EnvironmentAsia
The international journal by the Thai Society of Higher Education Institutes on Environment

EnvironmentAsia 14(1) 2021 1-12
DOI 10.14456/ea.2021.1
ISSN 1906-1714; ONLINE ISSN: 2586-8861

Characteristics and Dispersion Modeling of VOCs Emission Released from the Tank Farm of Petroleum Refinery Complex

Suwadi Saikomol[1], Sarawut Thepanondh[1,2*], Wanna Laowagul[3],
Wissawa Malakan[1], Jutarat Keawboonchu[1] and Vanitchaya Kultan[1]

[1] *Department of Sanitary Engineering, Faculty of Public Health, Mahidol University, Thailand*
[2] *Center of Excellence on Environmental Health and Toxicology (EHT), Bangkok, Thailand*
[3] *Environmental Research and Training Center, Department of Environmental Quality Promotion, Ministry of Natural Resources and Environment, Thailand*

* Corresponding author: sarawut.the@mahidol.ac.th

Received: June 22, 2020; Revised: August 8, 2020; Accepted: August 22, 2020

Abstract

Characteristics and dispersion modeling of VOCs emitted from the tank farm of petroleum refinery complex were evaluated in this study. Gas phase VOCs within aboveground storage tank from all types of petroleum raw materials and products were sampled by the Tedlar bags prior be transferred to 6-Liter evacuated canisters and analyzed to determine their types and concentrations using the Gas Chromatography Mass Spectrophotometer (GC/MS) in accordance with the US.EPA TO-15 compendium method. Results indicated that alkane was the dominant compound in which pentane is the major contributor in total VOCs. Fraction of the concentration of pentane in total VOCs was then used to estimate its emission for further used as an input to evaluate the ambient ground level concentration of pentane through the simulation of the AERMOD dispersion model. Predicted 1-hr average concentrations were calculated to the 5-minutes average using the concept of the peak to mean concentration with the objective to evaluate the extent and magnitude of odor impacts caused by pentane. Results indicated that the highest predicted concentrations of pentane within the modeling domain simulated under the existing operation of the refinery were exceeded their RfC and odor threshold. Alternative mitigation measures to reduce emission of pentane were evaluated and compared with the existing business as usual of the refinery. Results suggested that adding of the secondary seal to the floating roof of crude oil storage tank will be the most appropriate measure taking into consideration its success in decreasing both of the emission and ground level concentration of pentane as well as demonstrate as the cheapest capital cost per unit of ambient concentration reduction. This study highlights the important in elucidating the source-receptor relationship which will assist in quantification of the contribution of emission sources towards the ambient air concentrations. Effectiveness and appropriate of mitigation control scenarios to be applied for industrial air pollution management should be taking into consideration not only their success in emission control but also on their achievement in reducing level of pollutants in the environment.

Keywords: AERMOD; Emission; Odor; Petroleum refinery; Storage tank; VOCs

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1. Introduction

Odor released from refineries may cause both social and ecological problems, due to the complaints of residents who live near these sources (Zhang *et al.*, 2018). Some studies demonstrate that the exposure to odors to high level in a short term, especially volatile organic compounds (VOCs) (Jafarinejad, 2016), may cause different effects on human beings, ranging from emotional stresses such as states of anxiety, unease, headache or depression to physical symptoms

(Claeson *et al.,* 2013). Nausea, frequent diarrhea, and excessive tiredness have been associated with exposure to annoying odor (Herr *et al.,* 2009). Moreover, odorous gases emitted from storage tank can exert a negative influence on the surrounding environment and significantly lower the quality of life. Industrial growth and rapid urbanization, especially in developing countries, including Thailand, are of the main causes in deteriorating urban air quality in recent years. For this reason, odors are nowadays subject to control and regulation in many countries (Nicell, 2009).

Organic storage farm is one of the units of the petroleum and petrochemical industries potentially release the odorous compounds. Several studies reported the necessity to control this emission source particularly when the odor nuisances were concerned. Operation of petroleum refinery which relevant to various types of VOCs emission from their storage tanks including both raw materials (such as crude oil) and their petroleum refined products was evaluated in this study. Qualitative and quantitative analysis of the characteristics of VOCs released from each petroleum products was analyzed through the direct measurements. The dominant VOCs were selected to evaluate for its extent and magnitude towards the potential odor impacts which could be affected to the people living in the vicinity of the refinery. The appropriate mitigation measures to reduce emissions and concentrations of odor compound were proposed taking into consideration their cost-effectiveness of implementations.

2.Methodology

2.1 Study area

Aboveground storage tanks located in the Thaioil refinery complex were chosen as the study factory in this study. The refinery is own by the Thai Oil Public Company Limited. It is located in Chonburi province, Eastern region of Thailand as illustrated in Figure 1. The company provides a complex refinery utilizing modern technology to produce petroleum products primarily for domestic distribution. Totally, there were 63 aboveground storage tanks (fixed and floating roof types) contained various types of raw materials and petroleum products operated in this refinery.

2.2 VOCs within aboveground storage tank

Direct measurement of gas phase VOCs within aboveground storage tank was conducted to determine their types and concentration. Nine storage tanks representing storage tank of every petroleum products and raw materials of the studied refinery were selected for air samplings. The gas samples within each liquid storage tank were collected into the Tedlar sampling bags and then transferred to the pre-cleaned 6 Liters canister (Entech, USA) at the laboratory prior their analysis. The US EPA TO-15 method was used to quantify the concentrations of individual VOCs. Firstly, sample from each canister was

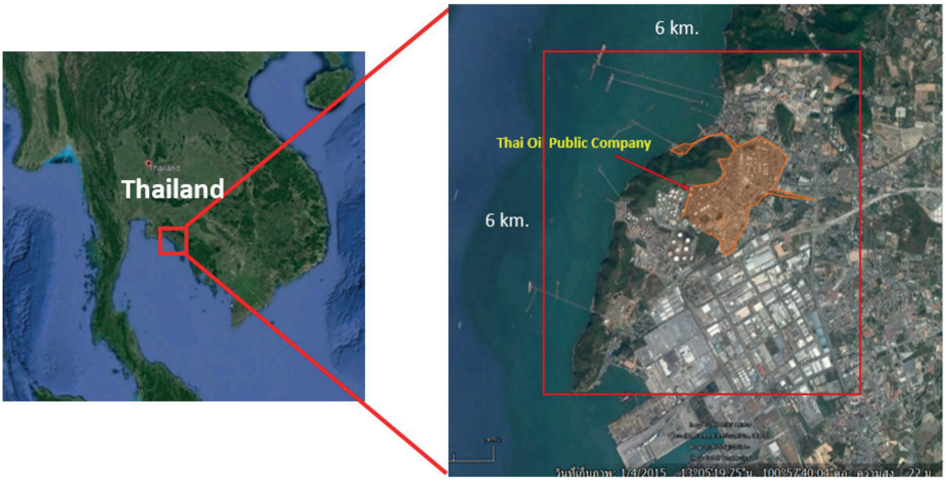


Figure 1. Study domain

loaded into a pre-concentration system (Entech 7200, USA). They were then introduced to a Gas Chromatography (GC) system (Agilent 7890B) where individual compounds were separated using chromatographic temperature profiles and detected by a mass spectrometer (MS) system (Agilent 5977A). Target VOCs were identified and quantified by using the specific retention time and peak area of the corresponding standard. Amount of each VOCs were determined by calculating their peak area obtained from preparing of the calibration curves using different concentrations of VOCs standard gases (Saikomol *et al.,* 2019).

2.3 Dispersion modeling

The AERMOD dispersion model was used in this study. It is a steady-state plume model proved to be effective for the simulation of the dispersion of odors (Wang *et al.,* 2006). The model calculates the vertical and horizontal dispersion of air pollutant concentration following the Gaussian distribution. The vertical distribution is described with a bi-Gaussian probability density function, but the horizontal distribution is also assumed to be Gaussian. AERMOD was preferred for a short-range (<50 km) to predict the dispersion and ambient concentration of air pollutants in normal and complex terrain as well as the dispersion in convective conditions (Dimitrakakis *et al.,* 2013). The model requires two different kinds of input data: sites-specific meteorological data, and local topographical feature. The modeling system consists of one main program (AERMOD) and two preprocessors (AERMET and AERMAP). The AERMOD meteorological preprocessor (AERMET) organizes the surface characteristics of the land surrounding the site together with the hourly surface meteorological data to produce the parameters that affect dispersion, such as albedo, Bowen ratio, and roughness for dispersion calculations in AERMOD. The AERMOD terrain preprocessor (AERMAP) uses gridded terrain data to calculate receptor and source elevation data and terrain height scale that are used by AERMOD when calculating air pollutant concentration (Ashrafi *et al.*, 2012; Silverman *et al.*, 2007). This model was developed to provide an estimation on ambient chemical concentrations primarily for regulatory purposes and has been intensively used in many countries including Thailand (Cimorelli *et al.,* 2004; Heckel and LeMasters, 2011; Jampana *et al.,* 2004; Poosarala *et al.,* 2009).

In this study, AERMOD was configured to simulate the ground level concentration of selected VOCs in the modeling domain of 6 km x 6 km from the center of the refinery. Finest grid spacing was set as 100 m. Emission data obtained from direct measurement and TANKS 4 calculation from all the 63 aboveground storage tanks were simulated (as point sources) as emission input to the model. Sequential analysis of 1-hr average ambient concentrations at 7 discrete receptors were evaluated using the local meteorological input from the 1st hour of the 1st January 2015 to the 24th hour of the 31st December 2015. Spatial distribution of the receptors is illustrated in Figure 2.

Figure 2. Discrete receptors within the study area

3. Results and discussion

3.1 Characteristics of VOCs released from aboveground storage tank

Direct measurements of gas phase VOCs inside the aboveground storage tank were conducted to determine their types and concentrations. Totally, they were 63 storage tanks in this refinery. Among them, 9 storage tanks were selected for air samplings as previously presented in Chapter 3.2. Characteristics of vapor in the storage tank in this study was presented in Table 1. Totally, there were 27 speciated VOCs species measured from samples. The major VOCs species from 9 storage tanks were mainly alkane such as pentane, cyclopentane and cyclohexane. Among the 7 alkane components, the concentration of pentane was the highest (46,030 ppbv), which was predominantly attributable to evaporation loss. The highest pentane concentration was emitted from crude oil (8,671 ppbv), followed by cyclopentane (30,973 ppbv) and cyclohexane (14,969 ppbv), respectively. These alkanes represented 91.6 % of total alkane concentration. Finding in this study is consistent with Li *et al.* (2018) which reported that alkanes were the dominant VOCs group from the petrochemical industry. In addition, toluene, styrene, and 1, 2, 4-trimethylbenzene were the most abundant in aromatic hydrocarbons. Emissions of these compounds were from the storage tank contained heavy vacuum gas oil and unleaded gasoline. In summary, concentrations of alkanes, alkenes, aromatic hydrocarbons, aldehyde, and others were 100,448 ppbv (62.88%), 49,274 ppbv (30.86%), 840 ppbv (0.51%), 48 ppbv (0.03%), and 9,112 ppbv (5.70%), respectively.

3.2 Spatial distribution of pentane emitted from tank farm of Refinery

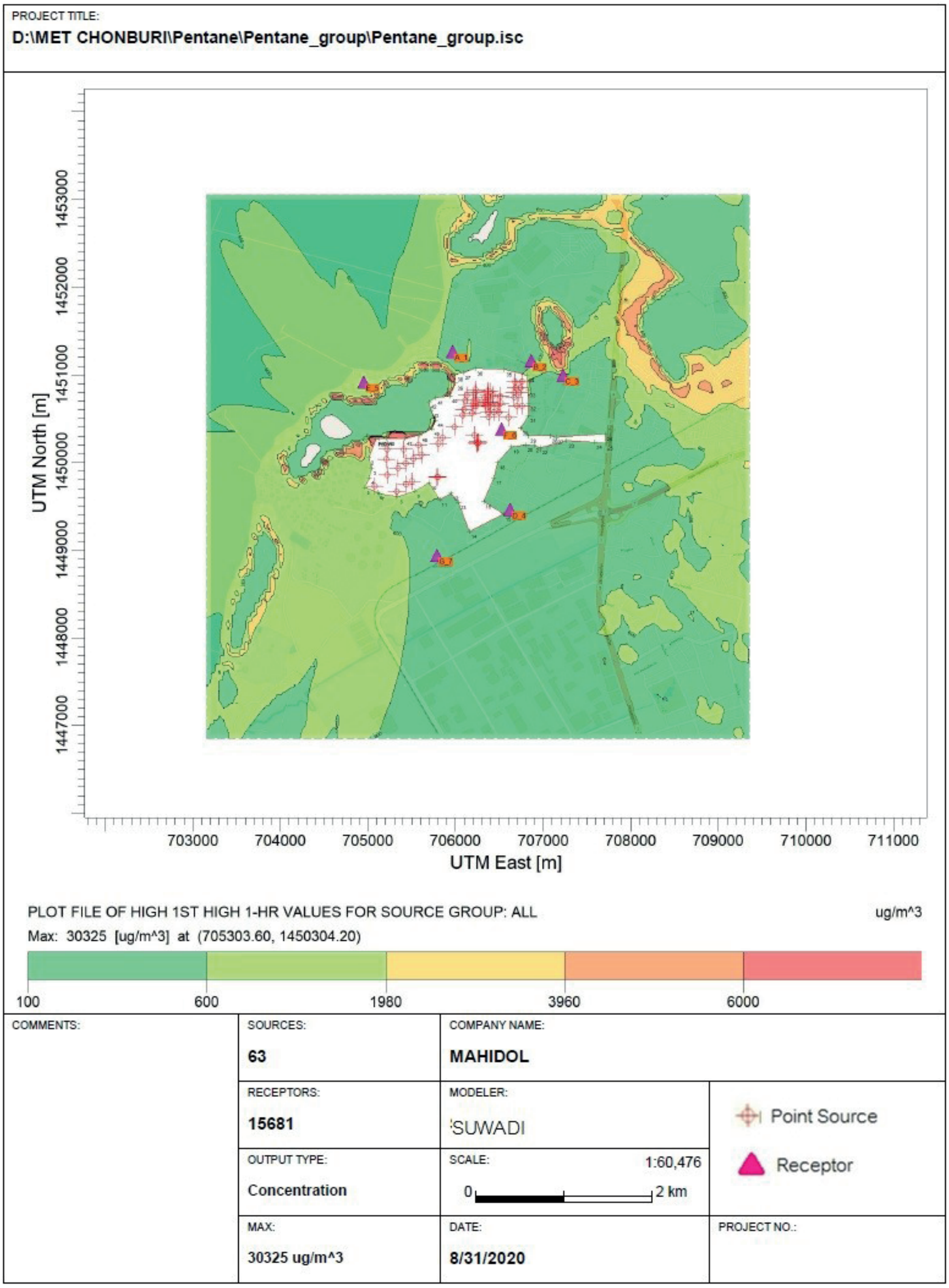
Results from direct measurement of vapor within the storage tanks revealed that pentane was the most abundant compound among measured VOCs. Details were elaborated elsewhere (Saikomol *et al.*, 2019). Therefore, pentane was chosen for the intensive analysis of VOCs dispersion and their possible impacts in this study. Spatial evaluations of pentane concentrations were carried out through the simulation of AERMOD model under 2 different scenarios. Scenario 1 represented the existing operation of the refinery (existing emission). Adding or modification of control equipment and technologies to the exiting storage tanks were tested for their success in emission and ambient concentration reductions under scenario 2.

Spatial distribution of maximum 1-h average pentane concentration under the exiting operation (scenario 1) is illustrated in Figure 3. Predicted highest concentrations at the receptors were lower than the reference concentration (RfC) of pentane (< 1,000 μg/m^3) and its odor threshold (6,492 μg/m^3). Therefore, the health and odor nuisance impact caused by pentane released from this emission source could be negligible. However, the highest concentration of pentane within the modeling domain was predicted as 30,325 μg/m^3. This level was almost 5 times higher than the value of pentane's odor threshold. We further evaluated the source contribution to this maximum concentration and found that Tank No. T3002 and T3079 (storage of crude oil) were the main contributors. Therefore, measures to reduce emission from these storage tanks were introduced and were evaluated for their success in the reduction of emission and ambient concentration under scenario 2. Mitigation measures under this scenario included a) installing of the vapor recovery unit (VRU); b) installing of the secondary rim seal to the tank and c) modification of the external floating roof to domed external floating roof.

As for scenario 2(a), analytical results indicated that the highest value of ground level concentration of pentane could be decreased to 22,370 μg/m^3 as illustrated in Figure 4. Maximum ground level concentration of pentane under scenario 2(b) and 2(c) were predicted at 22,301 and 22,279 μg/m^3 and are presented in Figure 5 and Figure 6, respectively.

Table 1. Chemical compositions of vapor in the storage tank (unti: ppbv)

VOCs	JET	Heavy vacuum gas oil	Gasoil	Kerosene	Crude oil	Crude slop	Fuel oil	High speed diesel oil	Unleaded gasoline
Alkane									
Pentane	4,865	3,833	2,385	1,219	8,671	4,623	5,562	6,987	7,885
Cyclopentane	4,504	2,637	2,248	1,433	3,609	2,777	3,564	4,666	5,535
Cyclohexane	1,555	1,055	719	545	2,199	2,421	2,181	3,466	828
Hexane	837	568	479	422	1,074	1,128	1,078	1,205	592
Isopropyl Alcohol	143	24	5.8	6.0	11	4.2	7.5	4.2	13
Dichloromethane	77	140	65	70	74	68	70	70	58
Propane, 2-Methoxy-2-methyl (MTBE)	12	2.7	8.0	4.3	-	0.31	0.62	0.39	154
Alkene									
Propene	455	8,368	620	96	2,814	2,615	12,116	1,265	874
Isobutene	188	2,906	188	91	1,204	1,228	12,185	1,091	929
Isoprene	2.7	5.0	2.6	2.3	3.5	3.4	5.4	3.5	12.9
Aromatic									
Toluene	27	46	33	23	27	19	24	17	30
Styrene	15	31	15	15	15	15	15	15	16
1,2,4-Trimethylbenzene	13	22	12	12	10	10	10	10	14
m/p-Xylene	15	21	13	11	8.0	7.7	7.7	7.7	16
1,3,5-Trimethylbenzene	8.2	14	7.5	7.2	6.3	6.1	6.2	6.1	8.6
o-Xylene	7.9	10	6.3	5.4	3.3	3.1	3.1	3.0	7.8
Ethylbenzene	3.4	2.8	2.2	1.8	0.67	0.61	0.59	0.55	3.4
1,2,3-Trimethylbenzene	9.4	17	8.9	8.7	8.2	8.1	8.1	8	10
Aldehyde									
Methacrolein	4.1	7.0	3.9	3.6	6.0	5.9	7.1	6.0	4.5
Alcohol									
1-Propanol	5.1	13	4.9	4.8	5.8	5.2	7.7	5.1	4.7
Chlorinated hydrocarbon									
1,2-Dichloropropane	-	-	3.6	-	6.3	-	8.4	10.6	3.2
Ketone									
Methyl vinyl ketone	716	593	445	338	1040	1110	1065	1470	515
3-Hexanone	47	43	27	34	17	31	29	41	40
Halogenated compound									
Chloroform	3.9	1.2	2.6	1.3	11	12	18	12	5.1
Organochloride									
1,1,2-Trichloroethane	82	61	46	67	110	113	110	114	63
Alkyl aldehyde									
Hexanal	25	28	18	16	28	23	28	23	21
Total	13,693	20,473	7,393	4,453	21,005	16,271	38,172	20,554	17,686



PROJECT TITLE:
D:\MET CHONBURI\Pentane\Pentane_group\Pentane_group.isc

PLOT FILE OF HIGH 1ST HIGH 1-HR VALUES FOR SOURCE GROUP: ALL

Max: 30325 [ug/m^3] at (705303.60, 1450304.20)

COMMENTS:

SOURCES: 63

COMPANY NAME: MAHIDOL

RECEPTORS: 15681

MODELER: SUWADI

OUTPUT TYPE: Concentration

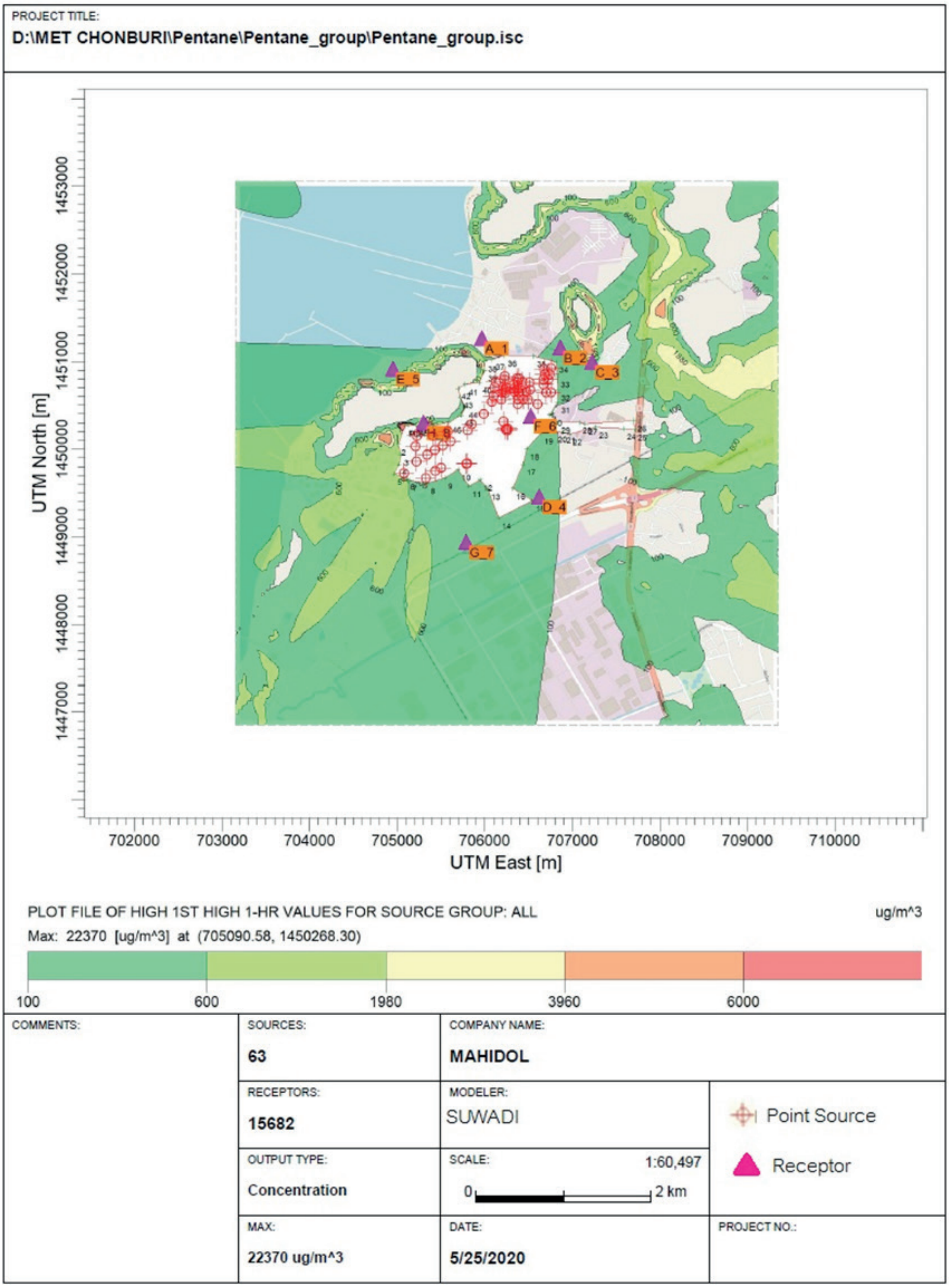
SCALE: 1:60,476

MAX: 30325 ug/m^3

DATE: 8/31/2020

PROJECT NO.:

Figure 3. Spatial distribution of maximum 1-h average pentane concentrations (Scenario 1: existing operation)



PROJECT TITLE:
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PLOT FILE OF HIGH 1ST HIGH 1-HR VALUES FOR SOURCE GROUP: ALL ug/m^3
Max: 22370 [ug/m^3] at (705090.58, 1450268.30)

COMMENTS:

SOURCES: 63

COMPANY NAME: MAHIDOL

RECEPTORS: 15682

MODELER: SUWADI

OUTPUT TYPE: Concentration

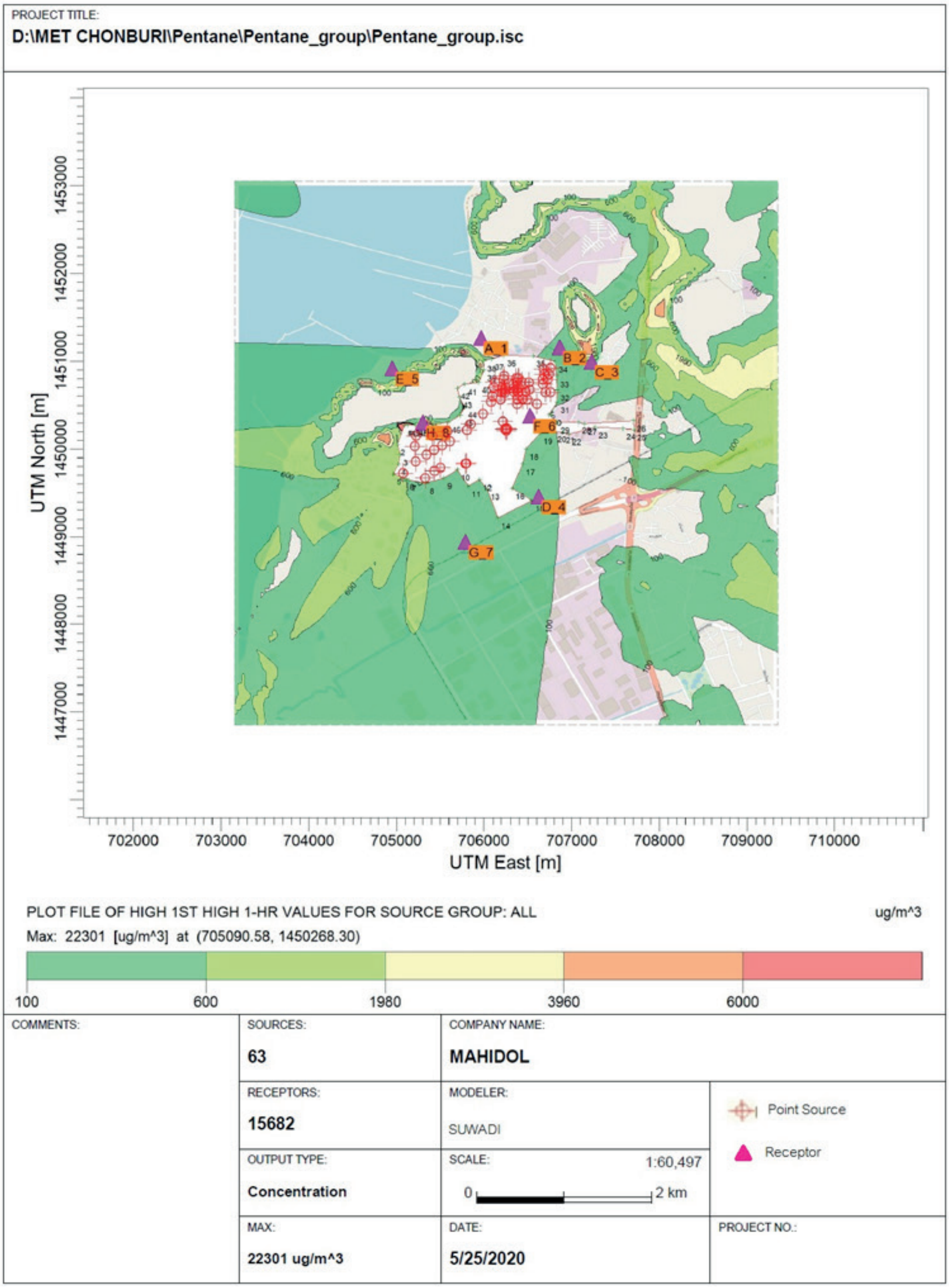
SCALE: 1:60,497 0 2 km

MAX: 22370 ug/m^3

DATE: 5/25/2020

PROJECT NO.:

Figure 4. Spatial distribution of maximum 1-h average pentane concentrations (Scenario 2(a): after installation of VRU)



PROJECT TITLE:
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PLOT FILE OF HIGH 1ST HIGH 1-HR VALUES FOR SOURCE GROUP: ALL ug/m^3
Max: 22301 [ug/m^3] at (705090.58, 1450268.30)

COMMENTS:

SOURCES: 63

COMPANY NAME: MAHIDOL

RECEPTORS: 15682

MODELER: SUWADI

OUTPUT TYPE: Concentration

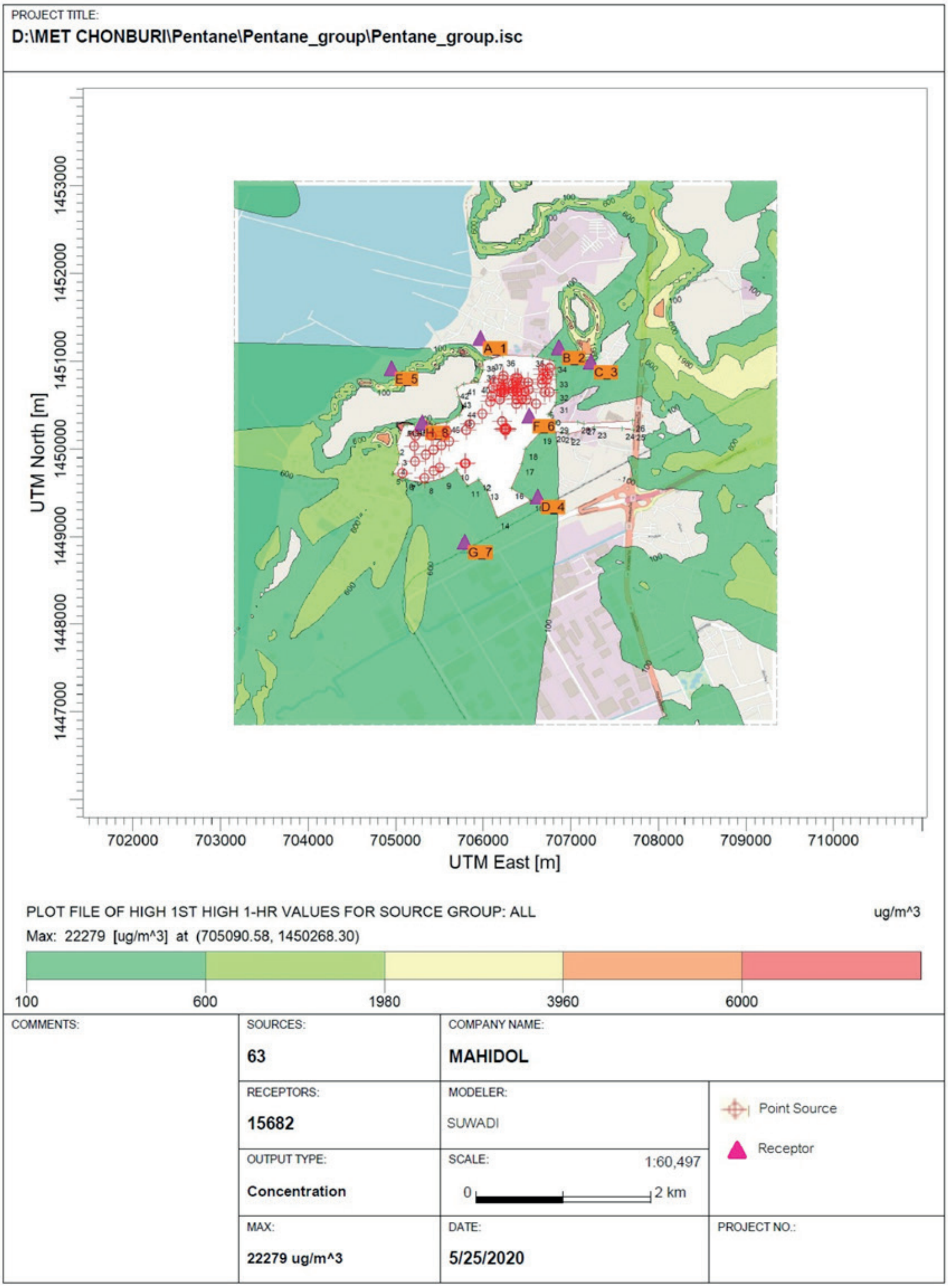
SCALE: 1:60,497
0 2 km

MAX: 22301 ug/m^3

DATE: 5/25/2020

PROJECT NO.:

Figure 5. Spatial distribution of maximum 1-h average pentane concentrations (Scenario 2(b): after installation of secondary seal)



PROJECT TITLE:
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PLOT FILE OF HIGH 1ST HIGH 1-HR VALUES FOR SOURCE GROUP: ALL
ug/m^3
Max: 22279 [ug/m^3] at (705090.58, 1450268.30)

COMMENTS:

SOURCES: 63

COMPANY NAME: MAHIDOL

RECEPTORS: 15682

MODELER: SUWADI

OUTPUT TYPE: Concentration

SCALE: 1:60,497
0 2 km

MAX: 22279 ug/m^3

DATE: 5/25/2020

PROJECT NO.:

Figure 6. Spatial distribution of maximum 1-h average pentane concentrations (Scenario 2(c): modification to domed external floating roof)

Table 2. Mitigation measures analysis (US$)

No.	source ID	Total capital cost (US$)	Emissions		Concentrations		Cost per unit of emission reduction		Cost per unit of ambient concentration reduction		Prioritization
			Before (kg/y)	After (kg/y)	Before (ug/m^3)	After (ug/m^3)	Cost US$/kg	Percentage of reduction from total emissions	Cost (US$/1ug/m^3)	Percentage of reduction in ambient concentrations	
2(a)	VRU installation	909,090	4,405.6	220.28	30,325	22,370	217	95.00	114.2	26.23	3
2(b)	Secondary Seal	30,303		2,221.15		22,301	14	49.58	3.7	26.46	1
2(c)	Domed external floating roof	454,545		1,300.60		22,279	146	70.48	56.5	26.53	2

Note: *calculated from the fraction of ambient concentrations contributed from the factory (not include from other factories)

3.3 Appropriate mitigation scenarios analysis

Cost of implementations towards reductions of emissions (per emission amount) and ambient concentrations (per µg/m^3) were evaluated. Results were used to analyze for the appropriateness of measures. Prioritization of measures which should be implemented taking into consideration their effectiveness on managing of released VOCs and economic aspects were presented for further management of VOCs in the factory. Output from the data analysis under this concept is as presented in Table 2. It is found that even though the measure 2(a) "installation of VRU" can lead to a great success in emission reduction but it has less sensitive to the reduction of predicted ambient concentration. On the other way, increasing of seal fabric to two layers implemented as scenario 2(b) which having the lowest capital cost could be the most cost effective measure in reducing both emission and ambient concentration as determined by its lowest cost per unit of emission and ambient concentration reductions. Therefore, this scenario was evaluated as the most appropriate measure to be implemented for the management of VOCs released from the aboveground storage tank of the petroleum refinery in this study.

4.Conclusion

Characteristics of VOCs emitted from the aboveground storage tank of petroleum refinery were evaluated in this study. Direct measurements of VOCs within the tank were conducted for all the raw materials and petroleum products of the refinery. Analysis of VOCs was performed using the gas chromatography/mass spectrophotometer (GC/MS) following the US EPA TO-15 method. Results indicated that pentane was the dominant species potentially released from this emission source. These concentration data were used to determine emission of pentane and were further used as an input data to the AERMOD dispersion model to evaluate the spatial distribution of ambient ground level concentration of pentane. It was found that the 1-hr average maximum ground level concentration predicted at selected discrete receptors were found below of the RfC and odor threshold values of pentane. However, the predicted highest concentration within the modeling domain was higher than reference limits. Therefore, the intensive analysis was conducted to evaluate the appropriate mitigation measures which should be implemented to control both emission and ambient concentration of pentane. Several control scenarios were tested against with the existing operation of the refinery. Appropriateness of the scenarios were evaluated taking into consideration both of their success in reduction of ambient concentration and their cost-effectiveness of the implementation. It was found that the increasing of seal fabric of the floating roof tank of crude oil to two layers was the most appropriate measure under this assumption. This study demonstrates the important in elucidating the source-receptor relationship which will assist in quantification of the contribution of emission sources towards the ambient air concentrations. Effectiveness and appropriate of mitigation control scenarios to be applied for industrial air pollution management should be taking into consideration not only their success in emission control but also on its achievement in reducing level of pollutants in the environment. Prioritization of the measures is necessity in order to identify the optimal levels of emission control and the require budget need to invest implementing those measures should be considered for their cost-effectiveness of implementation.

Acknowledgements

This study was conducted in collaboration with the Environmental Research and Training Center (ERTC) under the Department of Environmental Quality Promotion (DEQP) of Thailand. The authors would like to thank ERTC in supporting the direct measurement of VOCs. The Ph.D. scholarship was granted by the Research and Researchers for Industries-RRI program under the National Research Council of Thailand (NRCT). Our sincere thanks to the Thaioil Public Company limited for their support in conducting this research. This study was partially supported for publication by the Faculty of Public Health, Mahidol University, Thailand.

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