Source Contribution of 1,3 Butadiene in the Vicinity of Petrochemical Industrial Area

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Abstract

Emissions and ambient concentrations of 1,3 butadiene released from the synthetic rubber industries in the largest petroleum and petrochemical complex in Thailand were evaluated in this study. The industrial emissions in this analysis were those emitted from process fugitive, combustion stack, flare, and wastewater treatment facility. It was found that wastewater treatment units were the largest emission source among other potential sources. The contribution of emission from wastewater treatment plants were about 92% of total 1,3 butadiene emission. The extent and magnitude of 1,3 butadiene in ambient air were further evaluated through the simulation of AERMOD dispersion model using these emission data together with local meteorological and topographical characteristics. Predicted annual 1,3 butadiene concentrations at every receptor were lower than its ambient air quality standard ($< 0.33 \ \mu g \ m^{-3}$). Source apportionment analysis was performed with the objective to reveal the contribution of each emission source to the ambient concentrations at each receptor. Analytical results indicated that wastewater treatment units were the major emission source affected to the environmental concentrations of 1,3 butadiene in the study area. Evaluation of the potential adverse health impact of this chemical revealed that there may be a potential carcinogenic risk from inhalation exposure of 1,3 butadiene. Therefore, an effort in controlling emission of 1,3 butadiene should be given the priority to effectively manage the level of this compound in the environment.

Keywords: AERMOD; 1,3 Butadiene; Map Ta Phut; Source contribution; Synthetic rubber industry

Introduction

Volatile organic compounds (VOC) are any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate [1]. Emission sources of VOC include anthropogenic sources such as vehicles exhaust, industry process and fuel evaporation as well as biogenic emission

sources such as those released from broad-leave species [2–4]. Some of VOC species can have direct health impact and be considered as carcinogenic substance [5–7]. Some of them can also act as precursors of secondary air pollutants (tropospheric ozone and secondary organic aerosol) which indirect deteriorate to environmental quality [8].

1,3 butadiene is a volatile organic compound used in the production of synthetic rubber. The major end use of the synthetic rubber is automobile tires. 1,3-butadiene is also used to produce high impact polystyrene and acrylonitrile-butadiene-styrene (ABS) resin plastics. This manufacturing process is the major source of 1,3-butadiene released to the ambient air [9–11].

As for toxicity, 1,3 butadiene can cause irritation of the upper respiratory tract. Coughing and bronchospasm can occur, especially in susceptible individuals, such as persons with asthma. It is also classified as probable carcinogen in human (causing lymph and blood cancer in human) [9, 11].

In Thailand, the annual standard of 1,3 butadiene concentration in the ambient air has been designated as 0.33 $\mu g\ m^{-3}$ [12]. Monitoring data of 1,3 butadiene concentrations during the year 2013 – 2019 in the vicinity of the Map Ta Phut Industrial Estate (MTPIE), Rayong Province [13] where the major synthetic rubber industries are located is presented in Table 1. [14]. This monitoring data showed that the existing levels of 1,3 butadiene in this industrial area exceed their annual concentration. It was found existing 1,3 butadiene concentrations in this area were higher than annual standard. This research is aimed to evaluate the extent and magnitude as well as spatial distribution of 1,3 butadiene emitted from their industrial emission sources in the vicinity of MTPTE zone. Source apportionment of 1,3 butadiene is assessed through the application of the atmospheric dispersion model to identify the contribution of each emission source to the ambient concentration of 1,3 butadiene at the selected receptors and within the study domain.

Materials and methods
1) Emission data

Emission data used in this study were collected from the synthetic rubber industries in MTPIE. Emission sources of 1,3 butadiene used in the analysis included process fugitives, stack combustion, flare, wastewater treatment unit and storage tanks. Characteristics of each emission sources were also collected and be used as input data in the air dispersion model. Total emission amount of 1,3 butadiene used in this analysis was 1964.70 kg a^{-1}. This value was much higher than those reported in the Thai PRTR (Pollutant Release and Transfer Registration) of 579 kg a^{-1} [15]. This data clearly indicated that there are still lack of data completeness in the PRTR report. In this study, emission of 1,3 butadiene from wastewater treatment facilities were included. Total release from this source group was about 1798 kg a^{-1} (about 92% of total emission) as illustrated in Figure 1. Summary of emission rate of each source group is summarized in Table 2.
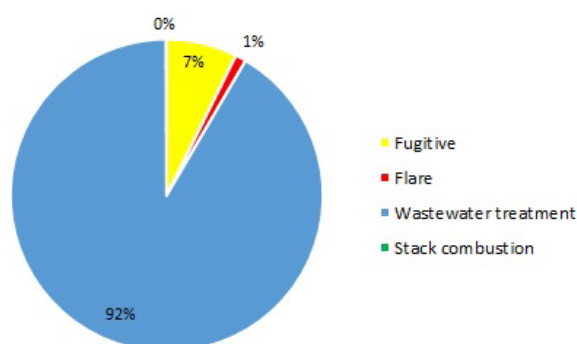
Figure 1 Total emission of 1,3 butadiene.

Table 1 1,3 butadiene ambient air concentration in the vicinity of the MTPIE zone

Station	Average annual 1,3 butadiene concentration ($\mu g\ m^{-3}$)						
	2013	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**
CBP (Chumchon Ban Phlong)	1.30	1.90	0.37	0.66	0.86	2.38	0.28
MMTP (Mueang Mai Map Ta Phut)	0.67	1.30	0.64	0.78	0.61	4.14	0.75
HMTP (Health Promoting Hospital Map Ta Phut)	0.70	0.48	0.04	0.58	0.20	0.95	0.52
MBN (Moo Ban Nopphaket)	0.12	0.06	0.56	0.05	0.05	0.21	0.08

Remark: Annual standard of 1,3 butadiene air concentration in Thailand is 0.33 $\mu g\ m^{-3}$

Table 2 Emission rate of 1,3 butadiene from each emission group

| Emission group	Emission rate	Unit	Emission loading calculation
Fugitive	2.45×10^{-5}	$g\ s^{-1}\ m^{-2}$	US.EPA method 21
Flare	7.00×10^{-4}	$g\ s^{-1}$	US.EPA AP42
Wastewater treatment	5.20×10^{-4}	$g\ s^{-1}\ m^{-2}$	WATER 9 model
Stack	2.89×10^{-5}	$g\ s^{-1}$	US.EPA AP42

2) Model configuration

AERMOD (Version 9.9.0) of the Lake Environmental was used in this study. This model was developed by the American Meteorology Society and United States Environmental Protection Agency (US EPA). It is a steady-state model which assumes that a plume disperses in the horizontal and vertical directions resulting in Gaussian (i.e., bell shaped) concentration distributions [16–17]. This model is a regulatory model used by the US EPA and has been widely applied as a useful tool to estimate source-receptor relationships of air pollutants as well as assessing the contributions from different emission sources to establish a control strategy [18–19].

The steps involved in AERMOD modeling are illustrated in Figure 2. The modeling domain in this study was centered at 47 N, X = 735550 mE and Y = 14027884 mN. covered an area of 25 × 25 km. The finest grid spacing was set up as Thai ONEP air model guideline (100 m grid resolution from fence up to 1.5 km radius, 250 m grid resolution from 1.5 km up to 3.0 km radius, and 500 m grid resolution from 3.0 km up to border of study area) [20]. Urban dispersion coefficient was selected together with the regulatory modeling options for model simulation in this research. Annual of 1,3 butadiene concentrations was calculated on elevated terrain height options.
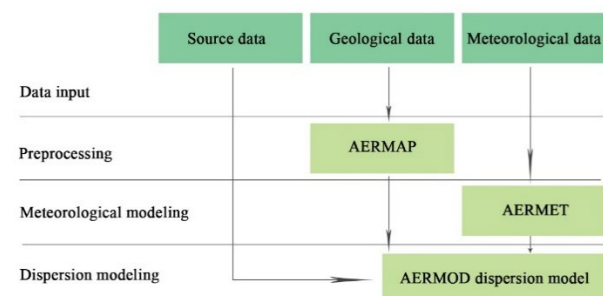

Figure 2 Data flow in the AERMOD modeling.

Meteorology input (surface met and profile met datum) were derived from the Weather Research Forecast meteorological model (WRF model). Model was simulated from the 1st hour in January 1, 2018, to the 24th hour in December 31, 2018. Meteorological variables used in air modeling analysis in this study was performed using the WRF (version 3.7) model. The simulation was performed through the nesting domain system covering the study area with the largest domain resolution of 36 × 36 km following by 12 × 12 km and the finest domain of 4 × 4 km.

The data were calculated at 44 vertical layers with the lowest layer of 20 m above ground to ensure comparability with observations from meteorological tower.

Terrain options (gridded data requited by AERMEP) were acquired from the Digital Elevation Model (DEM) data. Terrain characteristics were derived from the Shuttle Radar Topography mission (SRTM1) database (30 m resolution) maintained by the U.S. National Geospatial -Intelligence Agency (NGA) and the U.S. National Aeronautics and Space Administration (NASA).

3) Receptors and predicted concentrations

The Thai ONEP air model guideline (100 m grid resolution from fence up to 1.5 km radius, 250 m grid resolution from 1.5 km up to 3.0 km radius, and 500 m grid resolution from 3.0 km up to border of study area) was used as the criteria in setting up the receptor grid in this study. Twenty-one discrete points including school, government office, temple and community located within the study domain were selected as sensitive receptors to predict the ambient annual concentration of 1,3 butadiene in this study. The source contributions to ambient concentrations were also evaluated for each receptor spatial distribution of the receptors is illustrated in Figure 3.
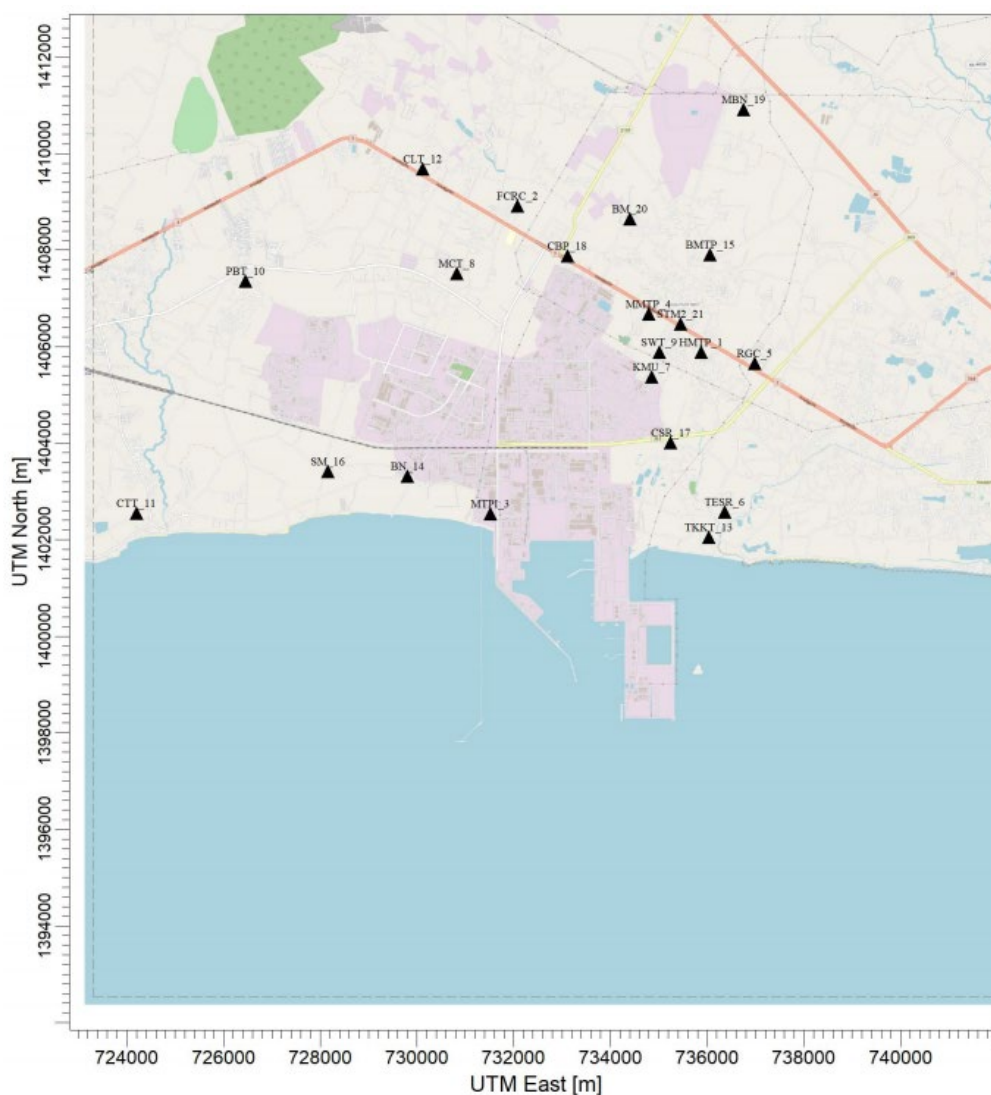
Figure 3 Location of receptors.

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4) Health risk assessment

To assess the potential harmful health risks of 1,3 butadiene in this study. It is necessary to determine in term of inhalation exposure pathway. Because of 1,3 butadiene is VOCs which high vapor pressure, inhalation is the exposure pathway of most concern for ambient VOC exposures. In this study, assessed the carcinogenic and non-carcinogenic risks associated with this pollutant exposures through inhalation in environment [21].

In carcinogenic risk was expressed as the inhalation unit risk (IUR) and the exposure concentration (EC), as shown in Eq. 1.

$$Carcinogenic\ risk\ =\ IUR\ \times\ EC \quad \text{(Eq. 1)}$$

In non-carcinogenic risk was assessed using the chronic non-cancer risk factor or the hazard quotient (HQ) and reference concentration (RfC), as shown in Eq. 2.

$$HQ\ =\ \frac{EC}{RfC} \quad \text{(Eq. 2)}$$

The exposure concentration (EC) was calculated by using Eq. 3.

$$EC\ =\ \frac{(CA \times EF \times ED)}{AT \times 365\ days/year} \quad \text{(Eq. 3)}$$

Where; IUR = Inhalation unit risk ($\mu g\ m^{-3}$), RfC = Reference concentration ($mg\ m^{-3}$), CA = Contaminant concentration in air ($\mu g\ m^{-3}$), EF = Exposure frequency (365 day $year^{-1}$), ED = Exposure duration during a lifetime (40 year) and AT = Averaging Time (70 year).

The IUR of 1,3 butadiene used for calculation of carcinogenic risk in this study were $3 \times 10^{-5}\ \mu g\ m^{-3}$. As for RfC of 1,3 butadiene used for calculation HQ in this study were $2 \times 10^{-3}\ \mu g\ m^{-3}$ [22].

Results and discussion

Emissions of 1,3 butadiene from each source group were estimated based on various procedures as summarized in Table 2. Direct measurements were utilized together with emission factor and chemical mass balance approaches in determining emission rate expressed in the unit of $g\ s^{-1}$ for each source. These data were used an emission input for the AERMOD dispersion model. Simulated results were presented as annual concentrations of 1,3 butadiene at each sensitive receptor and within the modeling domain as illustrated in Figure 4. The red colored plot in Figure 4. depicted the areas where predicted annual concentrations of 1,3 butadiene exceeded the Thai ambient air quality standard of this compound ($> 0.33\ \mu g\ m^{-3}$) [8]. However, it should be noted that these violated areas were located within the boundary of the MTPIE industrial complex.
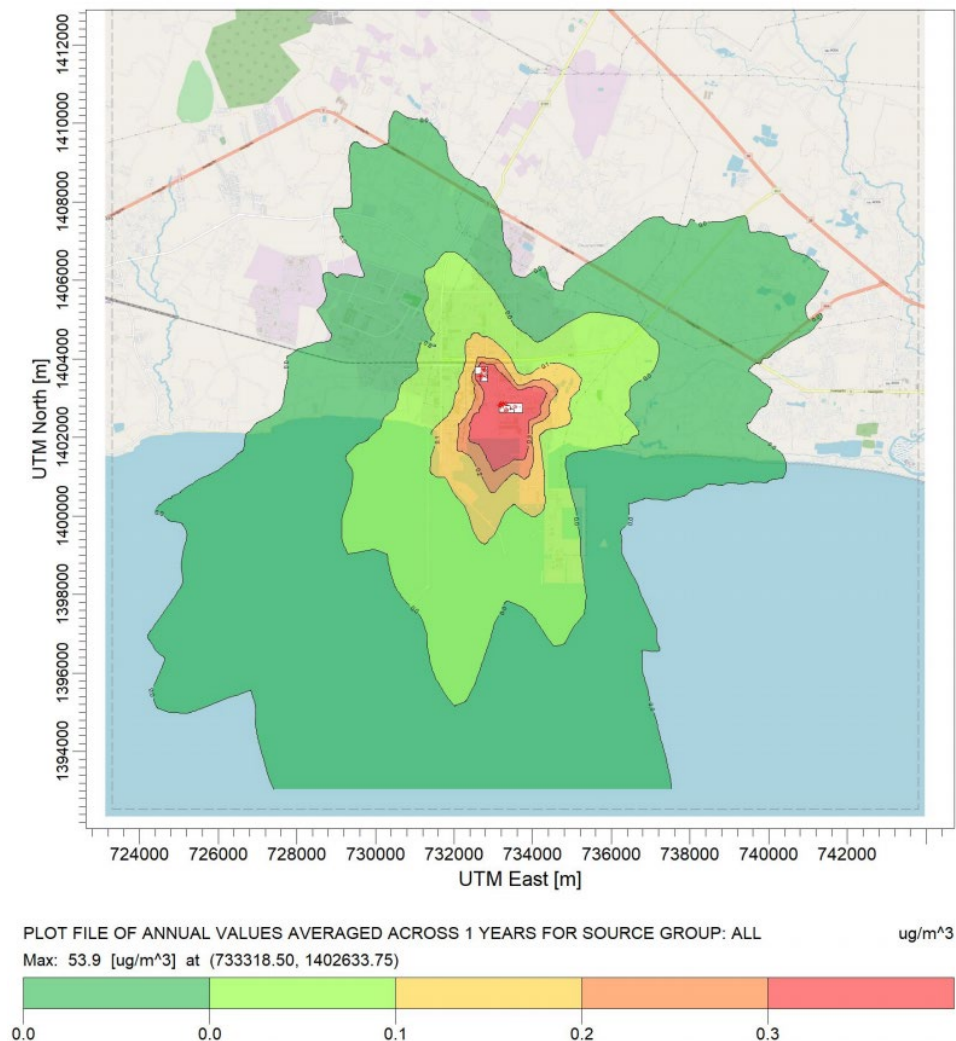
We further predicted the annual 1,3 butadiene concentrations and their source contributions at each receptor sites. It was found that predicted concentrations at every receptor were within the ambient air quality standard of 1,3 butadiene. The highest 1,3 butadiene concentration at receptor point was predicted at MTPI office (0.084 $\mu g\ m^{-3}$). As for the emission source contribution to the predicted ambient concentrations, it was found that wastewater treatment was the major source of 1,3 butadiene emissions which mostly affected to ambient concentrations at every receptor. The source contributions to ambient concentrations were estimated as 87–96 % from the wastewater treatment, 3–13% from the fugitive emission source, 1–2% from the combustion flare and ~ 0.5% contribution from stack combustion, respectively. Predicted concentration and the source contribution at each receptor is presented in Table 3.

In term of source contributions of 1,3 butadiene was carried out for each specific receptor to assist in the evaluation environmental impact to the population living in this area. Results

from AERMOD analysis predicted concentration at each receptor and percentage of source contribution to the 1,3-butadiene ambient concentration was shown in Table 3. This result clearly indicated that the synthetic rubber industries in this study area should give an effort as and priority in controlling emission from their wastewater treatment facilities to manage the ambient concentrations of 1,3 butadiene at those receptors, effectively.

In term of health risk assessment in this study was estimated using cancer risks and hazard quotient (HQ). Cancer risks of 1,3 butadiene was calculated by using annual average predicted concentration at each receptor point and inhalation unit risk factor (IUR). The results found that mostly of cancer risks of 1,3 butadiene at receptor point were lower than the acceptable limit of 1.00×10^{-6} except at receptor MTPI, CSR and TKKT cancer risks values of 1,3 butadiene is higher than acceptable limit (2.51×10^{-6}, 2.43×10^{-6} and 1.41×10^{-6}, respectively) as presented in Table 4. As for HQ of 1,3 butadiene was calculated by using annual average predicted concentration at each receptor point and reference concentration (RfC). Results found the HQ of 1,3 butadiene at receptor point were lower than the acceptable limit as presented in Table 4. This result reveal that the synthetic rubber industries in this study area may be a potential carcinogenic risk from inhalation exposure of 1,3 butadiene.

PLOT FILE OF ANNUAL VALUES AVERAGED ACROSS 1 YEARS FOR SOURCE GROUP: ALL   ug/m^3
Max: 53.9 [ug/m^3] at (733318.50, 1402633.75)

Figure 4 Spatial distribution of 1,3 butadiene concentration.

Table 3 Predicted concentration and analysis of source contribution at each receptor

Receptors	1,3 butadiene ($\mu g\ m^{-3}$) (Annual average)	% of emission source contribution to 1,3 butadiene concentration			
		Fugitive	Wastewater treatment	Flare	Stack
1. HMTP (Health Promoting Hospital Map Ta Phut)	0.014	12.61	87.17	0.14	0.07
2. FCRC (Field Crops Research Center)	0.009	7.12	92.34	0.54	0.00
3. MTPI (Map Ta Phut Industrial Estate)	0.084	12.64	87.21	0.07	0.07
4. MMTP (Mueang Mai Map Ta Phut)	0.006	14.56	84.91	0.35	0.18
5. RGC (Rayong Government Complex)	0.023	7.01	92.86	0.09	0.04
6.TESR Telephone Exchange Station Rayong (TESR)	0.033	5.22	94.69	0.03	0.06
7. KMU (King Mongkut's University)	0.015	14.86	84.87	0.20	0.07
8. MCT (Map Chalut Temple)	0.020	7.94	91.72	0.29	0.05
9. SWT (Sophon Wanaram Temple)	0.013	13.48	86.29	0.15	0.08
10. PBT (Prachummit Bamrung Temple)	0.004	7.48	91.77	0.75	0.00
11. CTT (Chon Tharam Temple)	0.005	7.84	91.95	0.21	0.00
12. CLT (Chak Lukya Templs)	0.008	7.79	91.03	1.18	0.00
13. TKKT (Ta Kuan Khongkharam Temple)	0.047	3.60	96.33	0.02	0.04
14. BN (Ban Nongfab)	0.021	9.15	90.57	0.19	0.09
15. BMTP (Ban Map Ta Phut)	0.006	11.23	88.43	0.17	0.17
16. BSM (Ban Samnak Mamuang)	0.011	8.13	91.52	0.27	0.09
17. CSR (Chumchon Soi Ruampattana)	0.081	4.68	95.24	0.04	0.04
18. CBP (Chumchon Ban Phlong)	0.010	5.23	94.47	0.20	0.10
19. MBN (Moo Ban Nopphaket)	0.001	11.81	85.83	2.36	0.00
20. BM (Ban Mapya)	0.005	5.11	94.50	0.39	0.00
21. STM2 (Soi Thoetthai-Muslim 2)	0.010	12.49	87.21	0.20	0.10

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Table 4 Cancer risk and Hazard quotient for 1,3 butadiene

Receptors	Cancer risk	Hazard quotient (HQ)
1. HMTP (Health Promoting Hospital Map Ta Phut)	0.43×10^{-6}	0.71×10^{-2}
2. FCRC (Field Crops Research Center)	0.28×10^{-6}	0.46×10^{-2}
3. MTPI (Map Ta Phut Industrial Estate)	2.51×10^{-6}	4.19×10^{-2}
4. MMTP (Mueang Mai Map Ta Phut)	0.17×10^{-6}	0.29×10^{-2}
5. RGC (Rayong Government Complex)	0.69×10^{-6}	1.16×10^{-2}
6. TESR Telephone Exchange Station Rayong (TESR)	0.99×10^{-6}	1.65×10^{-2}
7. KMU (King Mongkut's University)	0.45×10^{-6}	0.74×10^{-2}
8. MCT (Map Chalut Temple)	0.61×10^{-6}	1.02×10^{-2}
9. SWT (Sophon Wanaram Temple)	0.40×10^{-6}	0.66×10^{-2}
10. PBT (Prachummit Bamrung Temple)	0.12×10^{-6}	0.20×10^{-2}
11. CTT (Chon Tharam Temple)	0.14×10^{-6}	0.24×10^{-2}
12. CLT (Chak Lukya Templs)	0.25×10^{-6}	0.42×10^{-2}
13. TKKT (Ta Kuan Khongkharam Temple)	1.41×10^{-6}	2.34×10^{-2}
14. BN (Ban Nongfab)	0.64×10^{-6}	1.07×10^{-2}
15. BMTP (Ban Map Ta Phut)	0.17×10^{-6}	0.29×10^{-2}
16. BSM (Ban Samnak Mamuang)	0.34×10^{-6}	0.57×10^{-2}
17. CSR (Chumchon Soi Ruampattana)	2.43×10^{-6}	4.05×10^{-2}
18. CBP (Chumchon Ban Phlong)	0.29×10^{-6}	0.50×10^{-2}
19. MBN (Moo Ban Nopphaket)	0.04×10^{-6}	0.06×10^{-2}
20. BM (Ban Mapya)	0.15×10^{-6}	0.25×10^{-2}
21. STM2 (Soi Thoetthai-Muslim 2)	0.30×10^{-6}	0.09×10^{-2}

Conclusion

Emission data of 1,3 butadiene released from synthetic rubber industries in the largest petroleum and petrochemical industrial complex in Thailand was evaluated in this study. The emission sources consisted of stack combustion, combustion flare, wastewater treatment facility and process fugitive sources. It was found that wastewater treatment facility shared the highest contribution to the total emission of 1,3 butadiene in this industrial source (~ 92% of total emission). These emission data were used as input to predict ambient 1,3 butadiene concentrations through the simulation of AERMOD dispersion model together with local terrain features and meteorological characteristics. Predicted data is presented as pollution map to illustrate the spatial distribution of 1,3 butadiene over the modeling domain as well as the extent and magnitude of the predicted concentrations as compared with the ambient air quality standard. Results revealed that there were areas where predicted concentrations exceeded the ambient standard. However, those areas were located within the boundary of industrial estate. Therefore, comparing of predicted concentration in these areas with the environmental standard is not appropriate. Concentrations of 1,3 butadiene in external area from the boundary of the industrial zone were predicted. It was found that predicted data at the sensitive receptors were not exceed the Thai annual ambient standard of this compound. The source apportionment analysis revealed that wastewater treatment facility was the major emission source contributed to ambient concentrations at those receptors. However, when we calculated cancer risks of 1,3 butadiene by using annual average predicted concentration at each receptor point. Cancer risk values at some sensitive receptors were exceed the US EPA acceptable limit. Therefore, we recommend that this source should be given priority to manage and control the level of this carcinogenic sub-

stance which may be threaten to general human health living in the vicinity of this petrochemical industrial complex. Finding, methodology and analytical procedures used in this study can serve as a particularly useful tool to interpret the air pollution source-receptor relationships in other industrial areas.

Acknowledgements

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