京都大学	博士（　工学　）	氏名	Maihani Binti Ismail
論文題目	PUBLIC HEALTH RISK BASED PRIORITIZATION OF HAZARDOUS AIR POLLUTANTS FROM INDUSTRIAL SOURCES: A CASE STUDY FOR A PETROLEUM REFINERY IN SOUTHEAST ASIA（産業起源有害大気汚染物質の公衆衛生リスクに基づく優先順位付け：東南アジアの石油精製所におけるケーススタディ）		

（論文内容の要旨）

Industrial facilities are one of the major anthropogenic sources of air pollution. While emissions and concentrations of criteria air pollutants (CAP) are well monitored and controlled through regulatory enforcement, the status of other chemicals, including those potentially harmful to human health and the environment, known as hazardous air pollutants (HAP) is largely unknown. This research explores industry-induced HAP risk to public health, taking a petroleum refinery located in Southeast Asia as a case study.

Chapter 1: Introduction

The background and necessity of this research are briefly explained. The research objectives, scope, site description, and structure of the thesis are described in detail.

Chapter 2: Hazard Assessment for Emissions from Petroleum Refinery Using Multi-Country Regulatory Databases

This study aims to facilitate the prioritization of chemicals based on their carcinogenicity (C), mutagenicity (M) and reproductive toxicity (R) through hazard assessment using multi-country governmental regulatory databases. CMR classification for 176 chemicals reported as being emitted by petroleum refineries were obtained from 9 country databases. Out of 176 chemicals, Japan has the highest number of chemicals listed (84.7%). Although the classifications were based on the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), inconsistencies were observed in the classification of majority of the chemicals across countries. To quantitatively rank the chemicals, a scoring system was applied to the most stringent classification among the multi-country databases. As a result, Benzene tops the priority list followed by Benzo(a)pyrene, 1,3-Butadiene, Arsenic and Cadmium. The priority list provides justification for inclusion of chemicals in subsequent exposure assessment. Compared to a conservative and cost-effective approach, utilizing readily available information with assured data quality, this method is especially useful when resources and expertise are limited.

Chapter 3: Chemical Concentrations in Stack Emissions, Ambient PM2.5, and Soil Nearby Petroleum Refinery Operations

Stack total suspended particles (TSP) emission, ambient $PM_{2.5}$ and soil samples collected surrounding the refinery were analyzed for 12 metals and 16 polycyclic aromatic hydrocarbons (PAH). Stack metal results gives a snapshot view of the residual emissions from the processes and prompts the need to practice caution when using default emission factors. $PM_{2.5}$ concentrations during normal refinery operations (median=33.194ug/m^3, sd=10.222ug/m^3, n=33) was slightly higher compared to concentrations at locations farther away from the refinery (median=25.233ug/m^3, sd=10.474ug/m^3, n=23). This difference wass statistically significant by Mann-Whitney-Wilcoxon test, p-value < 0.05. Excluding haze samples, 81% of $PM_{2.5}$ concentrations exceeded the WHO 24-hour guideline (mean=38.230ug/m^3, standard error=0.188ug/m^3, n=89). Impact of construction on the refinery grounds was observed in the significant increase of $PM_{2.5}$, Cu, and Mo concentrations, and in the change in $PM_{2.5}$ -bound PAH profile. Seasonal and haze impact were also examined. A trend of decreasing concentration in soil as distance from the refinery increased in the predominant wind direction were observed particularly for mid to high molecular weight PAH, Zn, V, and Cr, making them good markers for refinery air deposition.

Chapter 4: Estimating Hazardous Air Pollutant Emissions from Petroleum Refinery

京都大学	博士（ 工学 ）	氏名	Maihani Binti Ismail

An emission inventory consisting of 75 chemicals from 147 refinery sources which include stationary combustion sources, flares, tanker loading, equipment leaks, storage tanks, cooling towers, and wastewater collection and treatment system was developed. The top 15 chemicals which consist of VOC and SVOC, accounted for approximately 98.3% of the total emissions by mass. The highest emissions come from the plant's wastewater collection and treatment system (48.0%), followed by storage tanks (20.9%), and tanker loading (17.6%). Fugitive emissions, which often left unreported, accounted for 78.4% of the total emissions, urging the need for inclusion in emission inventory and air quality monitoring. Compared to refineries with similar distillation capacity in the US, this refinery emits higher volume of VOC, which may in part be due to the difference in environmental factors, pollution prevention methods implemented, and estimation methodology applied. Although the emission inventory established is by no means exhaustive, it provides a good baseline for assessing the impact of refinery emissions to the air quality, and the potential health and ecological risks.

Chapter 5: Dispersion Model Evaluation for Hazardous Air Pollutants from Petroleum Refinery Emissions

The outputs of air dispersion model have the potential to impose significant public health, environmental, and economic impact. Hence, it is imperative for it to be evaluated to determine whether its results are of a quality adequate to serve as the basis for decision making. The aim of this research was to practically evaluate the adequacy of emission estimation and dispersion model strategies applied for modelling HAP, with focus on VOC, in areas with humid tropical climate. The model performance was evaluated based on its ability to identify the location of maximum concentration, the magnitude of upper-end of air concentration, bias, scatter, and fraction of data within acceptable range. Predictions for 1,2,4-Trimethylbenzene, Benzene, Ethylbenzene, and Toluene showed overall satisfactory performances. Xylenes and n-Hexane were overpredicted, while Cyclohexane underpredicted beyond the acceptable range of factor of 2. Compared to VOC, $PM_{2.5}$-bound metals were severely underpredicted. Potential cause for the discrepancies between model-predicted and observed data, and improvements necessary to close the gaps were discussed.

Chapter 6: Inhalation Risk Modelling of Exposure to Petroleum Refinery Emissions

Deterministic and probabilistic health risk assessment (HRA) was conducted for 76 refinery air emissions. Benzene and Xylenes were identified as acute health risk drivers. Naphthalene, Benzene, Ethylbenzene and Arsenic were identified as cancer risk drivers, with cancer risk estimates of $6.2x10^{-5}$, $3.2x10^{-5}$, $1.6x10^{-5}$ and $3.6x10^{-6}$, respectively. Total cancer risk for 21 carcinogens was estimated at $1.1x10^{-4}$. Naphthalene was identified as chronic non-cancer risk driver with hazard quotient (HQ) estimate of 1.4. The hazard index (HI) for nervous and respiratory systems, both driven by Naphthalene, were estimated at 1.72 and 1.68, respectively. Uncertainties in the risk assessment, how they were addressed or can be improved, were discussed. The HRA results urge the need for emission control of VOC. AERMOD simulation shows that Naphthalene, Benzene and Ethylbenzene contributed to 99.4% of the total cancer risk estimated at location of highest impact, with 88% of its exposure originating from the tanker loading activity.

Chapter 7: Conclusion and Recommendations

Summarizes the findings and concludes the entire research. Recommendations and suggestions for industry and government, as well as scope for future research are provided.

氏　名	Maihani Binti Ismail

（論文審査の結果の要旨）

本論文は、工業活動に起因する公衆衛生への有害大気汚染物質のリスクについて、東南アジアの石油精製所での実測データに基づくケーススタディを通じて検討したものである。得られた主な成果は以下のとおりである。

１）　9種の GHS（化学品の分類および表示に関する世界調和システム）に基づくデータベースを利用して、各化学物質の発癌性、変異原性、生殖毒性に基づく優先リストを作成することで、石油精製所から放出される可能性がある 176 化学物質の毒性アセスメントを実施した。その結果、Benzene が最も優先度が高く、続いては Benzo(a)pyrene, 1,3-Butadiene, As,Cd の優先度が高かった。曝露アセスメントにおいては、このような優先度に基づいて評価することが妥当と考えられた。

２）　石油精製所通常操業状態における周辺の PM2.5 濃度は、石油精製所から遠く離れた場所における濃度に比べ有意に高く、ヘイズ時のサンプルを除いても PM2.5 濃度の 81%は WHO の 24 時間ガイドライン値を超えていた。また、石油精製所周辺の VOC 濃度は有意に高かったが、一部のホットスポットを除いては発癌リスクが問題となるレベルではなかった。

３）　石油精製所からの距離の増加による支配的風向における土壌中濃度の減少傾向が、中高分子量の PAH, Zn, V, Cr で観測されたことから、これらの物質は石油精製所から放出された物質の大気沈降の良い指標であると推定された。

４）　147 の石油精製所からの排出インベントリーを調べ、大気拡散シミュレーションにより、決定論的、そして確率論的健康リスク評価を 76 の化学物質について実施した。その結果、急性リスクが問題となる物質として、Benzene と Xylenes が、発癌リスクが問題となる物質として Naphthalene, Benzene, Ethylbenzene,ヒ素が同定された。また、21 個の発癌物質による総発癌リスクは、1.1×10^{-4} と推定された。

以上の結果は、石油精製所に起因する大気汚染物質の放出実態に関する貴重なデータを提供するものであり、また、周辺住民の健康リスク評価方法確立にも大きく貢献するものであって、学術上、実際上寄与するところが少なくない。よって、本論文は博士（工学）の学位論文として価値あるものと認める。また、令和３年１月２５日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。なお、本論文は、京都大学学位規程第 14 条第 2 項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める。