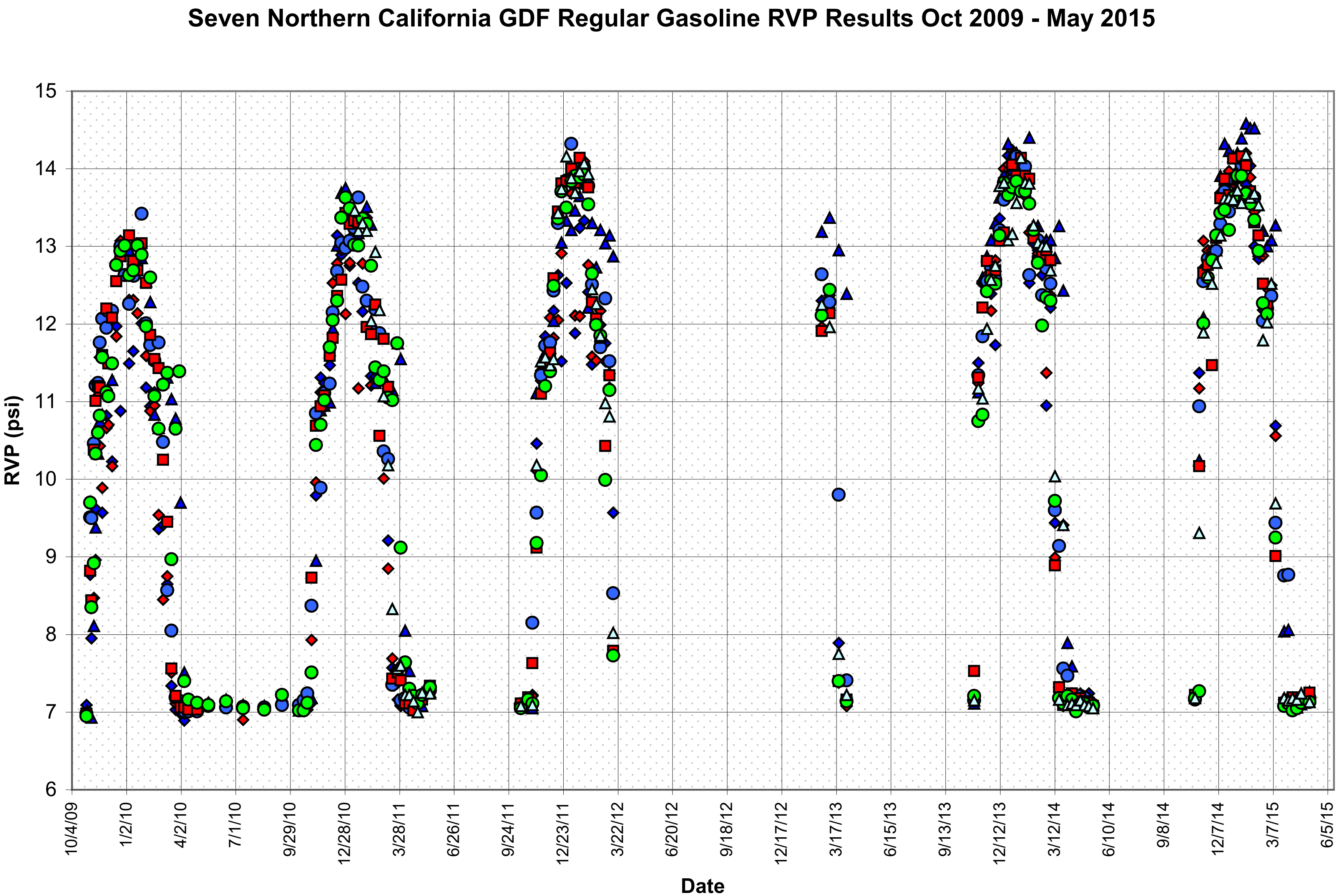

High Thoughput Sacramento GDF
Temp, RVP, TVP vs Date
temp RVP TVP
Fuel Temperature (deg. F)
Vapor Pressure (PSI)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
15.00
13.00
11.00
9.00
7.00
5.00
3.00
True Vapor Pressure Min. Ave. Max
Winter (11/3 - 3/30) 3.46 5.74 6.75
Summer (4/8 - 10/28) 3.28 4.19 4.76
Winter
Summer
11/3/2009
12/23/2009
2/11/2010
4/2/2010
5/22/2010
7/11/2010
8/30/2010
10/19/2010
12/8/2010
1/27/2011
Date

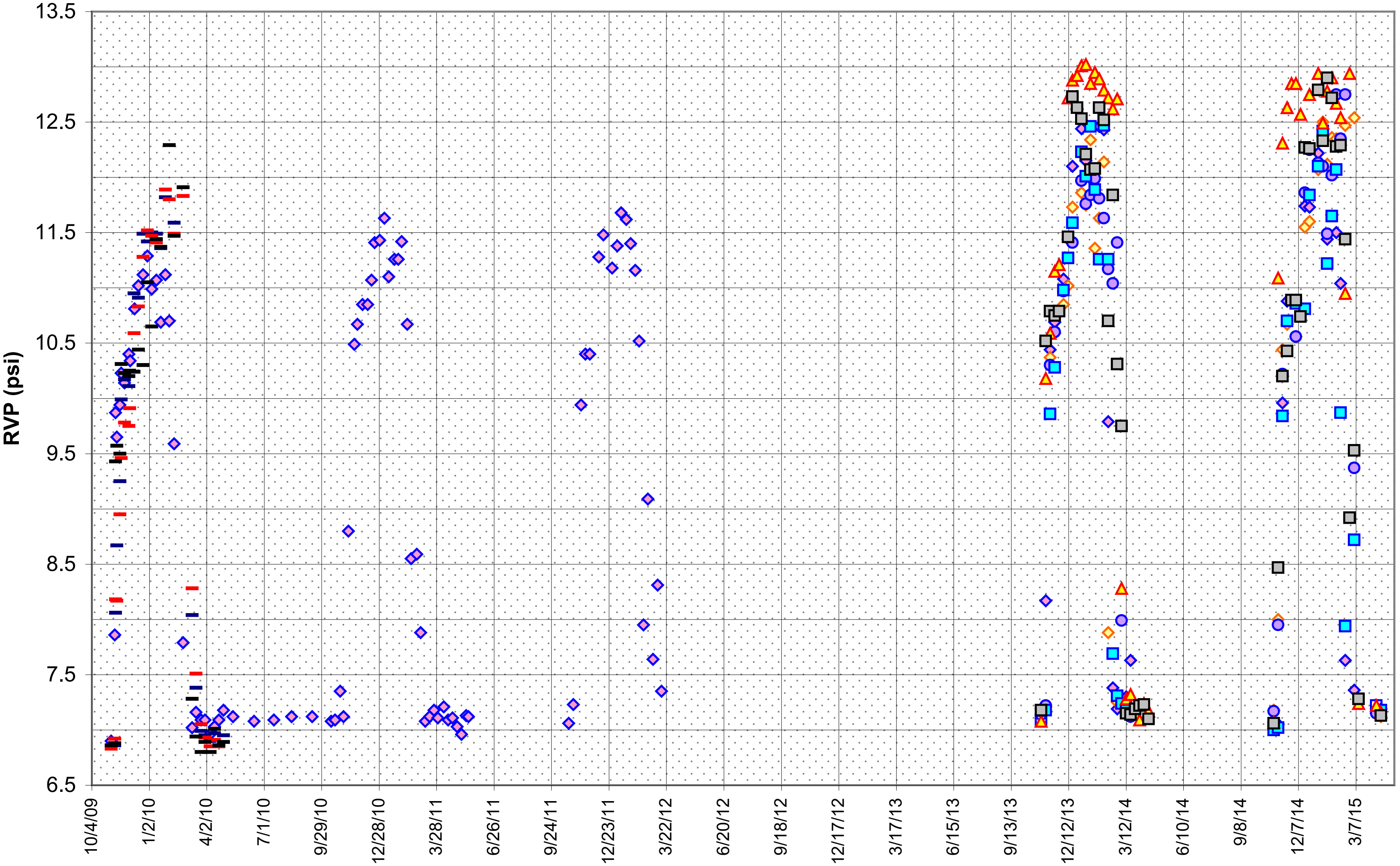
Figure 4



Seven Northern California GDF Regular Gasoline RVP Results Oct 2009 - May 2015
RVP (psi)
15
14
13
12
11
10
9
8
7
6
10/4/09
1/2/10
4/2/10
7/1/10
9/29/10
12/28/10
3/28/11
6/26/11
9/24/11
12/23/11
3/22/12
6/20/12
9/18/12
12/17/12
3/17/13
6/15/13
9/13/13
12/12/13
3/12/14
6/10/14
9/8/14
12/7/14
3/7/15
6/5/15
Date

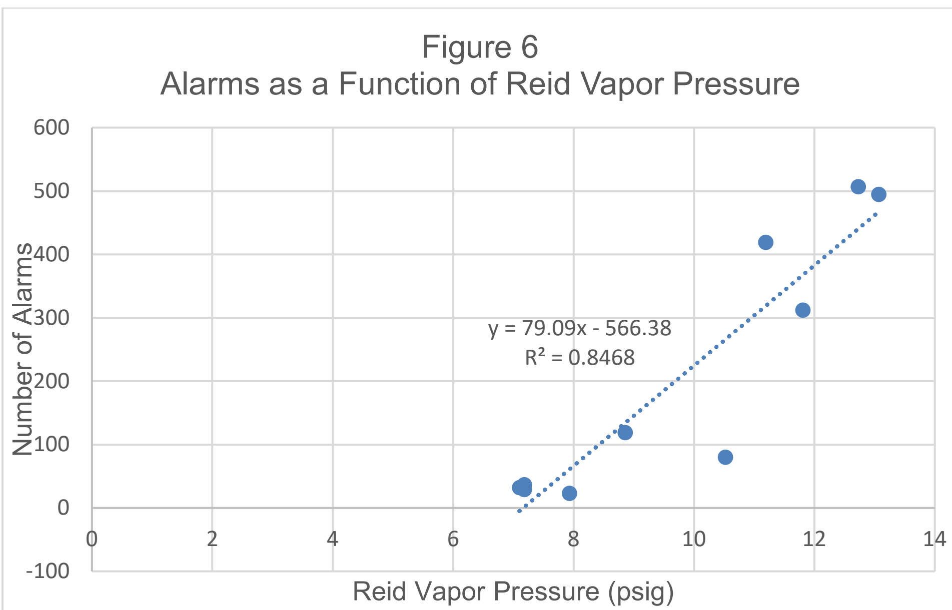
Figure 5

Seven Southern California Regular Gasoline RVP Results Nov 2009 - May 2015



IV. Discussion of Results

The correlation between gasoline volatility and the incidence of overpressure is quite strong. This is supported statistically by a least square regression analysis of average RVP values and number of alarms, where the coefficient of determination (r^2) is 0.85[2] from two independent data set (Figure 6). The incidence of overpressure can be quantified by observing the frequency of ISD overpressure alarms on a monthly basis. CARB staff collected ISD alarm history data covering the period from October 2011 to June 2015. Data were analyzed for 329 GDFs: 210 equipped with assist Phase II vapor recovery systems, and 119 equipped with balance Phase II vapor recovery systems. These GDFs were located in eleven air districts distributed across California. The total number of alarms registered for these GDFs in each month is shown in Figure 7. This graph shows over a four-year period that overpressure alarms are the highest during the months of November through February when the gasoline RVP is the highest. When RVP drops to 7 between April and October, the frequency of alarms is typically reduced to less than 100.



The RVP data reveals that yearly peak RVP increased somewhat over the course of the RVP study period. Figures 8 and 9 illustrate the maximum RVP by date in Northern and Southern California, respectively, value during each year of the study period. The

[2] Based on average monthly RVP values and monthly alarm data collected between March 2013 and May 2014.

selection of maximum RVP values for the charts is to show that values were increasing each year during the study period. The line shown on the chart is the best-fit linear regression of the data. Figure 8 is derived from all the data collected from seven GDFs located in Northern California. The data displayed in Figure 9 are derived from a single Southern California site, as this is the only site in Southern California where RVP was sampled for the full study period. A review of Figure 5 shows that the maximum RVP for a Southern California site was 13.02 psig and occurred on January 8, 2014, at one of the GDFs added to the study in the last two years of sampling.

The vapor growth and potential for OP alarms is much greater when higher fuel RVP and/or temperature lead to higher true vapor pressure. RVP and temperature data for two CARB study GDFs are shown in Figures 2 and 3. TVP is calculated using the equations from USEPA AP-42 [5]. The analysis below demonstrates how air ingestion leads to vapor growth and higher UST pressures for winter fuel compared to summer fuel.

Table 1 presents true vapor pressure from the data shown in Figures 2 and 3. These data illustrate the variation in the true vapor pressure of gasoline in the winter and summer seasons.

Table 1 Variation in True Vapor Pressure at GDF Study Sites

	TVP	Vol % HC at Saturation
Summer – RVP 7		
Low on 4/13/2010	3.3	22.3%
Average	4.2	28.6%
High on 08/13/10	4.8	32.4%
Winter – RVP 8 to 13.6		
Low on 12/03/10	5.3	36.3%
Average	6.1	41.5%
High on 01/20/11	6.8	45.9%

The following relationships show how TVP can affect the pressure in the tank. The analysis assumes constant temperature and ideal gas behavior, and an atmospheric pressure of 14.7 psi. The calculated vapor volume resulting from the saturation of one volume of air shows that the maximum winter season TVP results in 25% more saturated vapor volume than for the maximum summer season TVP.

1) TVP / Pbar = Vol % HC at Saturation
2) Vol % HC at Saturation = vapor volume / vapor volume + air volume

Equation 2 can be rearranged to solve for the vapor volume that will evaporate into 1 volume of air.

3) Vol % HC / (1 – Vol % HC) = Vapor Volume to Saturate 1 volume of Air

The data and equations above are used to calculate the potential volume increase that occurs as ingested air becomes saturated with gasoline vapor.

<u>Summer Fixed RVP 7</u>
Low TVP = 3.28, Vol % = 22.3%: 1 volume of air will become 1.29 volumes of vapor at saturation.
High TVP = 4.76, Vol % = 32.4 %: 1 volume of air will become 1.48 volumes of vapor at saturation.

<u>Winter Variable RVP ~8 to ~ 14.5</u>
Low TVP = 5.34, Vol % = 36.3%: 1 volume of air will become 1.57 volumes of vapor at saturation
High TVP = 6.75, Vol % = 45.9 %: 1 volume of air will become 1.85 volumes of vapor at saturation.

Figure 7
Correlation of RVP and the Frequency of Overpressure Alarms

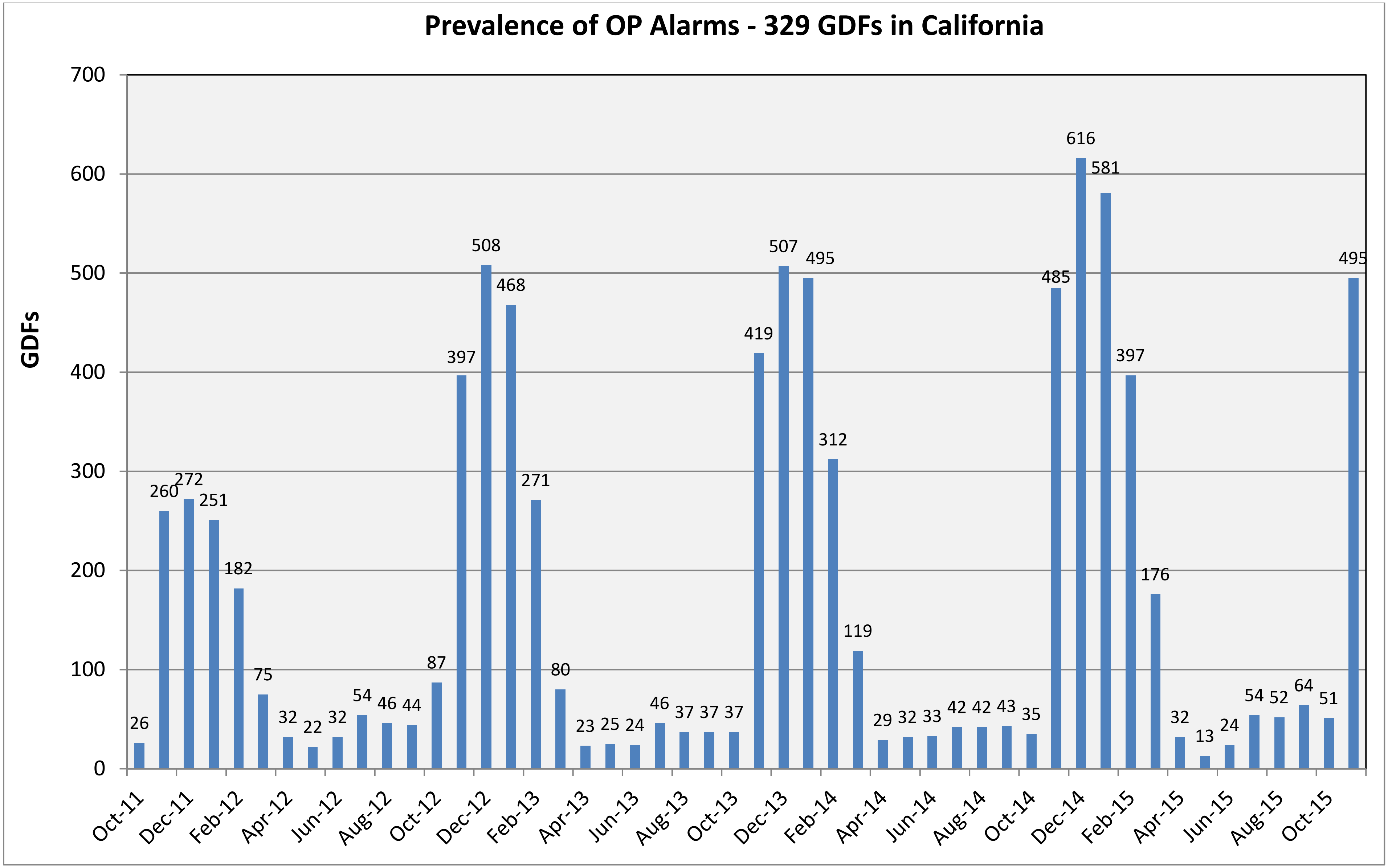


Figure 8

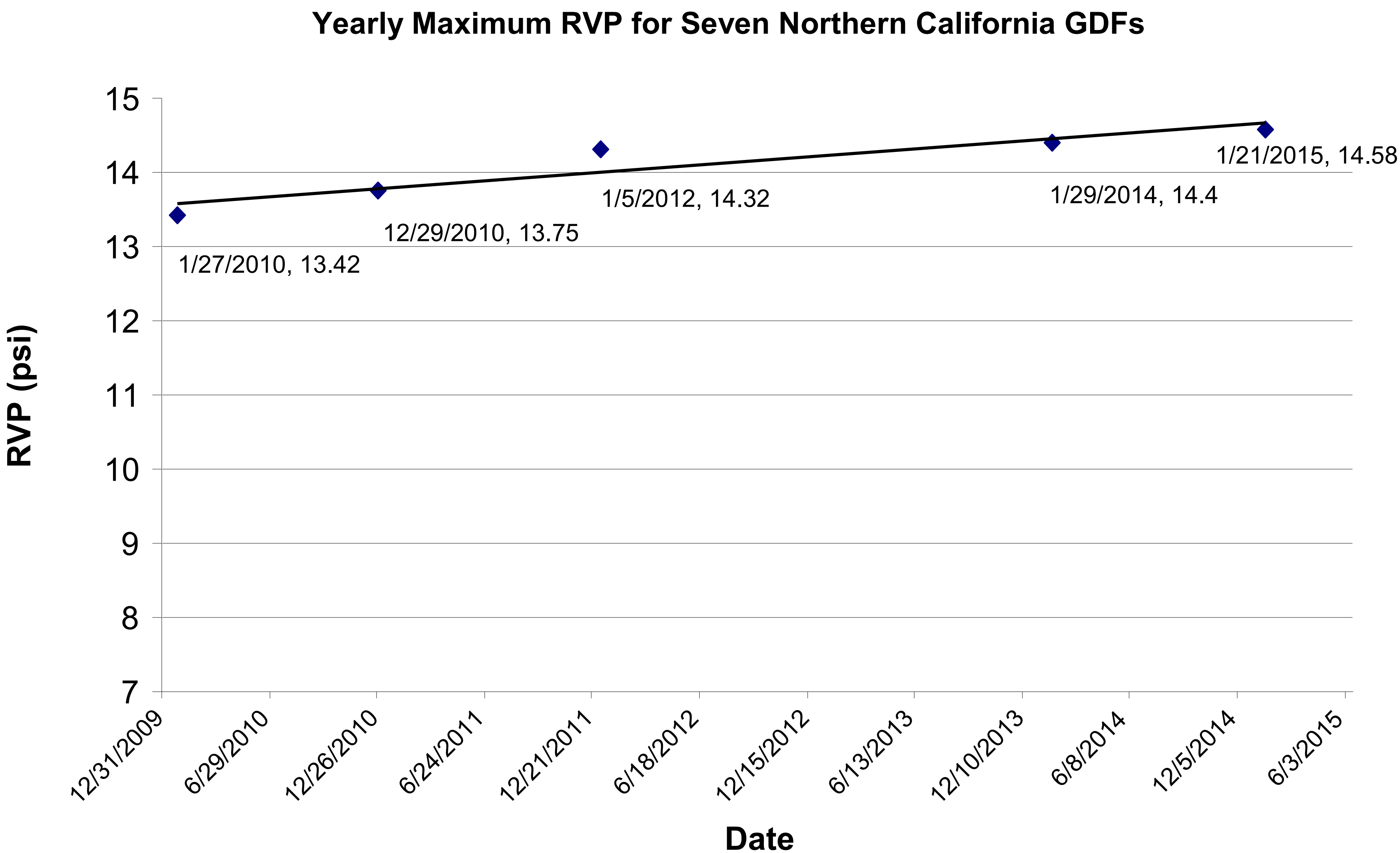
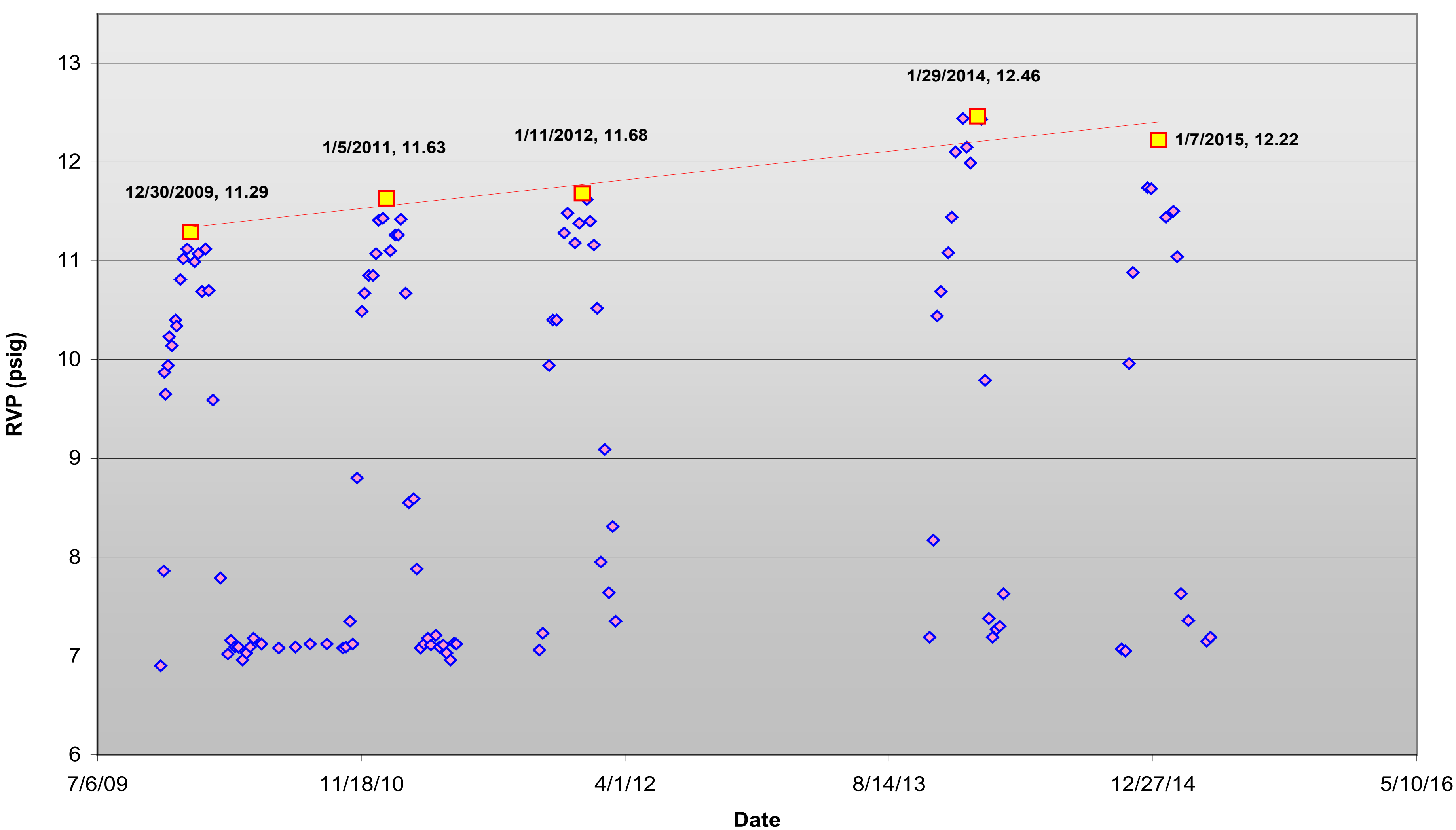

Yearly Maximum RVP for Seven Northern California GDFs
RVP (psi)
15
14
13
12
11
10
9
8
7
1/27/2010, 13.42
12/29/2010, 13.75
1/5/2012, 14.32
1/29/2014, 14.4
1/21/2015, 14.58
12/31/2009
6/29/2010
12/26/2010
6/24/2011
12/21/2011
6/18/2012
12/15/2012
6/13/2013
12/10/2013
6/8/2014
12/5/2014
6/3/2015
Date

Figure 9

Yearly Maximum RVP for 1 Southern California GDF



V. Conclusions and Recommendations

The RVP data collected show that gasoline volatility and saturated vapor concentrations are significantly higher for California gasoline in the winter months. There is a strong correlation between the frequency of ISD overpressure alarms and RVP of the gasoline stored and dispensed at GDFs in California.

A slight upward trend in maximum winter season RVP may have contributed to increased frequency of overpressure alarms seen over the same five-year period. CARB staff believes other factors involving newer vehicle fill pipe designs have increased the amount of fresh air being returned to the UST during ORVR vehicle refueling, further contributing to increased OP alarm frequency.

The observations of RVP, temperature and TVP at two OP study sites indicate that winter season RVP would have to be severely limited (perhaps as low as 10 psig) to limit vapor growth to levels similar to those predicted for summer fuel. Factors including cost of reformulating fuels, air quality benefits, vehicle drivability and other issues would need to be assessed before a decision could be reached regarding a winter fuel RVP limitation.

References

1. California Code of Regulations, Title 13, Sections 2250-2273.5, California Reformulated Gasoline Regulations, https://www.arb.ca.gov/fuels/gasoline/100912CalRFG_regs.pdf, 2012.

2. ASTM D4814 - 16b Standard Specification for Automotive Spark-Ignition Engine Fuel https://www.astm.org/Standards/D4814.htm

3. California Code of Regulations Title 13, Section 2298, Motor Fuel Sampling Procedure, https://govt.westlaw.com/calregs/Document/ID99A8290D46911DE8879F88E8B0DAAAE?viewType=FullText&originationContext=documenttoc&transitionType=CategoryPageItem&contextData=(sc.Default), 2012.

4. California Air Resources Board, Procedure For The Determination Of The Reid Vapor Pressure Equivalent of Gasoline, Standard Operating Procedure Mv-Fuel-125, Revision No. 2.3, http://www.arb.ca.gov/testmeth/slb/sop125v2_3.pdf, 2009.

5. USEPA AP-42, Compilation of Air Pollution Emission Factors, Nov. 2006, Chapter 7, Organic Liquid Storage, Section 7.1 pages 55-56

Appendix

Appendix 1 – RVP Results for Fuel Sample Collected for Overpressure Study

Appendix will be provided upon request.