Air Quality Report on the April 27, 2013 Fire Incident at Marathon Petroleum of Detroit

Michigan Department of Environmental Quality
Air Quality Division

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Introduction

This report summarizes and evaluates air quality data relevant to the time period of a fire that occurred at Marathon Petroleum's Detroit refinery on April 27, 2013. The fire started at approximately 6:00 PM and involved a small tank containing sour water from the refining process. The fire was extinguished at approximately 8:00 PM. During the incident, the wind was primarily out of the southeast, blowing toward Melvindale.

Both regional and near-source air quality data are summarized in this report to ascertain the impact of the fire. The impact upon regional air quality was evaluated by tabulating the Air Quality Index (AQI) from the Michigan Department of Environmental Quality's (MDEQ) permanent air monitoring stations located in Allen Park, Dearborn and Detroit (at Southwestern High School). The AQI values used were based upon ozone, sulfur dioxide (SO_2) and fine particulate matter less than 2.5 micrometers in diameter ($PM_{2.5}$) for three weeks before and three weeks after the incident.

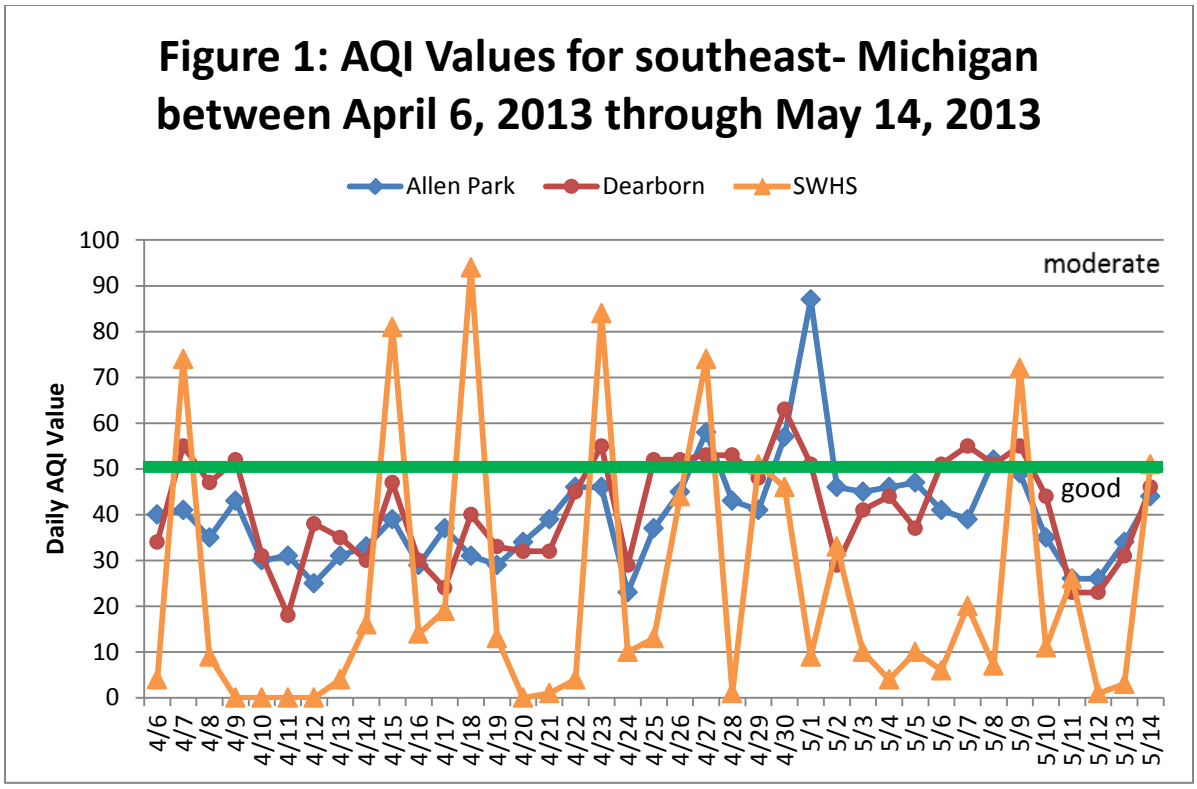
The near-source impact of the fire was evaluated by reviewing the continuous monitoring data during the fire from four stations operated by Marathon Petroleum for particulate matter less than 10 micrometers in diameter (PM_{10}), carbon monoxide, sulfur dioxide, and total reduced sulfur (TRS). Two 5-minute "grab" samples were collected soon after the incident and were analyzed for volatile organic compounds (VOCs). Data was also reviewed from the regularly scheduled 24-hour VOC sampling that took place at the four facility stations on April 28, 2013.

Summary of Findings

Impact Upon Regional Air Quality

To evaluate the overall impact on air quality in southwest Detroit, approximately three weeks of data before and after the fire was analyzed using the AQI. The higher the AQI value, the greater the level of air pollution and the greater the level of concern with regard to public health. An AQI value of 50 or less represents good air quality with little potential to affect public health. An AQI value in the range of 51 to 100 represents moderate air quality, meaning air quality is acceptable; however, for some pollutants, there may be a moderate health concern for a very small number of people.

Figure 1 shows that the regional ambient air quality was similar on April 27, 2013 to the time periods before and after the fire. For the entire time period analyzed, the AQI was in the Good or Moderate range (see Appendix A). This suggests that the Marathon fire did not have a large or long-term impact on the region's overall air quality.



Impact on Local (Near-source) Air Quality

The Marathon 2A-West monitor was directly downwind of the fire and therefore was the most impacted. The data collected from this station were reviewed to determine: 1) if there were any differences in VOC, PM_{10} or TRS concentrations compared to the other monitors in the area; and 2) how these pollutant concentrations measured at the monitors compared to established health criteria.

April 27, 2013 was not a scheduled sampling day for VOCs. However, Marathon personnel collected two special, 5-minute ambient VOC samples (grab samples). These two samples were taken approximately two hours after the fire was extinguished. One was taken downwind of the fire location at the corner of Leo and Flora Streets at 10:10 PM, and the other was taken upwind of the fire location at the corner of Patricia and Leonard Streets, at 10:27 PM. April 28 was a scheduled sampling day for VOCs, so 24-hour integrated samples were taken at all four of Marathon's monitoring stations and at the MDEQ's Dearborn monitor.

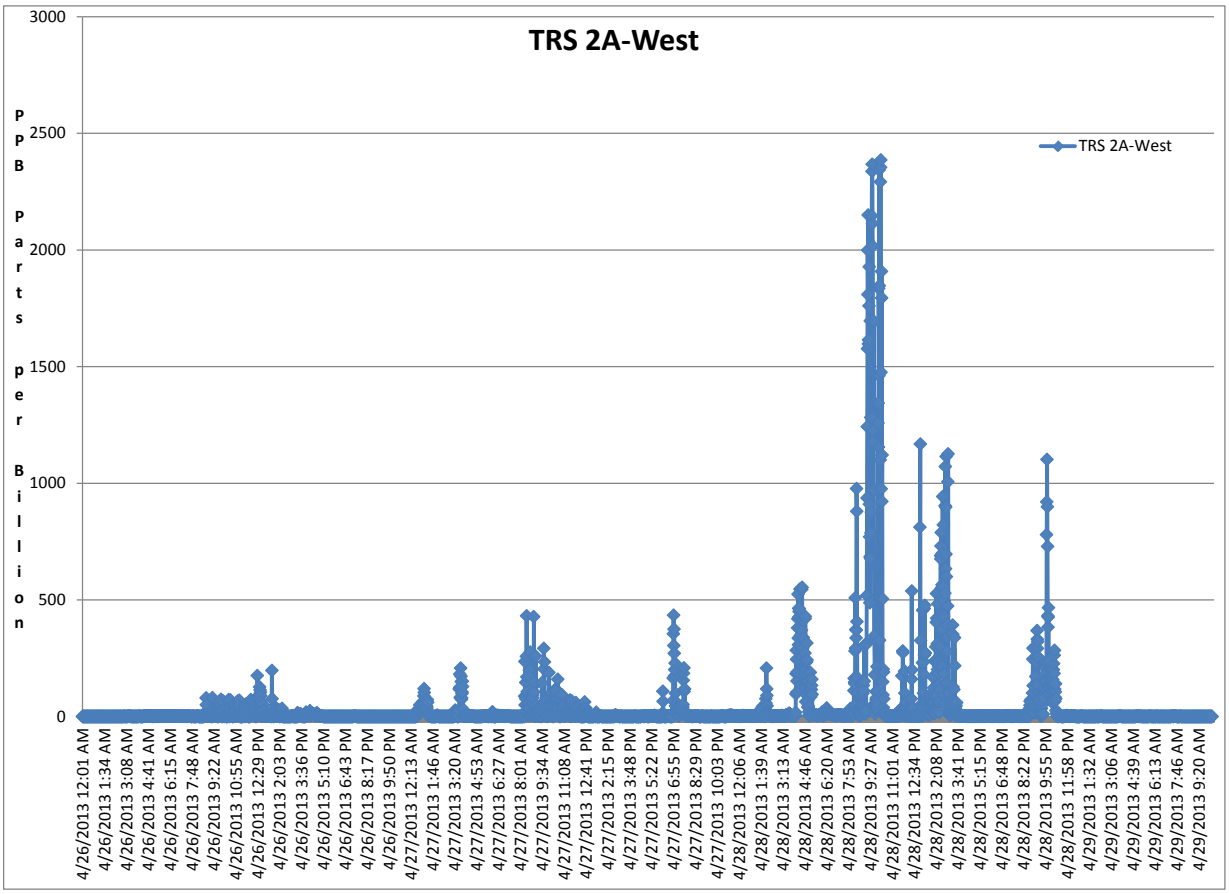
While some of the VOC levels at the Marathon property line and in the adjacent neighborhoods after the fire were higher than those observed at the Dearborn monitor, none of the concentrations were in excess of established health criteria. Of the 73 VOC compounds that were analyzed, 59 were found to be below their respective detection limits.

A review of 1-hour average PM_{10} levels at the beginning of the incident (6:00 to 7:00 PM) on April 27 shows that the maximum PM_{10} level at any of the four Marathon Petroleum monitors was 60 micrograms per cubic meter ($\mu g/m^3$), up from a maximum of 46 $\mu g/m^3$ the hour before. Between 7:00 and 8:00 PM, the maximum observed level was 14 $\mu g/m^3$ and between 8:00 and 9:00 PM, the maximum 1-hour average at any of the Marathon PM_{10} monitors was 24 $\mu g/m^3$. During the same 5:00 to 9:00 PM time period, hourly PM_{10} levels at the MDEQ's Dearborn monitor ranged between 18 and 23 $\mu g/m^3$. The National Ambient Air Quality Standard (NAAQS) for PM_{10} is 150 $\mu g/m^3$, averaged over a 24-hour period. While it appears that the PM_{10} at the Marathon Petroleum property line during the start of the fire was elevated compared to Dearborn, the 24-hour averages at the four Marathon Petroleum sites were well below the 150 $\mu g/m^3$ NAAQS.

Short-term (1-minute average) ambient values for TRS measured at the heavily impacted Marathon 2A-West monitoring site reached levels as high as 2,300 parts per billion (ppb), while maximum TRS levels at the Marathon 1-North monitor upwind were only about 22 ppb (see Figure 2). However, at each site, peak TRS levels occurred several hours after the fire incident.

It is unclear what reduced sulfur compounds were emitted during the fire, but the TRS monitoring methodology collectively measures dimethyl sulfide, dimethyl disulfide, hydrogen sulfide, and methyl mercaptan. These substances have a very disagreeable odor at levels as low as 1 ppb. Dimethyl disulfide and methyl mercaptan have the lowest health protective values. For worker protection, dimethyl disulfide has an occupational exposure limit of 500 ppb, averaged over eight hours. The MDEQ has set a health protective initial threshold screening level (ITSL) for methyl mercaptan at 5 ppb based on a 1-hour averaging time, for the protection of the general public including sensitive groups. The value is based on the 15-minute occupational ceiling level of 500 ppb, for the protection of workers. While there were no aggregated 8-hour periods during the incident where TRS levels were measured above 500 ppb (Figure 2), there were 84 nonconsecutive, one-minute periods that were higher than 500 ppb. If the TRS measurements are assumed to consist of only methyl mercaptan, then the highest measured TRS levels exceeded the methyl mercaptan occupational ceiling level and the ITSL. These health protective criteria are designed to protect from acute irritancy effects.

Figure 2. Chart of TRS Levels in Parts Per Billion (ppb) from the 2A-West Monitor from 4/26/2013 12:01 AM to 4/29/2013 9:20 AM (one-minute data)



Conclusions

It should be noted that, in an unexpected incident, the available air monitoring data can never be totally complete with regard to the timing and placement of the monitors or the parameters monitored. However, the MDEQ believes that, in the case of the April 27 Marathon Petroleum Refinery fire, the available data are extensive enough to draw conclusions as to the overall impact of the fire.

Evaluation of routine air monitoring data from the MDEQ's permanent air monitoring stations in southeast Michigan shows that the fire did not have an impact upon the region's air quality as a whole. Marathon Petroleum's monitoring network allowed the MDEQ to evaluate the local impact of the fire on communities adjacent to the refinery.

At the most impacted monitor location, the peak levels of dimethyl disulfide, dimethyl sulfide, hydrogen sulfide, and methyl mercaptan could have caused a very disagreeable odor, with possible eye, skin, and respiratory tract irritation, which would be reversible, short-lived effects. These levels could have caused coughing, sore throat, nausea, headache, and shortness of

breath. In asthmatics and sensitive individuals, the levels could cause airway constriction. If the TRS measurements are assumed to consist of only methyl mercaptan, then the highest measured TRS levels exceeded the methyl mercaptan occupational ceiling level and the ITSL. These health protective criteria are designed to protect from acute irritancy effects.

Of the VOCs detected from sampling on the evening of the fire and during the 24-hour monitoring on the day after the fire, there were no compounds that were above the MDEQ established ITSLs. As the ITSL is a health protective value, no adverse effects from the VOCs would be expected, based on the available data.

Similarly, the PM_{10} values did not exceed the National Ambient Air Quality Standard (NAAQS). As the NAAQS were established to provide for the protection of public health, including the health of sensitive sub-populations such as asthmatics, children, and the elderly, the PM_{10} data do not suggest any public health concern.

APPENDIX A

AQI value, pollutant and category for Allen Park, Dearborn and Detroit before and after April 27, 2013 (highlighted).

	Allen Park AQI			Dearborn AQI		SWHS AQI	
	Value	Pollutant	Category	Value	Category	Value	Category
4/6/2013	40	O_3	Good	34	Good	4	Good
4/7/2013	41	$PM_{2.5}$	Good	55	Moderate	74	Moderate
4/8/2013	35	$PM_{2.5}$	Good	47	Good	9	Good
4/9/2013	43	$PM_{2.5}$	Good	52	Moderate	0	Good
4/10/2013	30	$PM_{2.5}$	Good	31	Good	0	Good
4/11/2013	31	O_3	Good	18	Good	0	Good
4/12/2013	25	O_3	Good	38	Good	0	Good
4/13/2013	31	O_3	Good	35	Good	4	Good
4/14/2013	33	O_3	Good	30	Good	16	Good
4/15/2013	39	O_3	Good	47	Good	81	Moderate
4/16/2013	29	$PM_{2.5}$	Good	30	Good	14	Good
4/17/2013	37	SO_2	Good	24	Good	19	Good
4/18/2013	31	O_3	Good	40	Good	94	Moderate
4/19/2013	29	O_3	Good	33	Good	13	Good
4/20/2013	34	O_3	Good	32	Good	0	Good
4/21/2013	39	O_3	Good	32	Good	1	Good
4/22/2013	46	O_3	Good	45	Good	4	Good
4/23/2013	46	$PM_{2.5}$	Good	55	Moderate	84	Moderate
4/24/2013	23	$PM_{2.5}$	Good	29	Good	10	Good
4/25/2013	37	$PM_{2.5}$	Good	52	Moderate	13	Good
4/26/2013	45	$PM_{2.5}$	Good	52	Moderate	44	Good
4/27/2013	**58**	**O_3**	**Moderate**	**53**	**Moderate**	**74**	**Moderate**
4/28/2013	43	$PM_{2.5}$	Good	53	Moderate	1	Good
4/29/2013	41	$PM_{2.5}$	Good	48	Good	51	Moderate
4/30/2013	57	$PM_{2.5}$	Moderate	63	Moderate	46	Good
5/1/2013	87	SO_2	Moderate	51	Moderate	9	Good
5/2/2013	46	O_3	Good	29	Good	33	Good
5/3/2013	45	O_3	Good	41	Good	10	Good
5/4/2013	46	O_3	Good	44	Good	4	Good
5/5/2013	47	O_3	Good	37	Good	10	Good
5/6/2013	41	O_3	Good	51	Moderate	6	Good

	Allen Park AQI			Dearborn AQI		SWHS AQI	
	Value	Pollutant	Category	Value	Category	Value	Category
5/7/2013	39	$PM_{2.5}$	Good	55	Moderate	20	Good
5/8/2013	52	$PM_{2.5}$	Good	51	Moderate	7	Good
5/9/2013	49	$PM_{2.5}$	Good	55	Moderate	72	Moderate
5/10/2013	35	$PM_{2.5}$	Good	44	Good	11	Good
5/11/2013	26	O_3	Good	23	Good	26	Good
5/12/2013	26	O_3	Good	23	Good	1	Good
5/13/2013	34	O_3	Good	31	Good	3	Good
5/14/2013	44	O_3	Good	46	Good	51	Moderate

APPENDIX B

Marathon Petroleum of Detroit: Evaluation of the Public Health Significance of the Ambient Air Monitoring Data Associated with the 4/27/13 Fire Incident

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May 31, 2013

Overview and Summary

This paper evaluates the ambient air monitoring data pertaining to the fire incident at the Marathon Petroleum of Detroit Refinery which occurred on April 27, 2013 between approximately 6 PM and 8 PM. The fire occurred in one of the refinery's smaller tanks, which contained sour water from the refining process. The general wind direction at the time of the fire was from the southeast, resulting in smoke blowing toward Melvindale. The available ambient monitoring data from nearby sampling on April 27 to April 28 are herein reviewed and compared to available information on odor thresholds and toxicity, with a focus on total reduced sulfur (TRS) measurements and other air toxics. Although community health information was not sought or reviewed as part of this assessment, the measured levels of TRS (dimethyl disulfide, dimethyl sulfide, hydrogen sulfide, and methyl mercaptan) would be expected to have a very disagreeable odor, with possible eye, skin, and respiratory tract irritation, which would be reversible, transient effects. The measured levels of TRS could cause coughing, sore throat, nausea, headache, and shortness of breath. For asthmatics and sensitive individuals, the measured TRS levels could case airway constriction. Since the TRS monitor only detected total reduced sulfur, and there is no information on the individual percentages of sulfur compounds present, it is more difficult to interpret the data and indicate which effects may have occurred.

For consistency and better clarity, this report presents air contaminant levels of parts per billion (ppb), or, micrograms per cubic meter ($\mu g/m^3$), even though this results in the relatively large magnitude of some values as compared to presenting them in other units such as parts per million (ppm).

The levels of PM_{10} (particulate matter 10 microns or less in size) were also measured during the fire incident. "Particles less than 10 microns in diameter pose a health concern because they can be inhaled into and accumulate in the respiratory system…." (EPA, 2013). Sources of particulate matter include all types of combustion (e.g., motor vehicles, power plants, wood burning) and some industrial processes (EPA, 2013). The National Ambient Air Quality Standard (NAAQS) for PM_{10} is 150 $\mu g/m^3$ based on a 24-hour averaging time. During and after the fire incident the PM_{10} levels were below the NAAQS standard. The 24-hour average levels did not exceed the NAAQS of 150 $\mu g/m^3$ and therefore, the PM_{10} data do not suggest any public health concern.

Two hours after the fire incident Marathon representatives collected two 5-minute air canister samples of the air upwind and downwind of the fire. Also, the day after the fire, all four Marathon monitors and the Michigan Department of Environmental Quality (MDEQ) community monitor in Dearborn collected a previously scheduled 24-hour ambient air sample, which was tested for

volatile organic compounds (VOCs). Of all the VOCs detected, only the reported 24-hour acrolein levels were sufficiently high to be associated with potential health effects; however, the acrolein data may not be valid due to difficulties with the sampling and analysis of this substance (The U.S. Environmental Protection Agency's School Air Toxics Monitoring Program, Kilmer, personal communication).

Description of the Incident Monitoring Levels

The fire incident started at approximately 6 PM on 4/27/13 and lasted until shortly before 8 PM. The fire occurred closest to the monitor at the Marathon 2A West Site and the wind direction carried the smoke toward that monitor. The monitor at the 2A West Site measured total reduced sulfur (TRS) and particulate matter with a size of 10 microns or less (PM_{10}) at the time of the incident. This monitoring for TRS detects dimethyl sulfide (CAS# 75-18-3), dimethyl disulfide (CAS# 624-92-0), hydrogen sulfide (CAS# 7783-06-4), and methyl mercaptan (CAS# 74-93-1). The average ambient values for TRS measured at the relatively unimpacted Marathon 1-North monitor ranged from 0 to 22 ppb with a sample averaging time of 1 minute (Figure1). In contrast, TRS levels at the relatively more impacted 2A-West site ranged up to approximately 2,300 ppb (Figure 2). It should be noted that the vertical axis for the levels at the 1-North site shown in Figure 1 ranges from 0 to 25 ppb, while the vertical axis for the 2A-West site in Figure 2 ranges from 0 to 3,000 ppb. At each site, peak TRS levels occurred several hours after the fire incident. Although there is no NAAQS or other health benchmarks available for TRS, the toxicity information for the four component substances are summarized in Appendix C. For dimethyl disulfide, there were no one-minute periods where TRS levels were measured above the ACGIH TLV-TWA of 500 ppb (1,900 $\mu g/m^3$) based on an 8-hour workday, during the incident (figure 2), but there were 84 nonconsecutive one-minute periods that were higher than the dimethyl disulfide ACGIH TLV-TWA occupational exposure limit of 500 ppb, which is set for an 8-hour workday. The levels of dimethyl disulfide, dimethyl sulfide, hydrogen sulfide, and methyl mercaptan associated with the peak TRS level of 2,300 ppb could have caused a very disagreeable odor, with possible eye, skin, and respiratory tract irritation, which would be reversible, transient effects. The levels could have caused coughing, sore throat, nausea, headache, and shortness of breath. In asthmatics and sensitive individuals, the levels could cause airway constriction. Since the TRS monitor only detects total sulfur without speciation, the ratio of sulfur compounds released is unknown, and it is more difficult to interpret the data and indicate which effects may have occurred (see details in Appendix C).

A review of 1-hour average PM_{10} levels, from 12:00 AM on April 26 until 9:00 AM on April 29 indicates that the hourly PM_{10} levels ranged from 5 to 167 $\mu g/m^3$. At the beginning of the incident (6-7 PM) the PM_{10} level was 60 $\mu g/m^3$. That was an increase from 14 $\mu g/m^3$ for the 5-6 PM period. For the 7-8 PM period the level was 14 $\mu g/m^3$. The level was 24 $\mu g/m^3$ at 8-9 PM. The NAAQS PM_{10} is 150 $\mu g/m^3$ (24-hour averaging time). The NAAQS are values that provide for public health protection, including protection of the health of sensitive sub-populations such as asthmatics, children, and the elderly. Since the 24-hour average levels did not exceed the NAAQS, the PM_{10} data do not suggest any public health concern.

Soon after the fire incident, Marathon staff collected two 5 minute air samples by vacuum canister. One was taken downwind of the fire at the corner of Leo and Flora Street at 10:10 PM and the other was taken upwind of the fire at the corner of Patricia and Leonard Street at 10:27 PM. The samples were analyzed for volatile organic compounds (VOCs). The laboratory tested for 73 VOCs, of which 59 were below their respective detection levels. Table 1 lists the compounds that were detected at higher levels than were measured during 2011 at the Dearborn monitor which is used for comparison. The Dearborn monitor is a residential monitor with nearby industrial activity. It should be noted that these samples were taken more than two hours after the reported end of the fire incident.

Table 1. Volatile Organic Compounds Measured in the 5 Minute Sampling Events Upwind and Downwind of the Marathon Fire and Comparison to 2011 Air Quality Report Maximum 24-Hour Concentrations Measured at the Dearborn Monitor

Compound	Leo/Flora Street (µg/m^3) downwind (5-minute sample)	Patricia/Leonard Street (µg/m^3) upwind (5-minute sample)	2011 Dearborn Maximum Concentration (µg/m^3) (24-hour sampling time)
Acetone	55	81	0.000497
2-Butanone (MEK)	38	23	0.00522
Chloromethane	1.4	1.3	2.3
Dichlorodifluoromethane	3.1	2.7	3.1
Ethanol	45	68	No data
Methylene chloride	1.4	23	0.00198
n-Hexane	3.2	2.7	1.6
2-Propanol	Below detection level	14	No data
Propene	7.6	7.2	0.00143
Toluene	Below detection level	2.7	3.8

Before discussing the differences in the levels seen in the 5-minute air samples and the monitoring data located in Dearborn, it is important to note that the data for Dearborn represent sampling over 24 hours, whereas the grab samples were collected over only five minutes. This difference in sample duration makes it problematic for comparison purposes due to the uncertainties involved.

The levels of acetone were high both upwind and downwind of the fire when compared to the maximum concentration measured at Dearborn. Acetone is a common solvent used in laboratories, which raises the possibility of sample contamination. Assuming that the levels reported are valid, then it should be noted that the higher level of acetone was detected upwind of the fire. Ethanol and methylene chloride were also detected at higher levels upwind of the fire than downwind, which suggests that these compounds are coming from other emission sources and were not a result of the fire incident. Chloromethane was detected, but the levels are not as high as the maximum concentration detected at Dearborn. The levels of dichlorodifluoro-methane were similar to the maximum value detected at the monitor at Dearborn, and are not considered significant. The value for n-hexane is slightly higher downwind from the fire than upwind, and both were higher than the maximum value detected in Dearborn. The values for 2-butanone (MEK) were higher downwind of the fire than upwind, and both values are

significantly higher than the monitor in Dearborn. MEK is a common industrial chemical and is often found in mixtures with acetone, ethyl acetate, n-hexane, toluene, or alcohols. MEK has applications in the surface coating industry and in the dewaxing of lubricating oils (OEHHA, 1999). 2-Propanol and toluene were detected upwind from the fire, but not downwind of the fire, which suggests that these compounds are being emitted from other sources and not associated with the fire. Propene was detected at higher levels downwind of the fire than upwind, and both values are higher than the maximum value for this compound in Dearborn. In summary, the values for ethanol, n-hexane, 2-butanone (MEK), and propene may have been associated with the fire incident at Marathon and the potential health effects of these compounds will be discussed below.

Sunday, April 28, was a previously scheduled air monitoring day (for 24-hour sampling) for all four of the Marathon monitors and the Dearborn monitor. Table 2 below lists the compounds that had higher concentrations at the Marathon monitors than were detected at the Dearborn monitor in 2011. In Table 2 below, the Marathon MTMS site is the Mark Twain Middle School, which is located 1.29 miles southwest of Marathon Petroleum.

Table 2. Detectable Marathon Monitoring Data that were higher than the VOC Monitor Data Collected at Dearborn for April 28, 2013

Compound	Marathon MTMS ppbv (µg/m^3)* [24-hr]	Marathon 1-North ppbv (µg/m^3)* [24-hr]	Marathon 2-A West ppbv (µg/m^3)* [24-hr]	Marathon 4-East ppbv (µg/m^3)* [24-hr]	Dearborn ppbv (µg/m^3)* [24-hr]
Acetone	4.6 (11)	4.49 (10.7)	5.29 (12.6)	8.17 (19.4)	1.3 (3.1)
Acrolein	0.45 (1.0)	1.32 (3.03)	0.42 (0.96)	0.94 (2.2)	0.2245 (0.5147)
Benzene	<SQL†	0.44 (1.4)	0.55 (1.8)	0.53 (1.7)	0.2667 (0.8520)
2-Butanone (MEK)	0.64 (1.9)	0.7 (2)	0.87 (2.6)	1.54 (4.54)	0.148 (0.436)
Carbon disulfide	<SQL†	1.04 (3.24)	0.47 (1.5)	<SQL†	0.0268 (0.0835)
Ethylbenzene	0.06 (0.3)	0.08 (0.3)	0.12 (0.52)	0.09 (0.4)	0.0403 (0.175)
m&p-Xylenes	0.19 (0.82)	0.2 (0.9)	0.34 (1.5)	0.26 (1.1)	0.0985 (0.428)
o-Xylene	<SQL†	<SQL†	0.15 (0.65)	0.09 (0.4)	0.0384 (0.167)
Propene	<SQL†	<SQL†	3.42 (5.89)	1.25 (2.15)	0.2387 (0.4108)
Styrene	0.08 (0.3)	0.1 (0.4)	0.09 (0.4)	0.38 (1.6)	0.2047 (0.8720)
Toluene	0.91 (3.4)	1.63 (6.14)	1.01 (3.81)	1.2 (4.5)	0.2551 (0.9613)
1,2,4-Trimethyl-benzene	0.06 (0.3)	<SQL†	0.12 (0.59)	0.08 (0.4)	0.034 (0.17)

*The values listed under each monitor are the actual amounts detected for each compound in parts per billion (ppb), the values in the parenthesis are the same amounts converted to µg/m^3.

†(non-detectable) <SQL means that the value is less than the sample quantitation limit, which is the limit of quantitation multiplied by the sample dilution factor.

In the chart above, the validity of the acrolein data is unknown. There is a question about the validity of the data collected when using SUMA canisters in sampling for acrolein. SUMA canisters may have reactive sites that could allow for the production of acrolein even if a SUMA can is clean; older cans may still produce acrolein (U.S. Environmental School Air Toxics Monitoring program, Kilmer, personal communication; DATI, 2005).

The compounds listed in Tables 1 and 2 were compared with the known averages found in the 2011 Air Quality Report to determine if they fell outside of normally detected values in the Detroit Area. These compounds were also compared with the MDEQ Initial Threshold Screening Levels (ITSLs), which are health-based values that are human health protective. This information is presented in Table 3, below.

Table 3. Highest VOC Monitoring Data from Marathon Monitors or 5 Minute Sampling Data: Comparison with Dearborn 2011 Data and MDEQ ITSL.

Chemical	Highest Level Monitored at Marathon (µg/m^3)	Location of Highest Reading	2011 Air Quality Report Max. Concentration (µg/m^3)	MDEQ ITSL (µg/m^3) [Averaging Time]	Is the level above the ITSL?
Acetone	81	Patricia/Leonard Street	0.000497	5,900 [8-hr]	No
Acrolein	3.03	Marathon 1-North	No data	5 [1-hr]	Unknown
Benzene	1.8	Marathon 2A-West	1.5	30 [24-hr]	No
2-Butanone	38	Leo/Flora Street	0.00522	5,000 [24-hr]	No
Carbon disulfide	1.04	Marathon 1-North	0.000173	700 [24-hr]	No
Chloromethane	2.3	Dearborn	0.0296	90 [24-hr]	No
Dichlorodifluoro-methane	3.1	Leo/Flora Street and Dearborn	3.1	49,500 [8-hr]	No
Ethanol	68	Patricia/Leonard Street	No data	19,000 [8-hr]	No
Ethylbenzene	0.52	Marathon 2A-West	0.47	1,000 [24-hr]	No
Methylene chloride	23	Patricia/Leonard Street	0.00198	14,000 [24-hr]	No
m&p-Xylenes	1.5	Marathon 2A-West	1.6	100 [24-hr]	No
n-Hexane	3.2	Leo/Flora Street	1.6	700 [24-hr]	No
o-Xylene	0.65	Marathon 2A-West	0.53	100 [24-hr]	No
2-Propanol	14	Patricia/Leonard Street	No data	220 [24-hr]	No
Propene	7.6	Leo/Flora Street	0.00143	1,500 [24-hr]	No
Styrene	1.6	Marathon 4-East	0.0000981	1,000 [24-hr]	No
Toluene	3.8	Dearborn	3.8	5,000 [24-hr]	No
1,2,4-Trimethyl-benzene	0.59	Marathon 2A-West	0.89	50 [annual]	No

Of all the VOCs detected from sampling on the evening of the fire and the 24-hour monitoring on the day after the fire, there were no volatile organic chemicals that were over the ITSL. As the ITSL is a health protective value, no adverse effects from the volatile organic chemicals above would be expected.

Figure 1. Chart of TRS Levels in Parts Per Billion (ppb) from the 1-North Monitor from 4/26/2013 12:01 AM to 4/29/2013 9:20 AM (one-minute data)

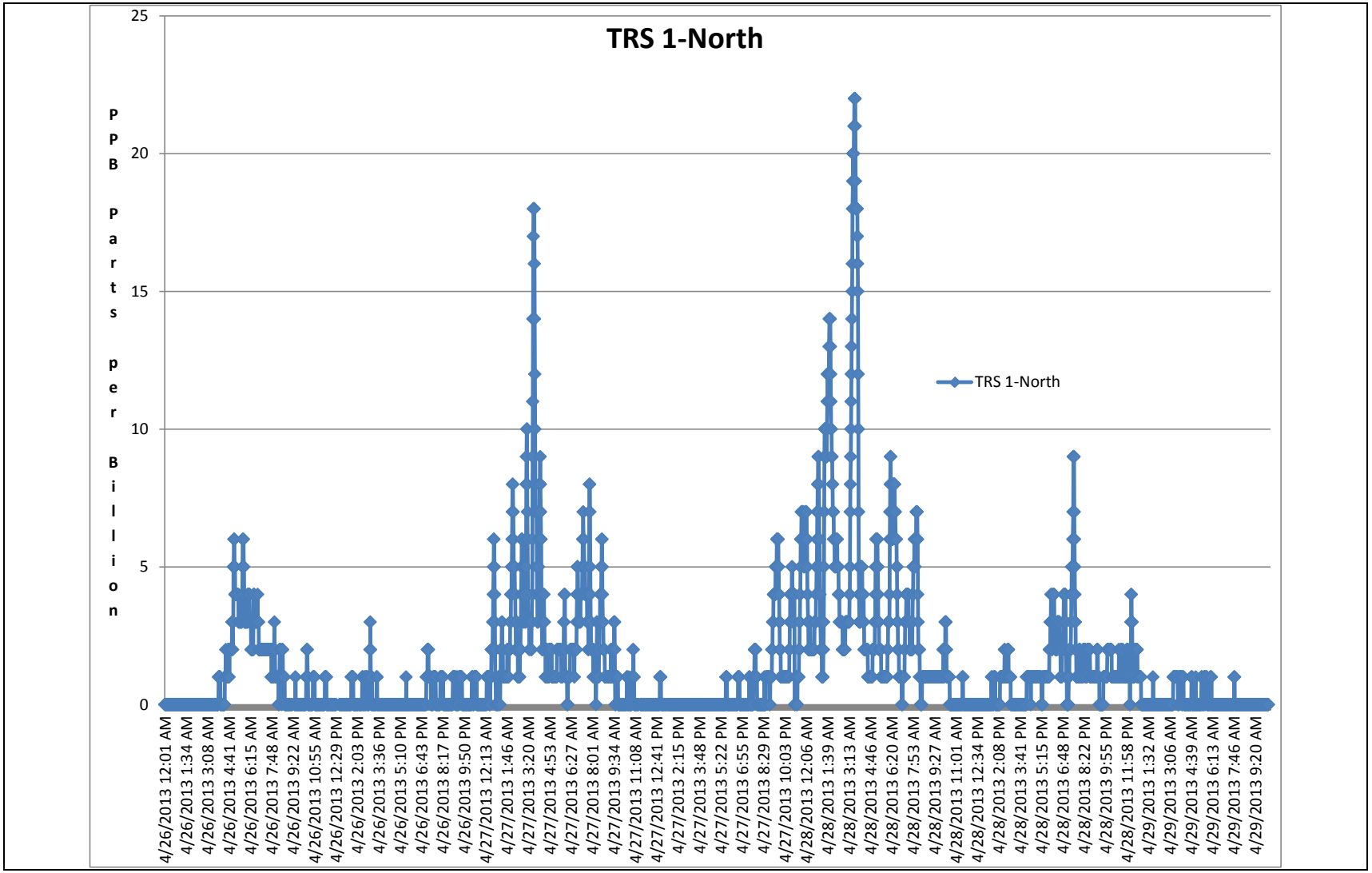
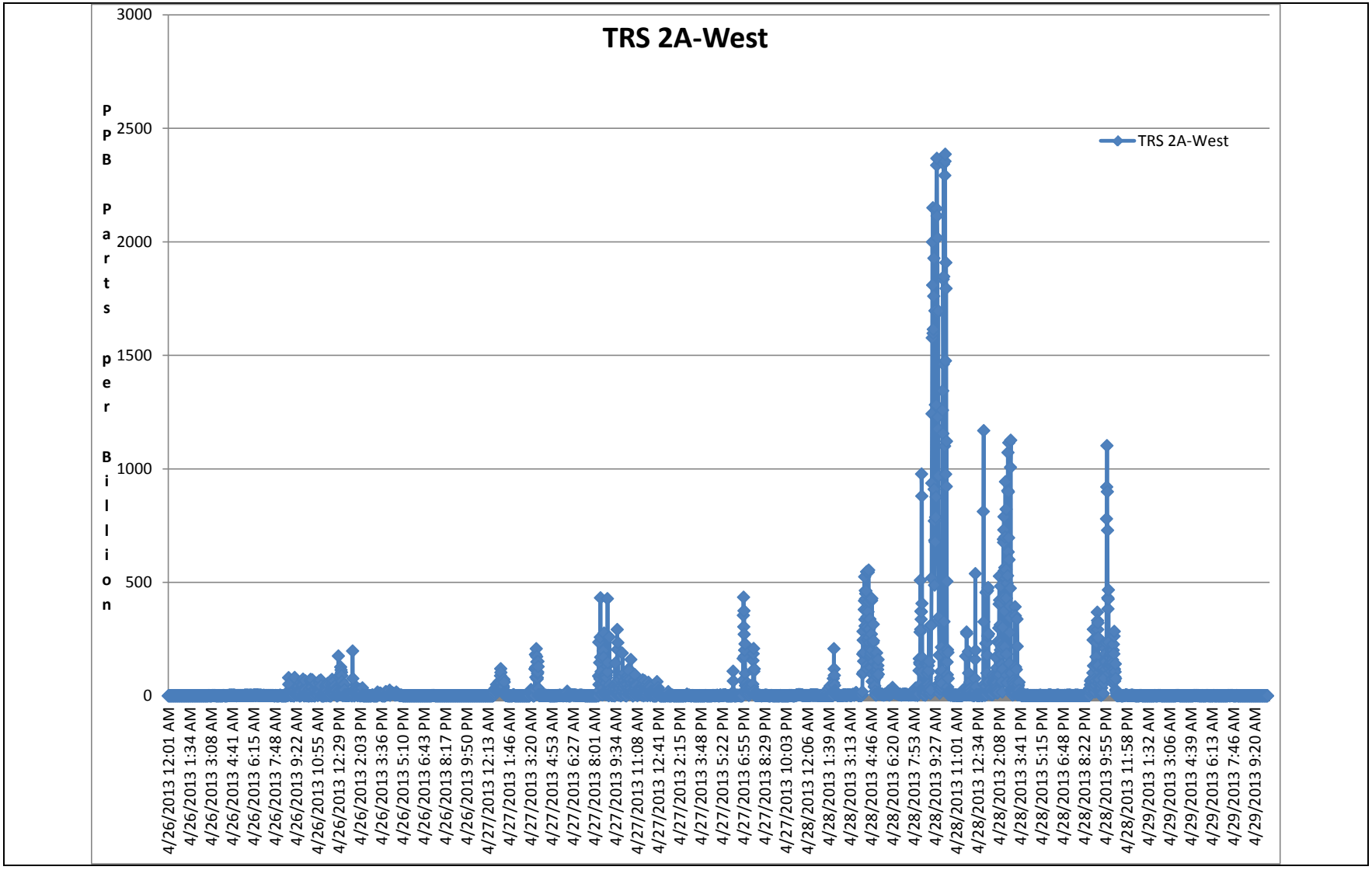


Figure 2. Chart of TRS Levels in Parts Per Billion (ppb) from the 2A-West Monitor from 4/26/2013 12:01 AM to 4/29/2013 9:20 AM (one-minute data)



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List of Abbreviations Used in this Paper

ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guideline Level
ATSDR	Agency for Toxic Substances and Disease Registry
BMD	Benchmark Dose
DATI	Detroit Air Toxics Initiative
DMDS	Dimethyl disulfide
DMS	Dimethyl sulfide
EPA	Environmental Protection Agency
FEV1	Forced expiratory volume in 1 second
FVC	Forced vital capacity
GRAS	Generally Recognized as Safe
HEC	Human equivalent concentration
ITSL	Initial Threshold Screening Level
LEC	Low effect concentration
LOAEL	Lowest Observed Effect Level
MCV	Motor nerve conduction velocity
MDEQ	Michigan Department of Environmental Quality
MEK	Methyl ethyl ketone (2-Butanone)
MRL	Minimal Risk Levels
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No Observed Adverse Effect Level
NTP	National Toxicology Program
OEHHA	Office of Environmental Health Hazard Assessment
OSHA	Occupational Safety and Health Administration
ppb	Parts per billion
Raw	Airway resistance
REL	Recommended Exposure Limit
RfC	Inhalation Reference Concentration
SGaw	Specific airway conductance
TLV-STEL	Threshold Limit Value-Short-Term Exposure Limit
TLV-TWA	Threshold Limit Value-Time-Weighted Average
TRS	Total Reduced Sulfur
$\mu g/m^3$	micrograms per meter cubed
VOCs	Volatile Organic Compounds

APPENDIX C

Toxicity and Odor Information on Individual Chemicals Including Occupational Exposure Levels and MDEQ ITSL

The chemicals listed in this Appendix were selected due to their higher detection in the 5-minute air samples for VOCs and the TRS monitored samples. More information about specific chemicals including general chemical information, occupational levels considered health protective and effects of exposure to the chemical are presented. Some of the health benchmark values cited here are guidelines from the American Conference of Governmental Industrial Hygienists (ACGIH), which is an organization of professional industrial hygienists who review all relevant scientific data on a specific compound and determine a threshold limit value (TLV), which is a value at which is considered health protective for workers exposed for 8 hours a day and a 40 hour workweek, for a working lifetime without any adverse effect (ACGIH, 2012). The Michigan Department of Environmental Quality (MDEQ) derives Initial Threshold Screening Levels (ITSLs); an ITSL is a "concentration of a toxic air contaminant in the ambient air which is used to evaluate noncarcinogenic health effects from a proposed new or modified process…." (NREPA, 1994). ITSLs are not ambient air quality standards. They are health protective benchmarks for the general public, and are routinely used by the Air Quality Division during the permitting process. The ITSL concentration is determined after studying the available scientific data and performing a risk assessment. ITSLs are designed to be health protective for the general public including sensitive subgroups over a lifetime of exposure to that chemical.

Acrolein

This chemical was detected in VOC monitors located at the four Marathon monitoring sites during a 24-hour sampling run on April 28, 2013, the day after the fire and was compared to the Dearborn 24-hour sampling run which also occurred on April 28, 2013. Acrolein is a colorless liquid with a piercing, disagreeable, acrid smell. The odor threshold for acrolein is less than 100 ppb (NRC, 2010). Acrolein is a highly reactive compound and is known to react with itself, as well as reacting with most compounds. It is produced industrially from propylene and mainly used as a biocide and an intermediate in the manufacture of other chemicals, such as methionine. Acrolein can also be produced from overheated cooking oil and burnt fats. Acrolein was detected at all four Marathon monitors operating on April 28, ranging from 0.96 $\mu g/m^3$ at the

Marathon 2A-West monitor to 3.03 µg/m^3 at the Marathon 1-North monitor. The Dearborn community monitor also detected acrolein on April 28 at 0.5147 µg/m^3. ATSDR has establish a Minimal Risk Level (MRL) for intermediate durations (15 to 364 days) for acrolein at 0.09 µg/m^3. The MDEQ has set an ITSL of 5 µg/m^3 based on a 1-hour averaging time. This ITSL is intended to ensure protection from the critical effect of eye irritation from peak short-term exposures. It is based on a human exposure study (Darley et al., 1960) with support from another human exposure study (Weber-Tschopp et al., 1977). In the Weber-Tshopp et al., (1977) study 17 males and 25 female volunteers (5 per group) were exposed to acrolein in three phases: (1) a continuous exposure at constantly increasing acrolein concentrations; (2) short exposures of 1.5 minutes to successively increasing concentrations of 0, 150, 300, 450, and 600 ppb (0, 300, 700, 1000, and 1400 µg/m^3); and (3) a 1-hour exposure to a constant concentration of 300 ppb (700 µg/m^3). After exposure they were administered a questionnaire. Unexposed students were administered a questionnaire as controls. After that, the eye blinking frequency and breathing frequency were measured for all individuals. The complaints about eye irritation were significantly higher than controls beginning at 90 ppm (210 µg/m^3). Throat irritation increased significantly at 430 ppb (1000 µg/m^3). Nasal irritation was significantly higher than controls beginning at 260 ppb (600 µg/m^3). In the Darley et al., (1960) study, 36 healthy human volunteers were exposed (eyes only) to multiple substances (separately) and concentrations to determine eye irritancy. Only one substance and concentration was run on any given day. Subjects were exposed to acrolein at either 0 ppb, 60 ppb (140 µg/m^3) 1300-1600 ppb (3000-3700 µg/m^3), or 2000-2300 ppb (4600-5300 µg/m^3), for five minute periods. During exposure, the subjects wore activated carbon respirators so that they breathed clean air and only the eyes were exposed to the test mixture. The three exposure levels resulted in average eye irritation scores of 0.471, 1.182, and 1.476 respectively. These were relatively higher than the control group's ratings, which for three tests were reported as 0.361, 0.265, and 0.088. The LOAEL of 140 µg/m^3 from the Darley et al., (1960) study was used along with a total uncertainty factor of 30 (10 for sensitive human populations and 3 for a LOAEL to NOAEL) to derive an ITSL of 5 µg/m^3.

There is some concern regarding the validity of the acrolein data as the quality assurance of acrolein data is unknown. There is a question about the validity of the data collected when using SUMMA canisters in sampling for acrolein. SUMMA canisters may have reactive sites that could allow for the production of acrolein even if a SUMMA can is clean; older cans may still produce acrolein (Kilmer, personal communication; DATI, 2005).

2-Butanone

This chemical was detected in two 5 minute air samples which were tested for VOCs. 2-Butanone (also known as methyl ethyl ketone or MEK) was detected at 38 µg/m^3 downwind of the fire and at 23 µg/m^3 upwind of the fire. The maximum detected level at the Dearborn monitor was 0.00522 µg/m^3 for a 24-hour measurement. 2-Butanone is a colorless, flammable liquid with an acetone-like odor. An odor threshold for 2-butanone of 5,400 ppb (16,000 µg/m^3) has been reported. ACGIH has a TLV-TWA of 200,000 ppb (590,000 µg/m^3) and a TLV-STEL of 300,000 ppb (885,000 µg/m^3) recommended for occupational exposure to 2-butanone. "These values are intended to minimize the potential for eye and upper respiratory tract irritation and adverse effects on the central nervous system and peripheral nerves" (ACGIH, 2008). 2-Butanone "is used as a solvent; in the surface coating industry; in the dewaxing of lubricating oils; and in the manufacture of colorless synthetic resins, artificial leather, rubbers, lacquers, varnishes, and glues" (ACGIH, 2008).

The MDEQ has set an ITSL for 2-butanone at 5,000 µg/m^3 based on a 24-hour averaging time. The ITSL is equal to the EPA RfC of 5,000 µg/m^3 established on increased incidence of misaligned sternebrae in mice from a study by Schwetz et al., (1991). Schwetz et al., (1991) exposed groups of 10 virgin Swiss CD-1 mice and 33 sperm plug-positive (gestation day 0) females to mean 2-butanone concentrations of 0, 398,000±9, 1,010,000±28, or 3,020,000±79 ppb (0, 1,174,000±27,000, 2,980,000±83,000, or 8,909,000±233,000 µg/m3) by inhalation for 7 hours/day on gestation days 6-15. Dams were sacrificed on gestation day 18. "A slight concentration-related increase in liver-to-body weight ratio (approximately 7% over control at 3,020,000 ppb) was observed in the dams. Two statistically significant developmental effects were observed: (1) a decrease in mean fetal weight (per litter) at 3,020,000 ppb (8,909,000 µg/m^3) in males (5% decrease compared with controls) and for male and female fetuses combined (4% decrease compared with controls), and (2) a positive trend for increasing the incidence of fetuses (total) with misaligned sternebrae with increasing exposure level (incidences were 31/310, 27/260, 49/291, and 58/323 for the control through 3,020,000 ppb exposure groups respectively). Developmental and maternal effect levels were established at 3,020,000 ppb (8,909,000 µg/m^3) for a small, but statistically significant, decrease in fetal weight among males, increased incidence of misaligned sternebrae, and an increase in maternal liver-to-body-weight ratio" (EPA, 2003b). This RfC uses BMD methodology using a low effect concentration, human equivalent concentration [$LEC_{(HEC)}$] of 1,517,000 µg/m^3 and an uncertainty

factor of 300 (3 for interspecies , 10 for susceptible individuals, and 10 for database deficiencies) to obtain the RfC of 5,000 µg/m^3. The highest level of 2-butanone (MEK) was 38 µg/m^3 detected downwind of the fire, this value is far below the ACGIH TLV-TWA of 200,000 ppb (590,000 µg/m^3) and below the ITSL of 5,000 µg/m^3. No effects from 2-butanone would be reasonably expected to occur at this level of exposure.

Dimethyl Disulfide

Dimethyl disulfide (DMDS) [CAS# 624-92-0] is one of the four compounds detected using the TRS monitor. DMDS is a pale yellow liquid, with a disagreeable "garlic-like" odor, with an odor threshold reported as 1.0 to 22 µg/m^3 and 31 to 39 µg/m^3 (ACGIH, 2008). This chemical is "encountered in the petroleum industry, the pulp and paper industry, and in water sewage treatment plants. DMDS is a product of the microbial degradation of sewage and is also produced by ruminant animals through their biotransformation of *S*-methyl-cysteine, an amino acid present in high concentrations in the *Brassica* family. DMDS is an approved synthetic flavoring substance and adjuvant. It is also a natural product found in garlic and in a variety of foodstuffs including; baked goods, condiments, and pickle products" (ACGIH, 2008). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value – time-weighted average (TLV-TWA) of 0.5 ppm (2,000 µg/m^3) is recommended for occupational exposures to DMDS, and was set to protect workers from mucous membrane irritation and central nervous system effects (ACGIH, 2008). The highest TRS concentration detected in the air at the 2A West Site Monitor was 2,300 ppb when measured using one-minute data. Though the elevated levels of TRS were detected over several hours on April 27th and April 28 well after the fire was extinguished, if one were to assume that the measured TRS consisted of only DMDS, then the mostly impact of this peak level would be a disagreeable odor.

The MDEQ has set an Initial Threshold Screening Level (ITSL) for DMDS at 28 µg/m^3 with an annual averaging time. The ITSL is based on a sub-chronic inhalation study on rats by Gage (1970). Groups of four rats per dose were exposed to 100,000 or 250,000 ppb (385,300 µg/m^3 or 963,200 µg/m^3) DMDS via inhalation for 6 hours/day, 5 days/week for 4 weeks (20 exposures total). The rats in the 250,000 ppb dose group exhibited lethargy, respiratory difficulty, low weight gain, and on necropsy revealed multiple organ congestion. No effects were noted in the 100,000 ppb (385,300 µg/m^3) group upon observation or necropsy. The 100,000 ppb value was used to derive an ITSL of 28 µg/m^3 based on an annual averaging time. Therefore, the TRS

levels measured during the incident (Figure2) had no 8-hour periods that were higher than the DMDS occupational exposure limit of 500 ppb (1,900 µg/m^3), which is set for an 8 hour work day. The measured TRS peak levels were also below the DMDS no-effect level in rats, which was seen at 100,000 ppb (385,300 µg/m^3). The day after the fire incident, (Figure 2) there were 84 nonconsecutive one-minute periods that were higher in comparison to the DMDS occupational exposure limit of 500 ppb (1,900 µg/m^3). The peak one-minute levels measured by the TRS monitor were much higher than the ITSL of 28 µg/m^3, which is protective for a continuous exposure over a lifetime. Therefore, if we were to assume that the peak TRS measurement of 2,300 ppb was only dimethyl disulfide, then this peak level would have a disagreeable odor, and may have caused mild irritation of the eyes and skin, cough, sore throat, nausea, and weakness.

Dimethyl Sulfide

Dimethyl sulfide (DMS) [CAS# 75-18-3] is one of the four compounds that may have been detected using the TRS monitor. DMS is a flammable, colorless liquid with a very disagreeable odor. In the workplace, DMS is emitted in the pulp and paper industry, oil refineries, and sewage treatment plants. DMS is produced in bacteria in periodontal pockets and is a product of intermediary metabolism from methionine. It is used in fragrance formulations and has been found in butter, white bread, American peppermint oil, and the oil of geranium. The U.S. Food and Drug Administration classified DMS as generally recognized as safe (GRAS) and approved its use in food. DMS has a low odor threshold of 2.5 µg/m^3. The ACGIH TLV-TWA of 10,000 ppb (25,000 µg/m^3) is recommended for occupational exposure to DMS. The highest TRS concentration detected in the air at the 2A-West Site Monitor was 2,300 ppb measured using one-minute data. The levels of TRS varied over the period of several hours on April 27th and April 28 well after the fire was extinguished. If one were to assume that only DMS was emitted, then this level of DMS would have a disagreeable odor. At levels above the TLV of 10,000 ppb, DMS may cause irritation of the eyes and skin, cough, sore throat, nausea, and weakness in workers.

The MDEQ has set an ITSL of 7 µg/m^3 based on an annual averaging time. The ITSL is based on a study by Butterworth et al., (1975) where groups of 15 male and female Wistar rats per dose group were administered 0, 2.5 25, or 250 mg/kg/day orally via intubation for 7 days/week for 14 weeks. At 250 mg/kg/day, a statistically significant increase in thyroid gland weight in

males, while a statistically significant decrease in thyroid gland weight occurred in females. The no adverse effect level (NOAEL) of 25 mg/kg/day was used to derive an ITSL at 7 µg/m^3 (annual average). This ITSL is the level that is estimated to be protective for all people with long-term exposure. The measured TRS of 2,300 ppb peak detection level is below the 10,000 ppb recommended exposure level for occupational exposure for workers, but higher than the ITSL of 7 µg/m^3, which is health protective for a continuous exposure over a lifetime. Therefore, If one were to assume that the peak TRS measurement of 2,300 ppb was only DMS, then this level of DMS would have a disagreeable odor without any other noticeable effects.

Ethanol

This chemical was detected in the air during two 5-minute air samples; one upwind of the fire and one downwind of the fire, and tested for VOCs. Ethanol (CAS# 64-17-5) is one of the VOCs measured. “Ethanol is a clear, colorless, flammable, volatile liquid with a sweet distinctive odor and a burning taste.”(ACGIH, 2008). An odor threshold of 84,000 ppb (160,000 µg/m^3) has been reported. ACGIH has a Threshold Limit Value – Short-Term Exposure Limit (TLV-STEL) of 1,000,000 ppb (1,900,000 µg/m^3) is recommended for ethanol vapor to protect from respiratory and ocular irritation. A TLV-STEL is a 15 minute exposure that should not be exceeded at any time during a workday. The highest value detected for ethanol was 68 µg/m^3 upwind of the fire, which is well below the odor detection limit and below the occupational workplace exposure limit for ethanol.

The MDEQ has set an ITSL for ethanol at 19,000 µg/m^3 based on an 8-hour averaging time. This value is based on the ACGIH TLV of 1,000,000 ppb (1,900,000 µg/m^3), which protects from respiratory and ocular irritation. The highest value detected for ethanol upwind of the fire was 68 µg/m^3, which is well below the MDEQ ITSL of 19,000 µg/m^3. No effects from ethanol would be reasonably anticipated to occur at this level of exposure.

Hydrogen Sulfide

One of the compounds that the TRS monitors for is hydrogen sulfide (CAS 7783-06-4). Hydrogen sulfide is a colorless, flammable, gas with a “rotten egg” smell. Some common names for the gas include sewer gas, swamp gas, and manure gas. It occurs naturally in crude petroleum, natural gas, and hot springs. In addition, hydrogen sulfide is produced by bacterial

breakdown of organic materials and human and animal wastes (e.g., sewage). Industrial activities that can produce the gas include petroleum/natural gas drilling and refining, wastewater treatment, coke ovens, tanneries, and paper mills. Hydrogen sulfide is heavier than air and may travel along the ground. It collects in low-lying and enclosed, poorly-ventilated areas such as basements, manholes, sewer lines, underground telephone vaults and manure pits. The primary exposure is by inhalation and the gas is rapidly absorbed by the lungs. The odor threshold for hydrogen sulfide is 0.5 to 300 ppb (0.7-420 µg/m^3) according to the ATSDR (2006). Hydrogen sulfide odors can persist in the air for an average of 18 hours; it is oxidized to sulfur dioxide and sulfuric acid (due to the length of time hydrogen sulfide reactions occur, sulfur dioxide and sulfuric acid arising from the fire incident would not affect the Detroit area).

The National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) is at 10,000 ppb (15,000 µg/m^3) for a ten minute period. This is the level recommended to limit the concentration of the potential hazard in the workplace to protect worker health. The Occupational Safety and Health Administration (OSHA) sets a permissible exposure limit (PEL) of 20,000 ppb (28,000 µg/m^3) for workplace safety with up to ten minutes at 50,000 ppb (70,000 µg/m^3) ceiling limit if there is no other exposure during a work shift. The TRS levels measured during the incident (Figure 2) had no minute periods that were above the NIOSH REL of 10,000 ppb either during the fire incident or after the fire incident. The highest TRS concentration detected in the air at the 2A-West Site Monitor was 2,300 ppb (3,200 µg/m^3). If one were to assume that the measured TRS consisted of only hydrogen sulfide, then at 2,000 to 5,000 ppb (2,800 to 7,000 µg/m^3), prolonged exposure may cause nausea, tearing of the eyes, irritation of the nose, throat, and respiratory system (e.g., cough, shortness of breath), headaches, or loss of sleep. Airway problems (bronchial constriction) could occur in some asthma patients with prolonged exposure. The effects can be delayed for several hours, or sometimes days. Repeated or prolonged exposures may cause eye inflammation, headache, fatigue, irritability, insomnia, digestive disturbances and weight loss (OSHA, 2013).

The MDEQ has set ITSLs for hydrogen sulfide of 2 µg/m^3 based on an annual averaging time and an acute ITSL of 100 µg/m^3 based on a 24-hour averaging time. The ITSL of 2 µg/m^3 (annual) is based on the EPA Reference Concentration (RfC). The RfC used a key study by Brenneman et al., (2000) exposed 10-week old male Sprague-Dawley CD rats (12 per exposure group) to 0, 10,000, 20,000, or 80,000 ppb (0, 14,000, 42,700, or 111,000 µg/m^3), hydrogen sulfide for 6 hours/day, 7 days/week for 10 weeks. At the end of the 10-week period, animals

were euthanized and their noses were examined. There were no effects in the animals given 10,000 ppb (14,000 µg/m^3) hydrogen sulfide. Olfactory mucosa lesions were observed in animals exposed to 30,000 ppb (42,700 µg/m^3) and 80,000 ppb (111,000 µg/m^3) hydrogen sulfide. The severity of the lesions increased with increasing dose. The US EPA used a no adverse effect level (NOAEL) of 10,000 ppb (14,000 µg/m^3) to calculate a human equivalent concentration (HEC) of 640 µg/m^3, then EPA used an uncertainty factor of 300 (10 for subchronic to chronic, 10 for sensitive individuals, and 3 for animal to human) yielding an RfC of 2 µg/m^3 (EPA, 2003a). MDEQ used the EPA RfC to establish an ITSL of 2 µg/m^3 (annual average).

The acute ITSL of 100 µg/m^3 (24-hour) was based on the ATSDR acute Minimal Risk Level (MRL) of 70 ppb (100 µg/m^3). The ATSDR MRL is based on a study by Jäppinen et al., (1990), which "evaluated lung function in three male and seven female subjects with bronchial asthma requiring medication for 1-13 years; none of the subjects had severe asthma. The subjects were exposed to 2,000 ppb hydrogen sulfide for 30 minutes. Respiratory function in response to a histamine challenge was assessed prior to exposure and after exposure. No statistically significant changes in forced vital capacity (FVC), forced expiratory volume in 1 second (FEV1), and forced expiratory flow were noted. Airway resistance (Raw) and specific airway conductance (SGaw) did not show statistically significant changes when examined as a group. In two subjects, there were changes of over 30% in both Raw and SGaw; these changes were suggestive of bronchial obstruction. Additionally, 3 of 10 subjects complained of headaches after exposure" (ATSDR, 2006). ATSDR used the 2,000 ppb (2,800 µg/m^3) concentration as a lowest observed adverse effect level (LOAEL) with an uncertainty factor of 27 (3 for LOAEL to NOAEL, 3 for human variability, 3 for database deficiencies – no studies in children) yielding an acute MRL of 70 ppb (100 µg/m^3) (ATSDR, 2006). MDEQ used the ATSDR MRL of 70 ppb (100 µg/m^3) to establish the acute ITSL of 100 µg/m^3. Therefore, the highest TRS concentration detected in the air at the 2A-West Site Monitor was 2,300 ppb (3,200 µg/m^3). If one were to assume that the measured TRS consisted of only hydrogen sulfide, then at 2,000 to 5,000 ppb (2,800 to 7,000 µg/m^3), prolonged exposure may cause nausea, tearing of the eyes, irritation of the nose, throat, and respiratory system (e.g., cough, shortness of breath), headaches, or loss of sleep. Airway problems (bronchial constriction) could occur in some asthma patients with prolonged exposure. The effects can be delayed for several hours, or sometimes days. Repeated or prolonged exposures may cause eye inflammation, headache, fatigue, irritability, insomnia, digestive disturbances and weight loss (OSHA, 2013).

Methyl Mercaptan

Methyl mercaptan (CAS# 74-93-1) is one of four reduced sulfur compounds that can be detected by the TRS monitor. “Methyl mercaptan is a flammable, water soluble, colorless gas that has a very disagreeable odor, which has been described as that of rotten cabbage…An odor threshold of 1.6 ppb (3.1 µg/m^3) has been reported” (ACGIH, 2008). Historically, Methyl mercaptan has been produced and added to natural gas due to its very low odor detection threshold; it was used to alert people to natural gas leaks. It has also been used as an intermediate in the production of pesticides, fungicides, and jet fuel, and in the synthesis of methionine and plastics. Methyl mercaptan is a by-product in the paper and pulp mill industries (ACGIH, 2013). Methyl mercaptan is a natural product of intestinal flora and can be metabolized to hydrogen sulfide (OSHA, 2013). The ACGIH TLV - TWA is 500 ppb (980 µg/m^3) with an 8-hour exposure for methyl mercaptan, while OSHA set a permissible exposure limit (PEL) at 500 ppb (1,000 µg/m^3) for the construction industry and maritime vessels and has set a PEL ceiling limit at 10,000 ppb (20,000 µg/m^3) for workplace safely for general industry. The NIOSH REL is 500 ppb (1,000 µg/m^3) ceiling for 15 minutes exposure. Of the three occupational exposure limits listed above, the ACGIH TLV of 500 ppb (980 µg/m3) has the best documentation to justify their value. ACGIH based their TLV on a rat inhalation study which showed body weight reductions and possible liver involvement at 57,000 ppb, but not at 17,000 ppb. There was a report of exposure in humans, students were accidentally exposed to about 4,000 ppb for several hours, experienced headaches and nausea. The next day, all exposed students but one, who had complained of headaches and nausea were normal. One exposed student still complained of headache the next day (Clayton et al.,1981). Some investigators have reported that the toxicity of methyl mercaptan is similar to hydrogen sulfide while others report the toxicity to be somewhat less than hydrogen sulfide (ACGIH, 2008).

The MDEQ has set an ITSL for methyl mercaptan at 10 µg/m^3 based on a 1-hour averaging time. Even though the documentation for the NIOSH REL was lacking it is a peer-reviewed occupational exposure level, therefore the ITSL is based on the NIOSH REL of 1,000 µg/m^3 (15-minute ceiling level) divided by an uncertainty factor of 100, and is designed to be protective against acute irritative effects on eyes, skin, and respiratory tract, which appear to be the most sensitive endpoints. But the odor threshold for this compound is so low that it would be a nuisance at levels well below the ITSL of 10 µg/m^3.

The highest TRS concentration detected in the air at the 2A-West Site Monitor was 2,300 ppb measured using one-minute data. The levels of TRS varied over the period of several hours on April 27th and April 28 well after the fire was extinguished. If one were to assume that the measured TRS consisted of only methyl mercaptan, the measured level and duration of TRS could quickly cause a disagreeable odor, there may be irritation of eyes, skin, mucous membranes, and respiratory tract; cough, sore throat; dizziness, headache; nausea; staggering gait, and shortness of breath. Using the student exposure case above as a guide, the symptoms headache and nausea would have dissipated by the day after exposure.

n-Hexane

This chemical was also detected during the 5-minute "grab" sample for VOCs. N-Hexane was detected at 3.2 µg/m^3 downwind of the fire and at 2.7 µg/m^3 upwind of the fire. The maximum detected level found at the Dearborn VOC monitor is 1.6 µg/m^3 for a 1-hour measurement. N-Hexane is a clear, volatile liquid with an odor threshold of 130,000 ppb (460,000 µg/m^3). ACGIH has set a TLV-TWA of 50,000 ppb (176,000 µg/m^3) as a recommendation for occupational exposure to n-hexane. "This value is intended to minimize the potential for neurotoxic effects, narcosis, and eye and mucous membrane irritation. A skin notation is also assigned, based on the reported human peripheral neuropathy following dermal contact and absorption of n-hexane" (ACGIH, 2008).

The MDEQ has set an ITSL for n-hexane at 700 µg/m^3 based on a 24-hour averaging time, which is based on an EPA Reference Concentration for Chronic Inhalation Exposure (RfC) of 700 µg/m^3 derived from a study by Huang et al., (1989) 16-week rat inhalation study that found a change in motor nerve conduction velocity in rats exposed to n-hexane. Male Wistar rats (8/group) were exposed to 0, 500, 1,200,000, or 3,000,000 ppb (0, 1,762,000, 4,230,000, or 10,574,000 µg/m^3) n-hexane for 12 hours/day, 7 days/week for 16 weeks. "The authors measured motor nerve conduction velocity (MCV) in the tail nerve along with body weight before exposure and after 4, 8, 12, and 16 weeks of exposure to n-hexane" (EPA, 2005). A dose-dependent, statistically significant reduction in body weight gain was observed at 8 weeks in 3,000,000 ppb (10,574,000 µg/m^3) rats and at 12 weeks in 1,200,000 ppb (4,230,000 µg/m^3) rat group. Rats exposed to 1,200 ppm (4,230,000 µg/m^3) and 3,000,000 ppb (10,574,000 µg/m^3) showed a reduction in MCV. This reduction was statistically significant during weeks 8 through 16 of the study when compared to controls. On histopathology, there was "increased incidence

of paranodal swellings, along with some evidence of demyelination and remyelination, which was present in the peripheral nerves at both" 1,200,000 ppb (4,230,000 µg/m^3) and 3,000,000 ppb (10,574,000 µg/m^3) (EPA, 2005). The NOAEL was 500,000 ppb (1,762,000 µg/m^3) for neurophysiological deficits and histopathological effects. The EPA used the benchmark dose methodology to determine a statistical lower confidence limit on the concentration at which an adverse effect may occur. The highest level of n-hexane detected downwind of the fire was 3.2 µg/m^3, which is significantly below the odor detection threshold of (460,000 µg/m^3) and well below the MDEQ ITSL of 700 µg/m^3. No effects from n-hexane would be reasonably expected to occur at this level of exposure.

Propene

This chemical was detected as part of a 5-minute air sample taken during the fire incident at Marathon. Propene (also known as propylene) was detected at 7.6 µg/m^3 downwind of the fire incident and at 7.2 µg/m^3 upwind of the fire. The maximum detected level at the Dearborn monitor is 0.00142 µg/m^3 for a 1-hour measurement. Propene is a colorless, flammable gas with an odor characteristic of olefins (ACGIH, 2008). Propene "is produced commercially as a byproduct of either ethylene manufacture or refinery operations" (ACGIH, 2008). The odor threshold has been reported as 17,000 ppb (29,000 µg/m^3) for detection, 58,000 ppb (100,000 µg/m^3) for recognition, and 80,000 ppb (140,000 µg/m^3) for 100% recognition (ACGIH, 2008). ACGIH has a TLV-TWA of 500,000 ppb (860,000 µg/m^3) as recommended for occupational exposure to propene. This value is intended to prevent changes in nasal mucosa, based on chronic animal studies.

The MDEQ has set an ITSL for propene at 1,500 µg/m3 based on a 24-hour averaging time. This ITSL is based on an NTP (1985) study where groups of 50 F344/N rats and 49 or 50 $B_6C_3F_1$ mice of each sex were exposed to propene at concentrations of 0, 5000000, or 10000000 ppb (0, 8600000, or 17000000 µg/m^3) for 6 hours/day, 5 days/week for 103 weeks. Increased incidence of squamous metaplasia of the respiratory epithelia of the nasal cavity was observed in female rats at the 5,000,000 and 10,000,000 ppb (8,600,000 and 17,000,000 µg/m^3) dose levels, and in male rats at the 10,000,000 ppb (17,000,000 µg/m^3) dose level. Increased incidence of chronic focal inflammation of the kidney was observed in male and female mice at the 5,000,000 and 10,000,000 ppb (8,600,000 and 17,000,000 µg/m^3) dose levels. A LOAEL of 5,000,000 ppb (8,600,000 µg/m^3) was identified from the NTP (1985) study

and was used to determine the ITSL of 1,500 µg/m^3. The highest level of propene was 7.6 µg/m^3 detected downwind of the fire; this value is far below the ACGIH occupational exposure level of 500,000 ppb (860,000 µg/m^3) and well below the MDEQ ITSL of 1,500 µg/m^3. No effects from propane would be reasonably expected to occur at this level of exposure.