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Doctoral Dissertation

博士論文

Urban impacts on tropospheric ozone chemistry and ozone abatement strategy using a CMAQ-PMF-based composite index

使用基於 CMAQ-PMF 的綜合指數探討對流層臭氧化學對都市的影響及臭氧減少策略

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大氣科學 學系/研究所 鄭顯威 研究生所提之論文 使用基於 CMAQ-PMF 的綜合指數探討對流層臭氧化學對都市的影響及臭氧減少策略係由本人指導撰述，同意提付審查。

指導教授________________ (簽章)

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Advisor's Recommendation for Doctoral Students

This thesis is by Jackson Chang Hian Wui of the graduate program in Department of Atmospheric Science, entitled: Urban impacts on tropospheric ozone chemistry and ozone abatement strategy using a CMAQ-PMF-based composite index, which is written under my supervision, and I agree to propose it for examination.

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This thesis titled "Urban impacts on tropospheric ozone chemistry and ozone abatement strategy using a CMAQ-PMF-based composite index" studying in the graduate program in Department of Atmospheric Science. The author of this thesis is qualified for a Doctoral degree through the verification of the committee.

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Abstract

Recent rapid urbanization has had a profound impact on local-scale atmospheric circulation but its impacts on the physical and chemical processes controlling the tropospheric ozone remain poorly resolved. In Taiwan, due to the strict emission policy, the ambient concentrations of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) have reduced by nearly 60% since 1994. However, such reduction in precursors has not been linearly reflected on the annual mean ozone concentration, but an increasing or flattening trend is seen in the last decade. Therefore, a comprehensive investigation on the urban impacts on tropospheric ozone chemistry is necessary for prescribing an effective ozone abatement strategy. Our study area focuses on southern Taiwan, a complex region of coastal urban and industrial parks and inland mountainous areas, where high ozone episode often occurs during the seasonal transition period (i.e. Apr-May and Oct-Nov). In this thesis, we modelled the spatial and temporal distribution of ozone and its precursors (i.e. NO_x and VOCs) using WRF-CMAQ model at urban scale resolution 1.0 x 1.0 km.

Firstly, we investigated the impacts of urban land-surface forcing and its interaction with local circulations on local meteorology and ozone air quality. Two simulations were performed with the same emissions but different land cover designations: URBAN scenario represents the current urbanized condition and NO-URBAN scenario replaces all urban grid cells with cropland. It was shown that when the urban-heat-island (UHI) convergent flow stalls over the city, a circulation flow is formed and traps the pollutants at an elevated height, increasing the reaction of hydroxyl radical with VOCs by 2.0-4.0 ppbv h^{-1} at 1000-1500 m. At nighttime, the deeper boundary layer of URBAN scenario diluted NO_x mixing ratio by 17 ppbv and weakened the titration effect, causing higher O_3 concentration by 15 ppbv in the urban area. When the UHI vertical mixing diminished, the O_3 aloft diffused downward to the surface level and further degraded the nighttime air quality.

Secondly, we examined the budget analysis of boundary-layer O_3, NO_x and NMHC over the urban and inland area of southern Taiwan. In the near-surface budget, chemical process and dry deposition are the main sink of O_3 with the contribution more than 10 ppbv h^{-1} and 15 ppbv h^{-1}, respectively; the major source of near-surface O_3 is vertical diffusion exceeding 30 ppbv h^{-1}. In the boundary-layer budget, chemical process is the main source while vertical diffusion becomes the sink for O_3. The physiochemical circulation involves the vertical transport of near-surface pollutants and enhances photochemical production of O_3 in the upper PBL level is dominant in urban areas. This vertical exchange is mainly attributed to the vertical diffusion process and gradually decreases with heights. Our results highlighted the important role of daytime sea breeze circulation pushing the polluted urban air masses into the inland region which greatly

enhanced the inland O_3 production due to the NO_x-limited condition. Thus, control of NO_x emission in inland area may be ineffective due to the dynamics role of land-sea breeze; whereas most of the urban areas are characterized by VOC-limited condition where control of VOCs emission is helpful to reduce urban O_3 concentration.

Thirdly, we developed a CMAQ-PMF-based composite index to identify the key VOC source-species for effective ozone abatement strategy. First-order, second-order and cross sensitivities of ozone concentrations to domain-wide (i.e. urban, suburban and rural) NO_x and VOC emissions were determined for the study area using CMAQ-Higher Direct Decoupled Method (HDDM). Negative (positive) first-order sensitivities to NO_x emissions are dominant over urban (inland) areas, confirming ozone production sensitivity favors the VOC-limited regime (NO_x-limited regime) in southern Taiwan. Most of the urban areas exhibited negative second-order sensitivity to NO_x emissions, indicating a negative O_3 convex response where the linear increase of O_3 from decreasing NO_x emissions was largely attenuated by the non-linear effects. Due to the solidly VOC-limited regime and the relative insensitivity of O_3 production to increases or decreases of NO_x emissions, this study pursued the VOC species that contributed the most to ozone formation. PMF analysis driven by VOCs resolved 8 factors including mixed industry (21%), vehicle emissions (22%), solvent usage (17%), biogenic (12%), plastic industry (10%), aged air mass (7%), motorcycle exhausts (7%), and manufacturing industry (5%). Based on the CMAQ-PMF-based composite index, our results indicate that VOC control measures should prioritize (1) solvent usage for painting, coating and the printing industry, which emits abundant toluene and xylene, (2) gasoline fuel vehicle emissions of n-butane, isopentane, isobutane and n-pentane, and (3) ethylene and propylene emissions from the petrochemical industry.

摘要

近年來快速的城市化對局部範圍的大氣環流產生了深遠的影響，但對於控制對流層臭氧濃度的物理及化學反應機制仍然沒有完整的解釋。台灣由於嚴格的排放政策，相較於 1994 年，現今氮氧化物（NO_x)和揮發性有機化合物（VOC_S)的環境濃度已減少將近 60%。然而，減少這些前驅物並未使臭氧的年均濃度呈現線性的變化，在過去的十年間反而出現增加或趨於平緩的趨勢。因此，必須廣泛調查城市對於對流層臭氧化學的影響，以制定有效減少臭氧排放的方針。本研究針對台灣南部地區，其為一個由沿海城市、工業園區和內陸山區所組成的複雜區域，並經常於換季的時候（4-5 月及 10-11 月）發生高臭氧事件。在本篇論文中，吾人將使用城市規模解析度 1.0 x 1.0 公里的 WRF-CMAQ 模式，模擬臭氧及其前驅物（如：NO_x、VOC_S）的時空分布。

首先，吾人調查城市地表和當地環流的相互作用對當地氣候和臭氧空氣品質造成的影響。並對使用相同排放源但不同的特定地區進行了兩次模擬：城市情形代表當前城市化的現況；非城市情形則用農田取代所有城市網格。結果顯示，當城市熱島（UHI）氣流匯聚並停滯在城市上空時，會形成環流並將污染物困在較高的高度，並發現在 1000-1500 公尺的高空，羥基自由基與 VOC 的反應增加 2.0-2.4 ppbv h^{-1}。在夜間，城市情形因為較深的邊界層使 NO_x 混合比稀釋了 17 ppbv，同時也削弱滴定效應，導致市區臭氧濃度升高了 15 ppbv。當 UHI 垂直混合減弱時，臭氧會從高空向下擴散至地表並進一步降低夜間的空氣品質。

再者，吾人針對台灣南部城市及內陸地區邊界層內的 O_3、NO_x 和 NMHC 進行收支調查。在近地表的收支中，化學過程和乾沉降是使 O_3 匯入的主要原因，並且分別貢獻 10 ppbv h^{-1} 和 15 ppbv h^{-1} 以上；近地表的 O_3 垂直擴散超過 30 ppbv h^{-1}。在邊界層收支中，化學過程是 O_3 主要來源，而垂直擴散也會使 O_3 匯入。物理化學牽涉近地表污染物的垂直擴散並增強 PBL 層上層的光化學反應來產生 O_3，並佔據城市中 O_3 的主要地位。這種垂直交換的過程主要是因為大氣能夠垂直擴散的結果，並隨高度增加逐漸地減弱交換效率。本研究結果發現白天的海風環流會將城市中受污染的氣團推向內陸，並且因為 NO_x 的限制條件，大大增強了內陸臭氧的生成，因此即使控制內陸地區的 NO_x 排放，也會受海陸風影響而沒有成效，然而大部分的城市地區，由於 VOC 的限制條件，控制 VOC 排放有助於降低 O_3 的排放。

最後，吾人基於 CMAQ-PMF 開發一個綜合指數，用來確認 VOC 的來源種類對於減少臭氧生成的貢獻性。利用 CMAQ-Higher Direct Decouple Method (HDDM) 確認研究區域的臭氧濃度對全域（即城市、郊區和農村）所排放之 NO_x 和 VOC 的一階、二階交叉敏感性（cross sensitivities）。並發現南台灣城市地區（內陸地區）的臭氧生成敏感度因子，主要受在 VOC 限制條件（NO_x 限制條件下）

下的 NOx 負一階敏感度主導。大部分城市地區表明負 O_3 凸反應曲線對 NO_x 排放表現出負二階敏感度，其中 NO_x 因排放很大程度上被非線性效應減弱而使 O_3 線性增加。由於嚴格的 VOC 限制政策和減少或增加 NO_x 排放對生成 O_3 相對地不敏感，本研究追求對臭氧形成最大貢獻 VOC 種類。VOC 使用 PMF 分析並解決八個因素，包括混合工業（21%）、車輛排放（22%）、溶劑使用（17%）、生物源（12%）、塑膠工業（10%）、老化氣團（7%）、機車尾氣（7%）和製造業（5%）。研究結果顯示基於 CMAQ-PMF 的綜合指數，VOC 的控制措施應優先考慮以下排放源：（1）油漆、塗料及印刷業對容易的使用，會排放大量的甲苯和二甲苯；（2）汽油車所排放的 n-丁烷、異戊烷、異丁烷和 n-戊烷；（3）石化業排放的乙烯及丙烯。

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Chapter 1 Introduction

1.1 Background Study

In recent years, southern Taiwan has been facing severe ozone air quality pollution, particularly during the seasonal transition period under the weak synoptic weather condition. Due to the strengthened emission control policy, the mean $PM_{2.5}$ concentrations has significantly declined in the last decade but the ozone concentration did not follow the similar declining trend and rather an increasing or flattening trend, reflecting a greater urgency for ozone pollution abatement. Chou et al. (2006) showed that the ozone concentration in Taipei, Taiwan increased substantially during 1994-2003 despite its precursors nitrogen oxides (NO_x) and non-methane hydrocarbon (NMHC) decreased significantly in the same period. The annual average of ozone and daily maxima ozone increased by 58% and 26% respectively in Taipei from 1994 to 2003. Chang et al. (2017) also reported that ozone concentration in Taiwan continued to increase from 2000 to 2014 with the increasing rate of daily 8h maxima (+0.45 ppb yr^{-1}) is more than twice as great as the daytime average (+0.20 ppb yr^{-1}). A more recent study from Tsai and Lin (2021) showed that despite all pollutants (i.e. PM, SO_2, CO, NO_2) in Taiwan has a consistent declining trend from 2014 to 2020, annual average ozone has an increasing trend fluctuating in the range 54-60 ppb. Considering that near-surface ozone is greenhouse gases and harmful to human health (Yim et al., 2019), crop (Avnery et al., 2011; Tai and Val Martin, 2017) and ecosystem (Ashmore, 2005), it is essential to examine the possible reasons related to the increasing trend of ozone concentration both regionally and locally.

Tropospheric ozone is closely related to its precursors NO_x and NMHC emissions both anthropogenic and biogenic. It is a major secondary air pollutant, produced through a complex series of photochemical reactions involving NO_x and NMHC. High O_3 episodes are usually associated with hot sunny weather, low wind speed stagnant condition, and slow-moving high pressure system. The consequences of these systems can influence the long-lived pollutants such as NO_x, NMHC and CO in terms of spatial transport (Lu et al., 2019), accumulation and kinetic reaction (Chen et al., 2020), which are directly related to the ozone formation. The ozone production regime is characterized by its sensitivity production either VOC-limited or NO_x-limited. The split between NO_x-limited or VOC-limited regime is determined by the chemistry of odd hydrogen radicals of either peroxides (i.e. hydrogen peroxide (H_2O_2), organic peroxides (ROOH)) or nitric acid (HNO_3). When the peroxides are the dominant radical sinks, the ozone chemistry favors NO_x-limited regime; when the nitric acid is the dominant sink, VOC-limited regime is favored. It is crucial to identify the ozone production regime for effective ozone pollution control measures because reducing NO_x emission in VOC-limited regime could have the adverse effect of increasing the O_3 concentration, while reducing VOC emission in NO_x-limited regime has little to insignificant impact on O_3 concentration.

Urbanization is an irreversible process involves the change of land use land cover from natural surfaces to artificial impervious surfaces. One of the most well-known impacts of urbanization is urban heat island (UHI) effect. UHI is characterized by a strong temperature gradient between the urban core and its surrounding areas generating a convergent flow towards the urban center in the lower boundary layer and a divergent flow from the upper boundary to the urban outskirts (hereinafter referred as urban-breeze) (Oke, 1976; Saitoh et al., 1996). At local scale, weather condition such as high temperature and low wind speed are conducive to UHI development and can induce a persistent convergence favorable to ozone formation in the urban areas (Martinelli et al., 2020; Umezaki et al., 2020; Yoshikado and Tsuchida, 1996). For coastal city, the interaction of UHI with local circulations (i.e. land-sea breeze) further complicates the ozone and its precursors transport through complex recirculation patterns (Finardi et al., 2018). During the daytime when entrainment process is unfolded, ozone is injected into the rapidly growing boundary layer. The drop in boundary layer depth that occurred when sea breeze front moved inland, carrying polluted urban air of NO_x-rich air and facilitated near-surface ozone titration effect, also had an impact on the vertical ozone profile. During the nighttime when the land-breeze is prevalent, the advected urban polluted air mass is transported back to the urban area.

To mitigate the ozone pollution problem, several attempts are suggested and extensively reviewed in the literatures. These methods can be grouped into two categories: (1) passive control and (2) active control. Passive control of ozone is usually done by reducing the UHI effect to reduce the ozone formation rate meanwhile active control is related emission control that targeted on the ozone precursors such as NO_x and NMHC. In the passive control, Fallmann et al. (2016) evaluated the effectiveness of urban greening and highly reflective material roof (i.e. white roofs) on the ozone concentration inside the urban canopy layer and found that both urban greening and white roofs are able to reduce the urban temperature by about 1 K and the mean ozone concentration by 5-8%. Other passive control strategies include installing green roofs (Li et al., 2014) or using permeable material pavements for highly populated cities, and proposing effective mitigation strategies based on sea breeze patterns (Sasaki et al., 2018). In the active control, it is important to first identify the ozone sensitivity production regime of the area of interest. For instance, Chang et al. (2016) concluded that the controls of NO_x emissions would mitigate ozone air pollution in most of the suburban cities in United States due to the NO_x-limited condition but control of VOC emissions is more effective to curb ozone air pollution in highly populated cities of VOC-limited condition. In another study, Tang et al. (2017) reported that the implementation of emission control during the Beijing Olympics 2018 decreased the ozone precursors (i.e. NO_x and NMHC) throughout the boundary layer but elevated the ozone concentration in the central urban area by more than 8 ppb. This is likely due to the weakened titration effect stems from the reduced NO_x emission especially for area of highly VOC-limited condition. The study also highlighted the temporary Beijing Olympics 2018 emission control measures expanded the region controlled by both NO_x and VOC and decreased region controlled by VOC.

1.2 Problem Statement

Tropospheric ozone is a secondary pollutant formed when the nitrogen oxides (NO_x) and volatile organic compound (VOCs) react in the atmosphere in the presence of sunlight. While ozone in the stratosphere is useful to protect the planet's surface from the harmful ultraviolet radiation, but ozone in the troposphere or ground-level ozone is the main component of photochemical smog. When present in high concentration, it can cause adverse respiratory effects such as difficulty to breathe, increased susceptible to respiratory diseases, increased sensitivity to allergens (Karthik L et al., 2017), and long term exposure may result in permanent lung damage (Zhang et al., 2019). Ozone is also a plant toxic when enforced by the presence of SO_2 and NO_x can reduce the crop yields (Avnery et al., 2011; Tai and Val Martin, 2017), damage agricultural crops, forests and wilderness areas (Ashmore, 2005).

Over the past several decades, rapid urbanization with increased anthropogenic emissions have substantially increased the adverse effect of UHI as well as the local air quality (Ohara et al., 2007). The UHI effects on air quality stem from the impacts of urbanization on local meteorology. Local studies in Taiwan show that UHI can enhance the daytime sea-breeze and weaken the nighttime land-breeze and thus had a significant impact on the air pollution dispersion in Taiwan (Lin et al., 2008). Besides, UHI effects also play an important role in perturbing thermal and dynamic processes; the convergence system induced by UHI prevented water vapor from being transported by the sea-breeze to the mountainous area and thus delay thunderstorm development (Lin et al., 2011). Since the 1990s, ozone has shown an increasing trend and has become the main air pollutant in southern Taiwan (Chang et al., 2005) which is located in the western coastal region where local circulation is prevalent under weak synoptic weather condition. Kaohsiung city located in southern Taiwan hosted many heavy industries such as petrochemical, refinery, steel-making, and power generation plants. It is also the second largest city in Taiwan which is densely populated approximately 2.7 million inhabitants. The coastal area of Kaohsiung City has the worst air quality in Taiwan because to the several industrial parks that are scattered around the city. Three main power plants are also located within 35 km of the city. The impact of urbanization on local meteorology such as urban heat island effect is well documented in the literatures but very few studies extended to air quality investigations. Ambiguity on the interaction between the UHI effect and local circulations (i.e. land-sea breeze) as well as its possible impacts on ozone air quality remains poorly established.

Due to the stringent emission control policies implemented in the recent years, a decline in NO_x emission by -23% was estimated in Taiwan from 2010 to 2016 using Ozone Monitoring Instrument (OMI) tropospheric nitrogen dioxide (NO_2) retrievals during the Korea-United States Air Quality (KORUS-AQ) campaign over East Asia (Souri et al., 2020). The study also highlighted that Taiwan stand out as region experiencing lower MDA8 ozone levels due to the continuous NO_x reductions throughout the years, especially for areas primarily in NO_x-sensitive condition. Changes in NO_x and VOC emission could lead to increase or decrease in O_3 concentrations depending on the O_3 sensitivity regime. In addition, the local circulation and urban land-surface forcing further complicates the non-linearity of the complex reaction between O_3-NO_x-VOC, making the mitigation policy becomes difficult at urban scale. To reduce the severe photochemical pollution in southern Taiwan, control techniques are required due to the increasing atmospheric oxidation capacity brought on by ongoing urbanization. The large gap in the O_3 budget studies over southern Taiwan may result in the implementation of unsuitable policy. Our knowledge of the budget analysis of the O_3 and its precursors in the vertical profile still has many gaps and uncertainties, which results in a lack of precision in the O_3 pollution reduction strategy across southern Taiwan.

1.3 Proposed Workflow

This thesis adopted the WRF-MEGAN-CMAQ model to simulate the spatial and temporal distribution of O_3 and its predecessors (i.e. NO_x, NMHC) over southern Taiwan at urban scale resolution 1.0 km x 1.0 km. The urbanization in the model is invoked by implementing the single-layer urban canopy (SUCM) scheme in the modelling system. The accurate representation of the urban meteorology fields is crucial in the chemical transport modelling because the chemical production and physical transportation of air pollutants are closely linked with the meteorology at urban scale. Anthropogenic emission is provided by Model Inter-Comparison Study for Asia, MICS at the outer domain (i.e. East China) and Taiwan Emission Data System, TEDS at the inner domain (i.e. Taiwan). The emission inventory contains point, line and area sub-inventory sources which are further estimated into gridded and hourly emissions through the use of SMOKE model. Biogenic emission is provided by the MEGAN v2 model which is driven by the latest plant functional type