The contribution of transport and chemical processes on coastal ozone and emission control strategies to reduce ozone

Justin Lien, Hui-Ming Hung*

Department of Atmospheric Sciences, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, 10617, Taiwan

HIGHLIGHTS

- Leighton Ratio variation illustrates the transition of the ozone transport process.
- Transport causes the noontime O3 time lag under pseudo-steady state conditions.
- AOD and SSA are derived under the apparent photo-stationary condition.
- Sea breeze convergence increases O3 primarily via physical accumulation.
- A feasible emission control strategy is proposed by superposed isopleth diagrams.

ARTICLE INFO

Keywords:
Ozone
Photochemistry
Leighton ratio
Sea breeze
Ozone isopleth

ABSTRACT

The interaction between transport and chemistry is pivotal for local ozone (O3) concentration, especially for a coastal region where the upstream sources might change diurnally. In the current emission control policy, most pollutants, such as particulate matter, SO2, NOx, and CO, decrease while the annual O3 trend might increase due to the complex feedbacks of precursors. In this study, we investigate the influence of transport upon the wintertime O3 diurnal trend over ZuoYing Kaohsiung, an urban coastal site in southern Taiwan, by constructing a two-dimensional numerical model coupling both physical mechanisms and core chemical processes and provide a feasible emission control strategy. The transport process (i.e., import vs. export) for the daytime is determined using the Leighton Ratio (Φ), the ratio of O3-production over O3-loss rate, under the pseudo-steady-state condition. Φ shows a deviation of -9 to +13% from the photo-stationary state, and experiences a transition from import effect before 10:15 to weakening import or net export effect afterward associated with a net O3 production as sea breeze starts developing. The significantly higher Φ derived from observation than from simulation by a factor of 1.35 might be resulted from the over-reported NO2 due to NOy contribution on the NO2 measurement, and the influence of aerosol and cloud possibly reducing ~30% on applied NO2 photolysis rate constant, associated with aerosol optical depth of 0.75 ± 0.15 and single scattering albedo of 0.85 ± 0.15. In this studied NOx-saturated regime, the addition of sea breeze convergence over the land enhances the maximal O3 by ~10%, mainly due to the O3 accumulation (~88%). Furthermore, the ozone isopleth analysis as a function of non-methane hydrocarbons and NOx emissions provides an achievable strategy to decrease both maximum daily ozone and the increment of ozone from morning to maximum by reducing hydrocarbons and NOx emissions, which can also eliminate the additional nitrate contribution on the aerosols.

1. Introduction

Surface ozone (O3) is one of the strong atmospheric oxidants and produced via photochemical processes driven by a well-known NOx-VOCs (volatile organic compounds) framework happening mainly in urban areas [1,2]. High O3 concentration is harmful to human health and has negative impacts on the environment [3, 4, 5]. Sustainable Development Goals 11 in 2019 (SDG11) stated that 90% of humans living in the cities did not enjoy good air quality, which meets the World Health Organization's (WHO) guideline value [6,7]. The government has applied regulations on controlling anthropogenic emissions, and the long-term concentrations of CO and NOx have revealed a decreasing trend [8].

* Corresponding author.
E-mail address: hmhung@ntu.edu.tw (H.-M. Hung).

https://doi.org/10.1016/j.heliyon.2021.e08210
Received 23 July 2021; Received in revised form 13 September 2021; Accepted 15 October 2021
2405-8440/© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
However, the O$_3$ concentration may not have a corresponding response due to the increasing background O$_3$ concentration [9] and the complex feedbacks of precursor gases [10-12]. In addition to the photochemistry, physical mechanisms including the transport process and the evolution of planetary boundary layer height (PBLH) can also play crucial roles in local surface ozone levels by ventilation or accumulation [13-15].

The classical Leighton relationship is frequently applied to estimate O$_3$ concentration under the photo-stationary state as follows:

$$[O_3] = \frac{j_{NO2}[NO_2]}{k_{NOx}[NO]}$$  
(Eq. 1)

where $k_{NOx}$ is the rate constant for NO + O$_3$ to NO$_2$, $j_{NO2}$ is the photolysis rate constant of NO$_2$. The Leighton relationship holds when ozone is balanced by the rapid chemical production and loss processes [1]. Many studies addressed the ozone problem by assessing NO/NO$_2$ computation modeling relies on the Leighton relationship to lower the computational cost [1]. The Leighton Ratio ($\Phi$) is defined as

$$\Phi = \frac{j_{NO2}[NO_2]}{k_{NOx}[NO][O_3]}$$  
(Eq. 2)

and is ~1 for a system composed of NOx and O$_3$ only. For a zero-dimensional box model, the photo-stationary state can be easily reached with $\Phi = 1$ due to the fast chemical processes. The deviation of $\Phi$ from 1 might be caused by the additional pathways such as the conversion of NO to NO$_2$ in the presence of RO$_2$ or O$_3$ loss reactions other than NO + O$_3$ to have $\Phi > 1$ while a significant local NO emission might lead to $\Phi < 1$ [1, 16]. The sufficiently slow photolysis of NO$_2$ at sunrise and sunset might cause the failure of the photo-stationary state [17]. Moreover, Khalil suggested the deviation of $\Phi$ from 1 as an indicator to interpret the transport contribution for an open system using the observation data in Yanbu [15]. He pointed out the invalidity of photo-stationary state in real cases and suggested that the Leighton Ratio, defined as the rate ratio of O$_3$-production/O$_3$-loss, can be applied to differentiate the role of advection and chemistry under the pseudo-steady state assumption [14]. In other words, Leighton Ratio describes the deviation of $O_3$ from the hypothetical photo-stationary state of the system composed of NOx and O$_3$ mainly due to transport. If Leighton Ratio is larger than 1, the chemistry favors the O$_3$ production, which suggests a net export of O$_3$ to sustain the pseudo-steady state. On the other hand, if the net transport O$_3$ is positive (i.e., flux in > flux out), chemistry production is weakened to lead Leighton Ratio less than 1 in response [14, 15].

The air characteristics of the marine atmosphere are typically different from that of the inland atmosphere due to the lack of human activities [18]. The air quality of coastal regions may be subject to the sea-land breeze circulation, and the influence is estimated to be a few kilometers. On one hand, the developed sea breeze together with coastal outflow may ventilate pollution from the boundary layer even under high-pressure days [19]. On the other hand, in some areas, the sea breeze leads to severe ozone episodes under some meteorological conditions [18, 20]. Due to the complex feedbacks of precursor gases on ozone production, the causal linkage of local emissions and ozone concentration relies on the local environment and meteorological conditions.

Taiwan is an island with Central Mountain Range running from the North to the South. Approximately 90% of the population lives on the west side, having flat to gently rolling plains. In the wintertime, Taiwan is under the influence of northeast monsoon, which might bring polluted air to the residential area in the downwind [21, 22]. Kaohsiung, a heavy industrial city in southern Taiwan, suffers from severe air pollution issues and has the worst air quality in Taiwan, especially in winter, due to the meteorological conditions, such as low PBLH, persistent but weak north wind as monsoon, and limited rainfall, leading to poor air quality [22, 23]. Despite the diminishment of some pollutants such as particulate matter (PM), SO$_2$, and CO, ambient O$_3$ concentration has been revealed an increasing trend over the past decades [24, 25, 26]. Nonetheless, the increasing O$_3$ trend may be viewed as a penalty of NOx reduction [27] and the daily maximum O$_3$ increment can serve as an indicator to evaluate the effect of NOx reduction [27, 28, 29]. Hence, the increased O$_3$ and decreased maximum O$_3$ increment may imply a successful NOx reduction with overall O$_3$ concentration restoring the background value. Additionally, the decreased maximum O$_3$ increment reduces the hospital admission rate since the short-term enhancement in ozone corresponds to increased hospital admissions of respiratory diagnosis [30]. The previous study relies on a synoptic model or statistical approaches [27, 31, 32]; however, there is less investigation of the detailed causal relations.

To characterize the interaction of the ozone transport and chemical production, this study constructs the emission diurnal pattern of precursors and the reaction processes over a coastal region (ZuoYing area as shown in Figure 1) in southern Taiwan using a two-dimensional numerical model with time-dependent PBLH. Leighton Ratio is applied to distinguish the chemical and physical processes. Moreover, the influence of local emission and convergence of sea breeze upon winter ozone is discussed for the regional characteristics. With the analysis, a feasible local emission reduction strategy on precursors is proposed by analyzing the maximum daily O$_3$ and the daily maximum O$_3$ increment under different precursor emission scenarios.

2. Methodology

A two-dimensional numerical model, consisting of both physical mechanism (including advection, emission, and entrainment) and core chemical processes, was developed using Matlab2019b (The MathWorks, Inc) to simulate the mean winter diurnal O$_3$ profile in Southern Taiwan. The simulated results are compared with the observation of the ZuoYing Environmental Protection Administration (EPA) site (22.6749°N, 120.2929°E), ~2.8 km from the sea, in 2018 winter. The developed model is further used to evaluate the contribution of transport and emissions.
2.1. Model description and setup

For a small domain study without topography and the resident time of nonvanishing advection process <6 hr, the concentration $X_i$ of a given species $i$ (in a unit of molecules/volume) in the Eulerian framework under the well-mixing assumption is governed by the differential mass balance equation,

$$\frac{\partial X_i}{\partial t} = -\nabla \cdot (\mathbf{u}X_i) + \frac{E_{ni}}{h} (X_{ni} - X_i) + \frac{P_i}{h} \delta(h) + (P_i - L_i)$$  \hspace{1cm} \text{(Eq. 3)}

with negligible diffusion and dry decomposition, where $\mathbf{u}$ is the wind vector, $\nabla$ is the gradient, $E_{ni}$ is the local emission, $X_{ni}$ represents the background concentration, $h$ and $h'$ are the mixing layer height and its time-derivative, respectively, $\delta$ is the Heaviside step function, and $P_i$ and $L_i$ stand for the chemical production and loss, respectively. Simply speaking, the four terms in Eq. (3) correspond to the advection, emission, entrainment, and chemical processes, respectively. Emission term with a unit of molecules km$^{-2}$ hr$^{-1}$ describes the anthropogenic source from the surface. Entrainment characterizes the effect from the free troposphere when the mixing layer is rising, i.e., $\delta(h) = 1$ if $h' \geq 0$ and $\delta(h) = 0$ otherwise. The detailed chemical processes are illustrated in section 2.1.1. In this study, advection and chemical production are solved using the backward Euler method, while other processes are treated by the forward method.

The model takes time-dependent meteorological parameters (including wind field, temperature, and relative humidity (RH)), PBLH, emission profile, and the boundary and background conditions of each measured species (CO, NMHCs, CH$_4$, NO, NO$_2$, and O$_3$) as input for Eq. (3). The boundary and background conditions for non-measured species (e.g., radicals and HNO$_3$) are assumed to be zero. The spatial domain of this study takes over the region of 6.65 km x 7.5 km (22.7042 ± 0.0295 N, 120.2928 ± 0.0354 E) as shown in the map of Figure 1, and is partitioned into 11 x 11 rectangles with a spatial resolution of 604 m x 680 m. Because the system is independent of the initial condition after 6-hr simulation, the model is implemented at a 0.01-hr time step for a 48-hr simulation with the last 24-hr data for further analysis.

2.1.1. Core ozone chemical processes

The ozone-related chemistry involves the well-known NOx-VOCs (or CO) framework [2, 11, 15, 33]. In this study, only gas-phase reactions are taken into accounts for simplification since the resident time via advection is approximately 1 hr. The daytime O$_3$ is governed by the following cycle:

- NO + O$_3$ → NO$_2$ + O$_2$  \hspace{1cm} \text{(R1)}
- NO$_2$ + hv小事→NO + O$_3$  \hspace{1cm} \text{(R2)}
- P$_i$ + OH → → → RO$_2$ + other molecules  \hspace{1cm} \text{(R3)}
- RO$_2$ + NO →小事→RO + NO$_2$  \hspace{1cm} \text{(R4)}
- RO → → → HO$_2$ + other molecules  \hspace{1cm} \text{(R5)}

where $P_i$ denotes the precursor of $i$, such as CO, CH$_4$, or non-methane hydrocarbons (NMHCs), and RO$_2$ denotes HO$_2$ or organic peroxy radicals. Propene is applied as the representative NMHCs to initialize the NO cycle: the daytime O$_3$ is governing by the following reaction since the resident time via advection is approximately 1 hr. The cross-section and quantum yield are obtained from SAPRC-07 [34].

The rate constants of applied major reactions are summarized in Table S1. The photolysis rate constants are assumed to be proportional to the cosine of solar zenith angle and calculated with the reported actinic flux [1,2], while the cross-section and quantum yield are obtained from SAPRC-07 [34].

2.1.2. The use of observation data

The applied diurnal meteorological parameters are the mean winter condition of the ZuoYing EPA site as shown in Figures 2a and 2b. Temperature is in the range of 18-24 °C while the RH is 65-85%. There is ~1.73 m s$^{-1}$ of the prevailing north wind mainly due to monsoon, while the sea-land breeze circulation induces the west wind in the range from -0.19 m s$^{-1}$ to 2.36 m s$^{-1}$. The applied time-dependent mixing layer height shown in Figure 2c is based on the analysis of the Central Weather Bureau database [35]. Except for the case of sea-breeze convergence stated in sections 2.3 and 3.4, all meteorological parameters within the studied domain are assumed to be spatially invariant but time-dependent.

The boundary and background conditions of measured chemical species are based on the observation results (Figure S1) of the nearby Taiwan EPA sites with PengHu data for the whole west side, NanZih data for the northeastern corner, and FuGuiJiao data as the background value. For NMHCs and CH$_4$, the west side boundary data are adapted from FuGuiJiao’s data due to no measurement in PengHu. The northern boundary is estimated using linear interpolation between PengHu and NanZih data (locations are shown in Figure 1). The wind field applied in this study has no south wind and the span of east wind is within an hour, which has non-observable influence over ZuoYing, so the concentration of the south side is assumed to be zero and the east side in the domain is extended as the east boundary condition.

### Table 1. Emission in 2013 over Kaohsiung [36].

| Sources/Sectors          | CO (10$^3$ kg yr$^{-1}$) | NMHCs | NOx |
|--------------------------|--------------------------|-------|-----|
| Industry                 | 19092                    | 18428 | 38433 |
| Vehicle                  | 78784                    | 20594 | 27354 |
| Non-road transportation  | 911                      | 270   | 5827  |
| Commercial               | 937                      | 13338 | 260   |
| Construction             | 0                        | 5884  | 0    |
| Burning                  | 2553                     | 282   | 349   |
| Other                    | 941                      | 443   | 1808  |

Note: In the model, sources other than Industry and Vehicle in Table 1 are summed up and considered as “Others”.
2.1.3. Emission profile

The precursor emissions for Kaohsiung summarized in Table 1 are based on the annual emission from Taiwan Emission Data System (TEDS9.0) reported by Taiwan Environmental Protection Administration (TWEPA) [36] by assuming the same daily pattern through the whole year. To downscale the annual emission of Kaohsiung into a small domain, the relative daily emission trend is firstly retrieved based on the following assumptions, 1) the vehicle source is proportional to transportation flux reported by the local governments, 2) the industrial source is independent of time and the other sources are modeled by a sinusoidal wave, and 3) the relative amount of emission matches the emission ratio in Table 1. Then the diurnal emission rate is quantified by minimizing the deviation of modeled nighttime CO concentration. In particular, the studied domain is ~10 km away from the heavy industrial parks with limited diesel trucks passing, which might lead to a lower ratio of NO over CO emissions than the reported ratio in Table 1. Thus, an extra emission adjustment for NOx by a factor of 0.1 of the averaged Kaohsiung NOx emission adjustment for NOx by a factor of 0.1 of the averaged Kaohsiung NOx emission correction factor, as illustrated in section 2.1.

2.2. Leighton Ratio

To evaluate the contribution of chemical processes or transport to the O$_3$ profile, the Leighton Ratios for both observation (J$_{NO2}$ adapted from TEDS9.0) and simulation as a function of time are estimated using Eq. (4):

$$\Phi = \frac{\sum \text{Rate}_\text{Prod}}{\sum \text{Rate}_\text{Loss}}$$

(Eq. 4)

reduces the influence of chemical processes such as NMHCs. In this study, the pseudo-steady state condition holds during the daytime, with \( \frac{\partial O_3}{\partial t} \) less than 3.5% of the major transport and chemical processes, fulfilling the validity of a pseudo-steady state with \( \frac{\partial O_3}{\partial t} \) < 10% of major terms in Eq. (3) as stated by Khalil [15]. The detailed information regarding the contribution of each term is shown in Figure S2. As a remark, we emphasize Khalil’s framework in which the Leighton Ratio is reinterpreted as the contribution of the transport process since O$_3$ is controlled only by transport and chemical processes. In addition to the advection, the Leighton Ratio should be more precisely reinterpreted as the contribution of nonchemical processes due to the additional entrainment term in Eq. (3) in our framework. Nevertheless, the entrainment term is considerably smaller than others, as shown in Figure S2a.

2.3. Sensitivity analysis

With the established model, we multiply a factor from 0 - 2.0 to NMHCs and NOx emission, individually, in the “Full Processes” case to evaluate the influence of NOx-VOCs framework on the maximum daily O$_3$, denoted as O$_3$(Max), and the maximum O$_3$ increment from 8:00 to the maximum O$_3$ of the day, denoted as \( \Delta O_3 \) (i.e., \( \Delta O_3 = O_3(\text{Max}) - O_3(8:00) \)). Furthermore, the measured u-wind over RenWu (an EPA site, 4.1 km in the east of ZuoYing) of 0.58 m $s^{-1}$ smaller than that over ZuoYing during 14:00–15:00, might suggest a significant convergence as wind traversing toward the east. The convergence is estimated at ~1.41 \times 10^{-4} m s$^{-1}$ in the east-west direction likely due to the land roughness and the interaction with the northerly monsoon. For a clean marine condition, sea breeze might ventilate the pollution and act as a factor causing convergence to accumulate pollution in ZuoYing. The impact of convergence on O$_3$ concentration is evaluated by assuming that a hypothetical convergence happens at u > 0.5 m s$^{-1}$ and is proportional to the development of sea breeze, i.e., \( D_{\text{max}} = \frac{(u - 0.5)}{(u_{\text{max}} - 0.5)} \) with \( D_{\text{max}} = 5.2 \times 10^{-5} m s^{-1} \) as the maximum convergence.

3. Results and discussion

3.1. Model results

Figure 3 shows the diurnal variation of the monitored species for both observation and simulation results. The simulated emitted species considering all processes (i.e., “Full Processes” case) show a similar

![Figure 3](image-url)

Figure 3. The simulation results of two cases ("Full processes" and "No Chemistry") and observation over ZuoYing for (a) CO, (b) CH$_4$, (c) NMHCs, (d) NO, (e) NO$_2$, and (f) O$_3$. The error bar of observation stands for ± σ and the average is taken after removing outlier (> ± 1.5σ). "Full Processes" considers both physical processes and chemistry, while "No Chemistry" only takes physical processes into account. The crimson dashed line in (d) and (e) corresponding to the right axis is the simulation result with no NOx correction factor, as illustrated in section 2.1.
Table 2. The normalized mean bias factor of each monitor species.

| Species | $r$     | $B_{\text{NMABF}}$ | $E_{\text{NMABF}}$ |
|---------|---------|---------------------|---------------------|
| CO      | 0.9099  | -0.0604             | 0.0840              |
| NMHCs   | 0.9500  | -0.2689             | 0.2119              |
| CH4     | 0.9508  | -0.1046             | 0.0097              |
| NO      | 0.9738  | -0.1046             | 0.4335              |
| NO2     | 0.7828  | -0.1973             | 0.2200              |
| O3      | 0.9917  | -0.0126             | 0.1400              |

The normalized mean bias factor ($B_{\text{NMABF}}$) and the normalized mean absolute error factor ($E_{\text{NMABF}}$) are calculated as follows:

$$B_{\text{NMABF}} = S \left( \exp \left( \frac{\sum M_i - \sum O_i}{M_i} \right) - 1 \right)$$

$$E_{\text{NMABF}} = \frac{\sum |M_i - O_i|}{| \sum O_i | \sqrt{2}} - 1$$

where $M_i$ and $O_i$ are the modeled and observed values, respectively, and the summation is taken over the samples over the day.

The diurnal trend with the observation and have better consistency in the nighttime but underestimation over the afternoon period. Table 2 summarizes the correlation ($r$), the normalized mean bias factor ($B_{\text{NMABF}}$) and the normalized mean absolute error factor ($E_{\text{NMABF}}$) [39] between simulation and observation. The modeled values are highly correlated to observation with $r > 0.9$ for most species, but a lower correlation $r = 0.78$ for NO2 due to more substantial deviation during noontime. The negativity of $B_{\text{NMABF}}$ indicates the overall underestimation of simulation, which might be attributed to the model well-mixing assumption. The emission is mainly sourced from the surface level and requires time or turbulence motion to mix. The concentrations, in general, have a decreasing trend with respect to altitude even within PBL. The well-mixing assumption averages the higher concentration near the observation sites (~15 m above the ground level) along with the decreasing profile within the PBLH. Therefore, it might be expected that the observed concentrations are higher than the simulated concentrations.

Additionally, part of NMHCs understimation might arise from the lack of natural emission sources in TEDS9.0. $E_{\text{NMABF}}$ of CO, NMHCs, CH4, NO2, and O3 has a value <0.22 suggesting the bias is acceptable. As the only exception, NO seems to have a larger ENMAEF due to its significant low concentration (<1 ppbv) during nighttime, near the instrument detection limit of 0.5 ppbv as summarized in Table S2 [40]. Overall, the simulation reveals major ozone characteristics, the start of ozone elevation and the peak occurrence time, which are used in the following analysis.

The concentrations of CO, CH4, and NMHCs are relatively unaffected by the chemical processes in this small domain study since their lifetimes in the daytime are 60.8 days, 6.6 years, and 13.5 hr, respectively, significantly longer than the residence time of air in the domain, ~1 hr. Even though NMHCs have the lowest concentration compared with CO and CH4, it is the major contributor to ozone production due to the higher reactivity. In contrast, NO, NO2 and O3, having short lifetimes responding to the chemical processes (54 s, 2.7 min, and 8.7 min, respectively), are subject to chemistry even within the applied small domain. As anthropogenic activities progress, such as morning traffic, precursors can reach their peak occurrence time, which are used in the following analysis.

3.2. Ozone profile

3.2.1. Time-lag

Photochemistry is a key process to produce O3 in the troposphere. However, the ambient O3 profile usually shows a certain time lag with solar radiation [42]. As shown in Figure 4a, there is a 2-hr time-lag between the simulated O3 profile and the applied NO2 photolysis rate constant, $j_{\text{NO2}}$. This 2-hr time-lag can be deconvoluted into the contribution of several factors such as the transport, transformation of other chemical forms, and the quantity of oxidation production.

First, under no wind condition, the model almost reduces to a chamber system. It shows a 30-min time-lead than the maximum radiation (Figure S3), possibly due to the time-dependent emissions and PBLH. On the other hand, as all chemical processes are turned off, O3 achieves a peak value at 15:15 due to transport as shown in Figure 3f ("No Chemistry" case). In this case, O3 is governed by mere advection with negligible emission and entrainment terms. Intuitively, the two-dimensional wind field blows the northern boundary conditions (with peak ~ at 14:00) to Zuoying, with the resulting O3 profile delayed due to transportation time. Overall, the “Full Processes” case shows the combined effect of chemical processes (peak at 11:30) with the transport (peak at 15:15) leads to the peak at 14:00.

The chemical processes in the NOx-VOCs framework generate the HOx (i.e., $OH + RO + RO_2$) cycle, which not only produces O3 but also partially stays as NO2 for approaching the photo-stationary state via the fast NO + O3 reaction. Some HOx might be terminated as HNO3 or H2O2, having lower reactivity to affect ozone production. To access the net photochemical formation of O3, we modified the definition of Ox as $Ox = O3 + NO2 + 2 \times NO3 + 3 \times NOx + OH + 1.5 \times HNO3$, stated by Womack et al. [43]. Ox has a maximum value around noontime as shown in Figure 4a and the model result suggests that the major contributors of Ox are O3 and NO2.

The transport pattern over Zuoying, together with the composition of Ox, explains the O2 time-lag. During the period from 12:00 to 14:00, O2 is exported by the possible ventilation effect of the sea breeze as $\Phi > 1$ (see section 3.2.2). To retain the pseudo-steady state, it results in higher NO2 concentration to raise the production rate, balancing the exported O2. Therefore, despite the Ox maximum at noon, it partially stays in the form of NO2 instead of converting to O3. Likewise, a higher reactivity or a higher amount of reactive NMHCs can shift the O3 peak toward noontime (Figure S3) by adjusting the distribution of NOx-O3 while retaining the
pseudo-steady-state. Overall, the observed and simulated postponed O₃ peak away from the maximal photolysis rate is caused by the combined effect of transport and chemical processes (i.e., the production efficiency and the distribution of Ox to various species other than O₃).

### 3.2.2. Leighton Ratio

With the detailed chemical processes simulation, the derived Leighton Ratio (Φ) using Eq. (4) is less than that using Eq. (2) as shown in Figure 4b. That is mainly caused by an additional contribution of O₃ loss reactions (reactions 3, 5, 6, 12a, and 28, in Table S1) other than NO + O₃ in the denominator of Eq. (4). Nevertheless, the overall trends of Φ between Eqs. (2) and (4) are consistent despite the slightly different transition time for Φ = 1. The simplified version from Eq. (2) gives a fair estimation as compared with that derived from Eq. (4) to evaluate the pseudo-steady state of O₃ and to illustrate the net transport, Tₚₑᵗ (= Flux in – Flux out) (Figure S2b), so Φ discussion in the rest of this study is based on Eq. (2).

Figure 4b shows that the simulation has daytime Φ in the range of 0.9–1.13, slightly less than 1 in the morning (~0.9 at 7:00), and Φ slowly increases with time to have a value larger than 1 starting at ~10:15. Φ ~ 1 might imply that NOx-O₃ chemistry tends to adjust itself via photolysis (O₃). This phenomenon is not consistent with the observed lower O₃ concentration in the downwind before the transition under the assumption. In the measurement error aspect, NO has a relatively low concentration except for the morning peak as stated in section 3.1. Therefore, the round-off error of NO concentration might lead to an overestimation of jNO₂ corre-

The proximity of the observation site to the emission sources might have a stronger influence than the well-mixing process in the model since the fresh emission would cause a lower Φ [1]. The emitted NOx has a ratio NO/NO₂ = 9 while the daytime simulated NO/NO₂ ranges from 0.005 to 0.61, roughly in the observed range from 0.081 to 0.38. This may imply that the NO transforms rapidly to NO₂ once emitted if there is sufficient O₃. If the observation site captures the information close to the source, a lower Φ is expected, and the corresponding import is possibly due to vertical motion or other processes instead of horizontal transport. Nonetheless, a regular Taiwan EPA site, ~15 m above the ground level, may be able to capture the concentration close to photo-stationary state due to the rapid transition of NO, as the observed ratio NO/NO₂ is similar to the simulated ratio, obtained under the ideal well-mixing assumption.

Moreover, Φ from observation reveals an absorb peak (~1.7) in the early morning, which may be caused by various factors. For instance, as mentioned above, Kaohsiung has suffered from severe air quality issues, especially in the early morning. In winter, the abundant aerosols might constantly lower the morning jNO₂ to cause applied jNO₂ highly over-
estimated. Also, the applied jNO₂ is mathematically estimated with the intensity of solar radiation, which reaches its highpoint at 12:00, as stated in section 2.2.1. In reality, the peak may slightly differ due to the difference between local time and solar time. With a 15-min delay adjustment in jNO₂ (i.e., Φ(0) = jNO₂(t+15min) [NO₂]/(kNO-O₃)

The Leighton Ratio is re-calculated for observation has a similar trend as simulation without the absorb morning peak, as shown in Figure 4b. Nonetheless, the overall profile still exceeds 1.3, consistent with the aerosol influence stated above.

The 5. The simulated diurnal O₃ profile (solid lines) and Leighton Ratio (dotted lines) under different emission conditions; (a) normalized NMHCs emission, and (b) normalized NOx emission. The gray dashed line spec-
ifies Φ = 1.
Hence, the higher derived $\Phi$ from observation data is more likely resulted from the over-reported $\text{NO}_2$, and the applied higher $j_{\text{NO}_2}$, without considering the scattering or absorption of aerosols and clouds.

### 3.3. Ozone isopleths for emission control

Emission usually dominates the concentration of precursors and NOx in urban areas. Figure 5a shows that NMHCs emission primarily affects $O_3$ around 10:00–14:00, at which the photolysis is closed to its peak of the day, and has negligible influence on $O_3$ for the rest of time in particular, the morning time ozone $O_3(8:00)$. Therefore, both $O_3(\text{max})$ and $\Delta O_3$ respond positively to NMHCs emission change. On the other hand, Figure 5b suggests that the overall ozone profile responds negatively to NOx emission change in the whole day, since the titration effect is independent of the existence or the intensity of light. Therefore, it indicates that ZuoYing region is under NOx-saturated regime and $O_3(\text{max})$ is negatively related to NOx emission change. Nonetheless, under a half NOx emission change as an example (green line in Figure 5b), the noontime $O_3$ increases slightly less than ozone in the rest of time: though NOx emission is reduced by half in the whole day, $O_3$ partially converts back to NOx in the daytime. Thus, the difference of $O_3$ changes at different times leads to a decrease of $\Delta O_3$ so that $\Delta O_3$ responds positively to NOx emission change. Similar results were reported by Jhun et al., who suggested that NOx reduction narrowed the gap between $O_3(\text{Max})$ and non-peak $O_3$.

The dependence of $O_3(\text{Max})$, as a function of NMHCs and NOx emissions, was applied to investigate the different reduction strategies. Figure 6a presents the ozone isopleth plot of a typical NOx-saturated regime, but with linearized ozone isopleth. The behavior of ozone isopleths indicates that the environment of ZuoYing is still NOx-saturated even with the imported precursors only, consistent with the study of Peng et al. [49]. To shift the environment to NOx limited, we would need to adjust the boundary condition, which was not taken into accounts for simplification. Figure 6b shows $\Delta O_3$ isopleths under different NMHCs and NOx emission scenarios. As discussed in the preceding paragraph, the $O_3(\text{Max})$ and $\Delta O_3$ isopleths as a function of NMHCs and NOx emissions show different trends. By visualizing the emission control strategy as an arrow emanating from the base case (1, 1) on Figures 6a and 6b, the simultaneous decrease of $O_3$ and $\Delta O_3$ can be achieved if the arrow lies in the shaded area; that is, the following criteria is satisfied: $-0.25 \leq \Delta n_{\text{NOx}}/\Delta n_{\text{NMHCs}} \leq 0.5$ and $\Delta n_{\text{NMHCs}} < 0$, where $\Delta n$ is the change of normalized emission. However, it may not be wise to lower $O_3$ and $\Delta O_3$ via more NOx emission, so the criterion should be refined as follows:

$$0 \leq \Delta n_{\text{NOx}}/\Delta n_{\text{NMHCs}} \leq 0.5 \text{ and } \Delta n_{\text{NMHCs}} < 0 \quad (\text{Eq. 5})$$

Once the emission reduction satisfies Eq. (5), the simultaneous decreases of NMHCs, NOx, $O_3$, and $\Delta O_3$ can be achieved.

Moreover, to further examine the influence of NOx and NMHCs emission during transport, Figures 5a and 5b show the diurnal $O_3$ profile and Leighton Ratio under different emission rates, respectively. The transported or chemically produced $O_3$ is always partially titrated by NOx molecules. To retain a pseudo-steady state, higher $O_3$ results in a stronger net export effect, leading to a higher Leighton Ratio, and causes higher ozone concentration downstream due to $O_3$ production overcoming the titration via the emission adjustment. In terms of species, the Leighton Ratio is more sensitive to NOx emission change than to NMHCs change, corresponding to the fact that $O_3(\text{Max})$ is more sensitive to NOx emission change. Besides, Leighton Ratio is more sensitive and achieves a maximum value around 14:00, possibly due to high $j_{\text{NO}_2}$, the $O_3$ peak concentration, and the strongest sea breeze.

### 3.4. Influence of convergence and sea breeze

With the addition of convergence, Figure 7 shows a maximum of 10.0% $O_3$ increase during 10:45 to 19:30. This enhancement is attributed to the net effect of ozone accumulation and the chemical processes via the accumulated precursors. By taking 14:00 data for comparison, the $O_3$ increases 6.4% by convergence. As shown in Figure S6, the deviation of $\Phi$ due to convergence mainly follows from the deviation of the net transport contribution, as transport primarily accounts for an 8.4% $O_3$ increase while chemistry contributes to the remaining 1.2% increase. The chemical response to convergence event is the combined effect of accumulated NOx and NMHCs: the former lowers $O_3$ in a NOx-saturated regime while the latter rises $O_3$ in the noontime. As a result, the opposite chemical effects on ozone due to NOx and NMHCs accumulation (6.3% and 6.5%, respectively, at 14:00) are mostly canceled out in this NOx saturated environment. Therefore, the convergence increases local ozone concentration over ZuoYing mainly physically with minor influence by the chemical processes.
The Leighton Ratio in Figure 7 does not show an observable change under convergence. The 6.3% increase of NOx at 14:00 can be decoupled as the combination of a 1.2% decrease for NO and an 8.0% increase for NO2. The non-observable response of Leighton Ratio due to convergence might reflect the cancellation of opposite chemical effects of NMHCs and NOx. Besides, with the convergence, the accumulation leads to increased import contribution during the transition period 10:15–12:00 as shown in Figure S6. The chemical processes are slightly modified to reflect the accumulation of precursors and ozone, which is relatively small (less than 10%) to affect the Leighton Ratio.

The influence of convergence over the coastal ozone is strongly dependent on the environment. Liu and Chan reported that NOx dominated a severe air-pollution episode in Hong Kong while O3 retained low concentration during the convergence event caused by sea-land breezes [20]. In this Hong Kong case with NOx-saturated regime, because the upstream location was a power plant with significant NOx emission, the titration effect by excessive NOx accumulation was more significant than the possible opposite effects by NMHCs and O3 accumulation in the convergence zone, resulting in a much lower O3 concentration than the background values. More specifically, NOx dramatically increased during the convergence episode (e.g., NO ~ 480 ppbv & NO2 ~ 100 ppbv during the episode while the averaged concentration was NO ~ 24 ppbv & NO2 ~ 39 ppbv over Central/Western, a pollutant monitoring station in Hong Kong). In contrast, the convergence induced by the sea breeze and clean upstream source moderately increase O3 by a maximum of 10.0% in our study. Hence, the convergence chemically decreases ozone in the study of Liu and Chan [20]. Moreover, Wang et al. showed that the sea breeze circulation might lead to severe ozone episodes at the coastal site in Hong Kong [18]. In their domain of study, the marine site revealed a higher ozone concentration than the coastal site due to a stronger photochemical process and weaker titration effect. The cyclone or continental anticyclone might carry the air parcel containing human-emitted primary pollutants outside the land, and later the photochemistry resulted in a high ozone concentration. Under this setup, the ozone would be transported into the coastal sites by the sea breeze; in contrast, the sea breeze, in general, brings cleaner air over ZuoYing in the afternoon, combining with stronger photo-production of ozone, which results in a net export effect.

4. Conclusions and atmospheric implications

In this study, we evaluate the effect of transport on the ozone-related chemistry and provide a feasible emission control strategy over a NOx-saturated regime using a two-dimensional numerical model coupling both physical mechanisms and core chemical processes for the coastal wintertime O3 concentration simulation. The simulation results suggest that the daytime O3 chemistry is close to the photo-stationary state $\Phi \sim 1$, with a deviation of -9% to +13% mainly due to the transport process, $\Phi$ experiences a transition from import effect before 10:15 to weakening import or net export effect afterward associated with a net O3 production as sea breeze starts developing with ventilation effect. During the period of 12:00 to 14:00, the transport process postpones the O3 peak by keeping Ox in the form of NO2 under the pseudo-steady state condition. In addition, the significantly higher $\Phi$ derived from observation data than from the simulation by a factor of 1.35 suggests the over-reported NO2 and the possible aerosol and cloud influence, which reduces $\sim 30\%$ on $J_{NO2}$ associated with AOD of $0.75 \pm 0.15$ and SSA of $0.85 \pm 0.15$, under the apparent photo-stationary condition (i.e., $\Phi \sim 1$).

Under the hypothetical sea breeze convergence, the influence of sea breeze convergence leads to a maximum of 10.0% O3 increase primarily by the accumulation via the transport process in this study. The chemical response to convergence reflects the cancellation of accumulated NMHCs and NOx, leading to no significant changes of Leighton ratio with convergence. With the analysis of ozone isopleths under differential local emission control strategies, the annual increase of O3 may be attributed to the improper ratio of normalized NMHCs and NOx reductions due to their opposite effects on O3. The feasible emission control strategies as Eq. (5) can achieve simultaneous decreases of $O_3$(Max), $\Delta O_3$, NMHCs, and NOx. Furthermore, the same concept could be applied to evaluate the influence of feasible emission control strategies on the mitigation of other species such as Ox, and HNO3, which are also controlled by NOx and NMHCs and might have significant contributions to particulate matter [43, 49, 50]. The superposition of profiles for different species might propose a better emission control strategy to reduce all species.

Declarations

Author contribution statement

Justin Lien: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Hui-Ming Hung: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was supported by the Ministry of Science and Technology, Taiwan (108-2111-M-002-003 and 109-2111-M-002-003).

Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2021.e08210.

Acknowledgements

We would like to thank the anonymous reviewers for their constructive and valuable comments.

References

[1] B.J. Finlayson-Pitts, J.N.J. Pitts, Atmospheric Chemistry. Fundamentals and Experimental Techniques, John Wiley and Sons, New York, NY; None, 1986, p. 1125. Medium: X; Size.
[2] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics: from Air Pollution to Climate Change, Wiley, 2006.
[3] S. Anenberg, J. Schwartz, D. Shindell, M. Amann, G. Faluvegi, Z. Klimont, G. Janssens-Maenhout, L. Pozzoli, R. Van Dingenen, E. Vignati, et al., Global air quality and health Co-benefits of mitigating near-term climate change through methane and black carbon emission controls, Environ. Health Perspect. 120 (2012) 821–829.
[4] Y. Fang, V. Naik, L.W. Horowitz, D.L. Mauzerall, Air pollution and associated human mortality: the role of air pollutant emissions, climate change and methane concentration increases from the preindustrial period to present, Atmos. Chem. Phys. 13 (2013) 1277–1294.
[5] J.J. West, A.M. Fiore, L.W. Horowitz, D.L. Mauzerall, Global health benefits of mitigating ozone pollution with methane emission controls, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 3988–3993.
[6] United Nations (UN), Sustainable Development Goal 11, Available online: http://sustainabledevelopment.un.org/sdg11 (accessed on September, 2019).
[7] WHO, Ambient (outdoor) air pollution, Available online: https://www.who.int/en/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health (accessed on September, 2019).
[8] F.-Y. Cheng, C.-H. Hsu, Long-term variations in PM2.5 concentrations under changing meteorological conditions in Taiwan, Sci. Rep. 9 (2019) 6635.
[9] R.A. Vingarzan, Review of surface ozone background levels and trends, Atmos. Environ. 38 (2004) 3431–3443.
[10] K. Li, D.J. Jacob, H. Liao, L. Shen, Q. Zhang, K.H. Bates, Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, Proc. Natl. Acad. Sci. 116 (2019) 222.

[11] D.J. Jacob, Introduction to Atmospheric Chemistry, Princeton University Press, 1999.

[12] L.I. Kleinman, Low and high NOx tropospheric photochemistry, J. Geophys. Res.-Atmos. 99 (1994) 16631–16638.

[13] D.P. Lalas, D.N. Astmakopoulou, D.G. Deligiorgi, C.G. Helmis, Sea-breeze circulation and photochemical pollution in Athens, Greece, Atmos. Environ. 17 (1983) 1621–1632.

[14] M.A.K. Khalil, Steady states and transport processes in urban ozone balances, NJP Clim. Atmos. Sci. 1 (2018) 22.

[15] M.A.K. Khalil, C.L. Butenhoff, R.M. Harrison, Ozone balances in urban Saudi Arabia, NJP Clim. Atmos. Sci. 1 (2018) 27.

[16] D.M. Chate, S.D. Ghude, G. Beig, A.S. Mahajan, C. Jena, R. Srinivas, A. Dahiya, M.A.K. Khalil, C.L. Butenhoff, R.M. Harrison, Ozone balances in urban Saudi Arabia, Atmos. Environ. 36 (2002) 591–601.

[17] H. Liu, J.C.L. Chan, An investigation of air-pollutant patterns under sea breezes during a severe air-pollution episode in Hong Kong, Atmos. Environ. 33 (1999) 1821–1833.

[18] K. Li, D.J. Jacob, H. Liao, L. Shen, Q. Zhang, K.H. Bates, Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, Proc. Natl. Acad. Sci. 116 (2019) 222.

[19] N. Kumar, Deviations from the O3 photostationary state at Niwot Ridge, Colorado, J. Geophys. Res. Atmos. 91 (1986) 5361–5370.

[20] H. Pleijel, J. Klingberg, G. Pihl Karlsson, M. Engardt, P.E. Karlsson, Surface ozone in Copenhagen, W.H.O.R.O.f.E., Air Quality Guidelines for Europe, 2000, p. 184.

[21] J.B. Milford, D. Gao, S. Sillman, P. Blossey, A.G. Russell, Total reactive nitrogen (NOy) as an indicator of the sensitivity of ozone to reductions in hydrocarbon and NOx emissions, J. Geophys. Res. Atmos. 91 (1986) 5335–5342.

[22] S. Sillman, The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments, Atmos. Environ. 33 (1999) 1821–1845.

[23] J.-J. Kelly, C.L. Parworth, Q. Zhang, D.J. Miller, K. Sun, M.A. Zondlo, K.R. Baker, A. Wisthaler, J.B. Nowak, S.E. Pusede, et al., Modeling NH4NO3 over the san joaquin valley during the 2013 DISCOVER-AQ campaign, J. Geophys. Res. Atmos. 128 (2013) 4727–4745.