Inter-correlation of Chemical Compositions, Transport Routes, and Source Apportionment Results of Atmospheric PM_{2.5} in Southern Taiwan and the Northern Philippines

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ABSTRACT

This study investigated the inter-correlation of atmospheric PM_{2.5} between southern Taiwan and the northern Philippines. 24-hour samples of PM_{2.5} were simultaneously collected at two remote sites, Checheng (Taiwan) and Laoag (Philippines), during all four seasons. The water-soluble ions, metallic elements, carbonaceous content, and anhydrosugars in the PM_{2.5} were then analyzed to characterize the chemical fingerprint. Furthermore, principal component analysis, chemical mass balance (CMB) receptor modeling, and backward trajectory simulation were applied to resolve the source apportionment of PM_{2.5} at both of the sites.

The results showed that Checheng and Laoag were highly influenced by polluted air masses transported long-range from the north, producing elevated PM_{2.5} concentrations during winter and spring. The water-soluble ions (WSIs) were abundant in secondary inorganic aerosols (SO₄²⁻, NO₃⁻, and NH₄⁺), which accounted for 34.1–76.0%. Crustal elements dominated the metallic content in the PM_{2.5}, but the concentrations of trace elements originating from anthropogenic sources increased during the northwestern monsoon periods. More organic carbon (OC) than elemental carbon (EC) was found, with secondary OC (SOC) contributing approximately 23.9–38.9% to the former. Moreover, the level of levoglucosan highly correlated with those of K⁺ and OC, confirming that these three substances are key indicators of biomass burning.

The two sites exhibited similar chemical compositions for PM_{2.5}, indicating the possibility of transport between Checheng and Laoag, and a paired *t*-test obtained a *p*-value of 0.030 (*p* < 0.05), implying a potential inter-correlation for PM_{2.5} between southern Taiwan and the northern Philippines. The major sources of the PM_{2.5} were soil dust, mobile sources, sea salt, and biomass burning along the northerly transport routes during winter and spring. The contribution of anthropogenic sources (i.e., industrial boilers, waste incinerators, and secondary aerosols) to the PM_{2.5} frequently increased during winter and spring, unlike during summer, suggesting that the northerly transport of PM_{2.5} highly affected particulate air pollution at both of the sites.

Keywords: Inter-correlation of remote sites; Atmospheric fine particles (PM_{2.5}); Chemical fingerprints; Transport routes; Source apportionment.

INTRODUCTION

The detriment of ambient air quality could be influenced by local emissions and long-range transport from upwind polluted regions, which physically or chemically interacts to form secondary aerosols (Li *et al.*, 2016; Wang *et al.*, 2016). Poor air quality in urban areas in specific season is not only an important scientific research issue, but also attracts

massive attention by governments and non-government organizations (NGOs) to clarify the emission sources (Seinfeld and Pandis, 2006; Lee *et al.*, 2018b). Particularly, Chinese haze and Asian Dust often occurring in winter and spring are highly correlated to China's rapid industrial development and unrestricted agricultural expansion (Yuan *et al.*, 2006; Li *et al.*, 2016; Li *et al.*, 2018). Asian Dust could not only invade northeastern Asia such as China, Korea, and Japan, but might also reach Taiwan, Philippines, and Hong Kong, and other southeastern Asian regions in winter and spring (Fang *et al.*, 2013; Yuan *et al.*, 2013). Chinese hazes, namely PM_{2.5}, mostly occurred in northern mainland China were transported by the northeast monsoons toward the downwind regions (Yuan *et al.*, 2004). Furthermore, swidden burning

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often occurring in Southeast Asia and Southwest China in spring, could emit a huge amount of biogenic particulates carried by westerly wind and southwestern monsoons from Indochinese Peninsula, resulting in the deterioration of ambient air quality in downwind regions, such as Singapore, Vietnam, the Philippines, and Taiwan (Wang *et al.*, 2012).

With the rapid development of economy, industrial activities in East Asia are becoming more prosperous and the population is getting more intensive, leading to high energy consumption and air pollution emission. Additionally, biomass burning could emit more biogenic particulates to the atmosphere. Previous literature reported that northeastern monsoons could blow fine particles ($PM_{2.5}$) from northern China, Korea, and Japan to southern China, Okinawa, Taiwan, and probably even reach the Philippines and Hong Kong, resulting in poor regional and ambient air quality (Wang *et al.*, 2007; Li *et al.*, 2013a, 2013b; Kim *et al.*, 2018; Lee *et al.*, 2018a). Such phenomenon has been addressed by previous literature that long-range transport causes the deterioration of regional air quality in the downwind regions (Chuang *et al.*, 2012). Moreover, interaction of air pollutants may occur in the boundary areas neighboring Taiwan Strait and Bashi Channel (Li *et al.*, 2012; Bagtasa *et al.*, 2018).

Previous studies reported that $PM_{2.5}$ originated from southeastern or northeastern Asia could arrive at Dongsha Islands located at the northern South China Sea (Wang *et al.*, 2012; Yuan *et al.*, 2015). During the cultivation days in spring, the emissions of fine particles from the original swidden burning can possibly affect the ambient air quality of Singapore, Malaysia, and the Philippines. Polluted air masses launched from southern Taiwan and deteriorated its ambient air quality, while Luzon is also located along the transport routes of such polluted air masses. Moreover, the Philippines often complain that air pollutants emitted from southern Taiwan often cause poor ambient air quality of Luzon during the northeastern periods.

Sulfate (SO_4^{2-}) and nitrate (NO_3^-) are the dominant ionic species in the atmospheric fine particles (Yuan *et al.*, 2004; Li *et al.*, 2013, 2015, 2016; Yang *et al.*, 2017). Secondary inorganic aerosols are mainly converted from the oxidation of SO_2 and NO_x and other species (Chang *et al.*, 2006; Dai *et al.*, 2013). Metallic contents of $PM_{2.5}$ such as Ba, As, Cr, Cd, Ni, and Pb could be emitted from the exhausts of anthropogenic sources such as power plants, waste incinerators, and industrial processes. Crustal materials including Si, Ca, Fe, and Al dominate particulate matter in the atmosphere, even in $PM_{2.5}$. The concentrations of trace elements including Ba, Cr, Cu, Mn, Mo, Ni, Pb, Sb, V, and Zn at urban areas are mostly much higher than those at rural areas (Fang *et al.*, 2003; Dongarrà *et al.*, 2010; Chen *et al.*, 2015). The carbonaceous content of atmospheric aerosols comprised of elemental carbon (EC) and organic carbon (OC), both collectively are referred as total carbon (TC) (Lin *et al.*, 2001; Wu *et al.*, 2009). Elemental carbon, also known as black carbon (BC) or graphitic carbon (GC), was chemically stable in the atmosphere and mainly formed in the combustion processes. Consequently, EC is attributed to original carbonaceous particles, which can not only reduce the visual range significantly due to its effective absorption of visible light, but also plays an

important role in the formation of secondary organic aerosols (Yuan *et al.*, 2006; Wu *et al.*, 2009). EC is a highly potential toxic substantial media through the respiratory system, and thus enhances the cancer risk on human health (Na *et al.*, 2004; Liu *et al.*, 2015). Organic carbon could be also formed in the combustion process or during the photochemical reactions. Its primary sources include cooking fume, vehicular exhausts, forest fires, and tobacco burning as well. Organic carbon can be further divided into primary organic carbon (POC) and secondary organic carbon (SOC). SOC is founded by low-volatile organics from the chemical reactions between primary carbon and volatile organics (Pankow *et al.*, 2007; Ding *et al.*, 2008).

Currently, there are still many developing countries using primary fuels (e.g., coals, woods, and biofuels) for space heating, cooking, and agricultural debris burning worldwide. Biomass burning can be divided into non-human activity combustion (e.g., lightning causing forest fires) and human activity combustion (e.g., burning for expanding the agricultural land). Biomass burning occurs frequently worldwide and is concentrated in tropical countries or regions near the equator such as Southeast Asia and South Asia (Engling *et al.*, 2014). These countries or regions with dense population and primitive agricultural activities cause intensive biomass burning activities to be more frequent and severe.

Hazes occurring in Asian countries are commonly accompanied with monsoons which could transport air pollutants downward, causing the deterioration of regional air quality and the adverse effects on human health along the transport routes (Yang *et al.*, 2018). It has inevitably become one of the top global environmental issues. Biomass burning can emit large amounts of air pollutants, such as carbonaceous fine particles and greenhouse gases (CO_2 and CH_4) (He *et al.*, 2003; Ragosta *et al.*, 2008). In addition to the generation of fine particles during the combustion processes, it could cause an intrinsic hazard to human health. Previous literature reported that fine particles such as $PM_{2.5}$ or PM_{10} could induce respiratory and cardiovascular diseases such as asthma or allergy-induced symptoms especially for the sensitive groups of children and elderly (Sacks *et al.*, 2010; Loop *et al.*, 2018). Anhydrosugar is an indicator for the decomposing of cellulose, hemicellulose, and lignin during the combustion processes of woods and agricultural debris (Kuo *et al.*, 2011). As the combustion temperature reaches 300–600°C, cellulose could decompose to levoglucosan, while hemicellulose decomposes to galactosan and mannosan (Nirmalkar *et al.*, 2015).

Taiwan is located north of Luzon and east of mainland China. In the winter season, air pollutants emitted from the industrial regions along the coast of East China could be transported toward Taiwan and even cross Bashi Channel by the northeastern monsoons. In the spring season, biomass burning in Southeast Asia affected by the westerlies results in the long-range transport of fine particles to the northern part of South China Sea, and even arrived the Philippines. Consequently, characterizing atmospheric fine particles in the junctional area of Taiwan and the Philippines become more important to ascertain the transport of air masses between southern Taiwan and northern Philippines.

Therefore, this study aimed to sample atmospheric PM_{2.5} in southern Taiwan (Checheng) and northern Philippines (Laoag) and further analyzed their chemical composition to characterize the chemical fingerprint and identify the potential sources of PM_{2.5} and their contributions. Moreover, the inter-correlation of PM_{2.5} in the atmosphere of southern Taiwan and northern Philippines was further investigated.

EXPERIMENTAL METHODS

Sampling Sites

Two PM_{2.5} remote sites located at southern Taiwan and northern Philippines were selected to sample PM_{2.5} for this study. Checheng site (CC) was situated at the southern tip of Taiwan, while Laoag site (LO) was situated at northern Luzon in the Philippines. Both sites are approximately 400 km apart and separated by Bashi Channel as shown in Fig. 1. Checheng site with the longitude and latitude of 120°47'20" and 21°57'29" was located near a forest resort surrounding by hills and creeks with almost no anthropogenic sources and activities. Laoag site with the longitude and latitude of 120°59'04" and 18°50'93" was located along the coastline surrounding by hills at northwestern Luzon with limited human emissions except for agricultural activities. These two remote sites can be treated as the background sites of southern Taiwan and northern Philippines.

For this particular study, the sampling campaign of PM_{2.5} was simultaneously conducted at two remote sites in four seasons from August 2015 to May 2016. The sampling of PM_{2.5} was carried out in August (summer), November (fall), January–February (winter), and May (spring). In each season, the sampling of 24-h PM_{2.5} was performed for continuous two weeks (i.e., fourteen days for every season).

Sampling and Weighing Methods

In this study, PM_{2.5} samplers (PQ200; BGI) were used to collect atmospheric PM_{2.5}, which composed of an air inlet, an air conduit, a particle branch diameter, a filter cartridge, an air sampling motor, a flow rate control system, a flow rate

measuring device, an environmental and filter paper temperature monitoring system, a high-pressure power measurement system, a timer, an outdoor environmental protection shell and appropriate mechanical, and an electrical or electronic controller. Prior to sampling, the quartz fibrous filter was initially situated on the filter holder connecting to the air conduit. The filters were fixed and sealed in the PM_{2.5} sampler and the air flowed evenly downward through the filters. Particulate matter with aerodynamic diameter less than 2.5 µm (PM_{2.5}) were screened through a cyclonic separator. The filters of 47-mm diameter were initially conserved for at least 48 hours in a thermostatic chamber ($T = 20\text{--}25^{\circ}\text{C}$, $\text{RH} = 40 \pm 5\%$) before sampling. The volumetric flow rate of air sampling was set as 16.7 L min^{-1} . After sampling, the PM_{2.5} filters firstly put into a petri dish were temporarily stored at 4°C and then transported back to the central laboratory as soon as possible for further conditioning and weighing. The PM_{2.5} filters were preserved in a thermostatic chamber with a constant temperature of $T = 20\text{--}25^{\circ}\text{C}$ for at least 48 hours for conditioning. The filters before and after sampling were both weighed by an analytical microbalance (Model MSA6.6S-0CE-DM; Sartorius) with a precision of microgram (10^{-6} g). The difference of filter's weight before and after sampling was divided by the total air sampling volume to determine the concentration of PM_{2.5}.

Chemical Analytical Methods

After conditioning and weighing, one quarter of the PM_{2.5} filter was used for analyzing the water-soluble ionic species in PM_{2.5}. The filters were put into a 50-mL PE bottle poured with 30-mL D.I. H₂O with conductivity $< 18 \text{ M}\Omega$ to dissolve ionic species in an ultrasonic vibration process for approximately 120 minutes (2 hours). An ion chromatography (Model DX-120; Dionex) was applied to analyze the concentrations of anions (i.e., F^{-} , Cl^{-} , SO_4^{2-} , and NO_3^{-}) with 1.8 mM Na_2CO_3 /1.7 mM NaHCO_3 solution as eluent. Other ion chromatography (Model ICS 1100; Dionex) was used to analyze the concentrations of cations (i.e., NH_4^{+} , K^{+} , Na^{+} , Ca^{2+} and Mg^{2+}) with 20 mM methane sulfonic acid as eluent.

Fig. 1. Location of PM_{2.5} sampling sites at southern Taiwan (Checheng) and northern Philippines (Laoag).

Another quarter of the PM_{2.5} filter was used for analyzing metallic elements in PM_{2.5}. The filters were initially digested in a 20-mL mixed acid solution (HNO₃:HClO₃ = 3:7) at a high temperature of 150–200°C for 2 hours, and then diluted to 25 mL with D.I. H₂O. During the digestion, D.I. H₂O was added to the residual solution two or more times in order to eliminate the acid content of the digestion solution. The metallic elements in PM_{2.5} including Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, Mg, K, Ca, Ti, V, Al, and As were then analyzed with an inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Model Optima 2000DV; Perkin Elmer).

Moreover, two eighths of the PM_{2.5} filter were further used to measure the carbonaceous content of PM_{2.5}. The carbonaceous content including elemental, organic, and total carbons (i.e., OC, EC, and TC) were measured with an elemental analyzer (Model 1108; Carlo Erba). Prior to PM_{2.5} sampling, the quartz fibrous filters were initially preheated at 900°C for 1.5 hours to expel potential carbon impurities from the quartz fibrous filters. The preheating procedure could minimize the background carbon in the matrix of quartz fibrous filters, which might cause interferences with the analytical results, leading to an overestimation of the carbonaceous content in PM_{2.5}. The elemental analyzer (EA) was operated in the procedure of oxidation and reduction at 1020°C and 500°C, respectively, for continuous 15-min heating. Additionally, one eighth of the quartz fibrous filter was heated in advance using nitrogen gas at 340–345°C for at least 30 minutes to expel organic matter from the filters, after which the amount of EC was thus determined. Another one eighth of the quartz fibrous filter was analyzed without heating to determine the TC of PM_{2.5}. The amount of OC was then estimated by subtracting EC from TC.

Another quarter of the PM_{2.5} filter was firstly stored at a temperature of 4°C for further pretreatment of anhydrosugar analysis with a high-performance ion chromatography (HPIC; Model ICS 5000+; Dionex). The filters were extracted with D.I. H₂O (conductivity > 18.2 MΩ) in a PE bottle under ultrasonic vibration for 120 min with a preheated quartz fibrous filter (0.3-μm pore size). Anhydrosugars were then analyzed by using 18 mM NaOH solution as eluent in a flow rate of 1 mL min⁻¹.

Quality Assurance and Quality Control (QA/QC)

During the sampling process, sampling instruments require regular calibration of the volumetric flow rate of 16.7 L min⁻¹ in order to ensure the accuracy of the sampling flow rate. Inaccurate air sampling flow rate would cause either over- or underestimation of PM_{2.5} concentrations. Moreover, sampling staff needs to wear powderless rubber gloves for the installation of quartz fibrous filters onto the top of the filter holder to avoid potential exterior pollution. A stainless steel clip was used to move the quartz fibrous filter onto or out of the filter holder. The weather condition, sampling duration, and the description of sampling location were recorded in a recording sheet. After sampling, each quartz fibrous filter must be confined in a petri dish to avoid collision and then stored in a desiccator for at least 48 hours before weighing.

Both field and transportation blanks were further undertaken

for PM_{2.5} sampling, while filter blanks were applied for chemical analysis. Blanks were processed simultaneously with field samples. The blank test can be used to determine the background contamination from the analytical process. In this study, the background contamination was insignificant and can be ignored. Moreover, the determination coefficient (R²) of the calibration curve for the analysis of each chemical species was required to be higher than 0.995. The recovery efficiencies of chemical species were determined by spiking known quantity of chemical species' mass, while the reproducibility tests were performed by conducting the replicate analysis of 1 out of every 10 PM_{2.5} samples. Recovery efficiencies varied between 95% and 105%, and reproducibility tests had acceptable results within ±10% for the analysis of chemical species.

Backward Trajectory Simulation

In order to trace air masses transported toward the sampling sites, backward trajectories were plotted by using the wind field obtained from National Oceanic Atmospheric Administration (NOAA). A Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT) simulation is a widely used model that simulates the trajectory of a single air parcel originated from a specific source location and height above ground (i.e., 100, 300, and 500 m) over a period of time (24, 48, or 72 hours). The PM_{2.5} sampling sites were used as starting points to plot the backward trajectories. In this study, 72-h backward trajectories of air parcels transported toward the sampling sites in different sampling days were plotted respectively to assist for identifying their potential sources of PM_{2.5}.

Source Apportionment of PM_{2.5}

The source apportionment of ambient PM_{2.5} was assessed by using a receptor model based on the principle of chemical mass balance (CMB) (Kothai *et al.*, 2008; Li *et al.*, 2015). Since the detailed descriptions of CMB receptor model (CMB8.0) are available elsewhere, only a brief summary is presented below. The CMB receptor model is proposed by Winchester and Nifong in 1969 and uses the emission profiles of prominent sources to estimate their contribution to a specific reception site. It is assumed that the total amount of a particular chemical species in PM at the reception site is the linear summation of each individual contribution from various sources. The CMB receptor model simulation uses the results of the least-squares regression analysis of the PM_{2.5}'s chemical composition to resolve the most appropriate contributions of prominent sources. Therefore, this model consists of a least-squares solution to a set of linear equations. This solution expresses the concentration of each chemical species at the receptor site as a linear summation of the products of source profiles and source contributions. Source profiles (the fractional amount of each chemical species in the emissions from each source type) and receptor concentrations, each with realistic uncertainty estimates, serve as the input data to the CMB receptor model. The model output consists of the contribution from each source type to the total ambient PM_{2.5} mass, as well as to individual chemical species concentration. The CMB8 model results

are further evaluated by using several fit indices, such as R^2 (≥ 0.8), χ^2 (≤ 4.0), t -statistics (≥ 2.0), and the percentage of mass accounted for 80–120%. The source profiles used in this study were reported by USEPA, Southern California Air Quality Study, and the researchers conducted the chemical composition of $PM_{2.5}$ from local prominent sources in Taiwan.

Principal Component Analysis

Principal component analysis (PCA) is one of the methods of multivariate statistical analysis. The principles of PCA use the obtained eigenvalue and eigenvector which are screened for larger variance of each component (Han *et al.*, 2015; Turias *et al.*, 2006). The level of correlation loading factor is shown below:

- (1) high correlation—loading factor higher than 0.7,
- (2) moderate correlation—loading factor between 0.5–0.7, and
- (3) low correlation—loading factor less than 0.5.

Principal component analysis applied chemical analytical data to determine the main loading factors. The largest loading factor is the first principal component and followed by the sequence of the second, third, and fourth principal components. However, the main purpose of principal component analysis is to apply less variance to represent big data, usually simplify to 3–4 main loading factors.

Paired t -test

Paired t -test has been widely used to compare two population averages while we have two sample groups in which one sample can be paired with the observations in other sample. A paired t -test is more powerful than a 2-sample test because the latter includes additional variation occurring from the independence of the observations. A paired t -test is not subject to this variation because the paired observations are dependent. Moreover, a paired t -test does not require both samples to have equal variance. Therefore, if we can logically address our research question with a paired design, it would be beneficial to obtain more important statistical information for describing the correlation between two sampling groups.

RESULTS AND DISCUSSION

Seasonal Variation of $PM_{2.5}$ at Southern Taiwan and Northern Philippines

Table 1 summarizes the seasonal variation of $PM_{2.5}$ concentrations at Checheng and Laoag during the sampling

periods. In summer (August 22–September 3, 2015), the average $PM_{2.5}$ concentrations at Checheng and Laoag were 6.14 ± 1.44 and $11.89 \pm 1.97 \mu\text{g m}^{-3}$, respectively, which were relatively lower than those in other three seasons, resulting from better vertical dispersion due to unstable atmosphere. First of all, the regions of southern Taiwan and northern Philippines were mainly influenced by the prevailing winds of southwestern monsoons, by which clean air masses were blown from South China Sea, resulting in relatively lower $PM_{2.5}$ concentrations in summer. Secondly, the two sampling sites were just attacked by Typhoon Goni (August 18–20, 2015) several days before the sampling periods. Additionally, the vigorous thermal convection of local air flow due to strong solar radiation was beneficial for the dispersion of atmospheric particulates.

During the sampling periods in fall (November 5–19, 2015), the average concentrations of $PM_{2.5}$ at Checheng and Laoag were 7.84 ± 3.42 and $8.44 \pm 2.27 \mu\text{g m}^{-3}$, respectively, as shown in Table 1. The prevailing wind directions at Checheng and Laoag in fall were different since air masses were distinguished in the two sampling regions. At Checheng, air masses were originated from Mongolia or northern and northeastern China accompanying with northeastern monsoons, which transported air masses across central and southeastern China to the target regions. Consequently, the concentrations of $PM_{2.5}$ transported northerly toward Checheng in fall were relatively higher than those transported southwesterly in summer. At Laoag, the prevailing winds were mainly blown from West Pacific Ocean where air masses were much cleaner compared to those carried by northeastern monsoons.

During the sampling periods in winter (January 21–February 3, 2016), the average concentrations of $PM_{2.5}$ at Checheng were $7.06 \pm 3.42 \mu\text{g m}^{-3}$ which were two times lower than those observed at Laoag ($14.15 \pm 7.61 \mu\text{g m}^{-3}$), although the prevailing winds blown by northeastern monsoons could blow atmospheric $PM_{2.5}$ toward the target regions. Checheng site surrounding by hills is located at the southern tip of the Central Range with the heights ranging from 2,000 to 4,000 m. Obstructed by the Central Range, air masses containing $PM_{2.5}$ cannot easily cross over the Central Range and reached the Checheng site. Consequently, Checheng seldom violated the Taiwan's 24-h $PM_{2.5}$ standard of $35 \mu\text{g m}^{-3}$ during the winter sampling periods.

During the sampling periods in spring (May 10–24, 2016), the average $PM_{2.5}$ concentrations increased at both Checheng ($17.81 \pm 5.44 \mu\text{g m}^{-3}$) and Laoag ($21.59 \pm 6.55 \mu\text{g m}^{-3}$) caused by the prevailing northeastern monsoons originated

Table 1. Seasonal variation of $PM_{2.5}$ concentrations and chloride deficits at Checheng and Laoag.

Sampling sites	Sampling number		Summer	Fall	Winter	Spring
Checheng (CC)	53	$PM_{2.5}$	6.1 ± 1.4	7.8 ± 3.2	7.1 ± 3.4	17.8 ± 5.4
		Chloride Deficit	16.7%	20.5%	18.8%	28.3%
		$[Cl^-]/[Na^+]$	1.0	0.9	1.0	0.9
Laoag (LO)	49	$PM_{2.5}$	11.9 ± 5.0	8.4 ± 2.3	14.1 ± 7.6	21.6 ± 6.6
		Chloride Deficit	12.3%	10.8%	14.5%	26.4%
		$[Cl^-]/[Na^+]$	1.0	1.0	1.0	0.9

Unit of $PM_{2.5}$: $\mu\text{g m}^{-3}$.

from Northeast Asia, such as Mongolian Plateau and North China where a large amount of PM_{2.5} were emitted from coal burning for space heating and might transport to downwind regions including Taiwan, the Philippines, and Hong Kong. Lower PM_{2.5} concentrations at Checheng than those at Laoag were mainly attributed to the possible obstruction of air flow by southern Central Range lying in Taiwan. Another reason might be the potential sources around Laoag (e.g., biomass burning) emitted more PM_{2.5} than those at Checheng. Overall, the seasonal PM_{2.5} concentrations at both sites were ordered as spring > winter > fall ≈ summer. In terms of spatial distribution, Laoag had higher PM_{2.5} concentration than Checheng in all seasons.

Chemical Characteristics of PM_{2.5} at Southern Taiwan and Northern Philippines

During the sampling periods, PM_{2.5} collected at both sites were further analyzed for water-soluble ions, metallic elements, carbonaceous contents, and anhydrosugars. As shown in Table 2, secondary inorganic aerosols (SIAs) including SO₄²⁻, NO₃⁻, and NH₄⁺ accounted for 34.1–76.0% of water-soluble ions (WSIs). SIAs were the products of chemical reactions occurred in the atmosphere (Lonati et al., 2008; Masiol et al., 2015; Zhang et al., 2017; Jiang et al., 2019). It showed that the concentrations of SIAs at Laoag were commonly larger than those at Checheng. The seasonal average SIA concentrations were 6.4 μg m⁻³ (Checheng) and 7.2 μg m⁻³ (Laoag), and constituted of 68.0% and 76.0% of WSIs in spring, respectively. The seasonal variation of WSIs basically followed the similar trend of PM_{2.5} concentration. For all measured PM_{2.5} concentrations, the lowest PM_{2.5} concentrations of 1.4 μg m⁻³ was found at Checheng in summer and that of 2.4 μg m⁻³ was observed at Laoag in fall.

During the sampling periods, the average concentrations of SIAs in PM_{2.5} at Laoag were generally higher than those at Checheng. In summer and fall, the prevailing winds of southwestern monsoons could carry atmospheric PM_{2.5} from Southeast Asia to Laoag, however, in winter and spring, the prevailing winds of northeastern monsoons transported atmospheric PM_{2.5} from Japan, Korea, and North China toward Checheng and Laoag. Due to the obstruction of Central Range in Taiwan, the average SIA concentrations in PM_{2.5} at Checheng were generally lower than those at Laoag. Due to high frequencies of biomass burning of agricultural

debris around the Laoag site, the concentrations of K⁺ in PM_{2.5} increased gradually from summer to spring at Laoag, and similar trend was observed at Checheng, indicating that ambient air qualities at Checheng and Laoag were both influenced by the cross-boundary transport from neighboring countries or regions toward the target regions in different seasons. Similar chemical characteristics of PM_{2.5} were found at both Checheng and Laoag as illustrated in Fig. 2, indicating that the inter-correlation of WSI species in PM_{2.5} existed in the intersectional region of southern Taiwan and northern Philippines.

Sea salts (i.e., Cl⁻ and Na⁺) also played an important role in PM_{2.5} at both sites. The equivalent concentration ratio of Cl⁻ and Na⁺ showed that [Cl⁻]/[Na⁺] ranged from 0.9 to 1.0 at Checheng and from 0.9 to 1.1 at Laoag, respectively, during the sampling periods as shown in Table 1. Both [Cl⁻]/[Na⁺] equivalent ratios were close to unity at both sides, indicating that PM_{2.5} was highly influenced by sea salts. Previous literature reported that the mass ratio of [Cl⁻]/[Na⁺] is about 1.8 (Cheng et al., 2000). However, the mass ratio of [Cl⁻]/[Na⁺] in PM_{2.5} were always below 1.8, due to chloride deficit. Chloride (Cl⁻) in PM_{2.5} could react with acidic substances (e.g., HNO₃, H₂SO₄, and other acids) to form HCl which could be further evaporated to the atmosphere. The mass ratio of [Cl⁻]/[Na⁺] was thus reduced gradually while sea salts migrated toward inland in the atmosphere. Chloride deficit can be determined by Eqs. (1) and (2) (Kerminen et al., 1998):

$$\text{Chloride Deficit (\%)} = \frac{[\text{Cl}^-]_{\text{original}} - [\text{Cl}^-]}{[\text{Cl}^-]_{\text{original}}} \times 100\% \quad (1)$$

$$[\text{Cl}^-]_{\text{original}} = [\text{Na}^+] \times \frac{[\text{Cl}^-]_{\text{seawater}}}{[\text{Na}^+]_{\text{seawater}}} \quad (2)$$

where:

[Cl⁻]_{original}: original chloride ion concentration in the atmosphere;

[Cl⁻]: chloride ion concentration of PM_{2.5} in the atmosphere;

[Cl⁻]_{seawater}: chloride ion concentration in the seawater;

[Na⁺]_{seawater}: sodium ion concentration in the seawater.

Table 2. Secondary inorganic aerosol (SIA) concentrations at Checheng and Laoag during the sampling periods.

Seasons	Sites	SIAs (μg m ⁻³)			SIAs/WSIs		
		Avg.	Max	Min	Avg.	Max	Min
Summer	CC	1.4	1.6	0.9	55.8%	60.8%	47.9%
	LO	2.9	4.1	2.0	65.8%	69.0%	59.4%
Fall	CC	2.0	3.1	0.6	61.0%	69.8%	34.1%
	LO	2.4	4.1	1.6	65.7%	68.7%	61.2%
Winter	CC	1.8	4.4	0.9	65.3%	67.5%	61.7%
	LO	3.9	4.4	2.2	70.1 %	79.9%	61.4%
Spring	CC	6.3	11.8	2.5	68.0%	85.1%	42.0%
	LO	7.2	9.6	4.4	76.0%	81.4%	57.8%

CC: Checheng; LO: Laoag; Avg: average; Max: maximum; Min: minimum; SIAs: secondary inorganic aerosols; WSIs: water-soluble ions.

Fig. 2. Seasonal variation of water-soluble ions in PM_{2.5} at (a) Checheng and (b) Laoag.

The deficit of chloride in PM_{2.5} during the sampling periods is shown in Table 1 and Fig. 3. In winter and spring, the prevailing winds of northeastern monsoons caused higher chloride deficit at Checheng than those at Laoag. The chloride deficit of PM_{2.5} at Checheng was ordered as spring > fall > winter > summer. Influenced by air pollutants blown from southern Philippines, the chloride deficits of PM_{2.5} in summer were generally higher than those in fall at Laoag. During the sampling periods, the chloride deficits of PM_{2.5} at Laoag were ordered as spring > winter > summer > fall. The chloride deficits of PM_{2.5} had a tendency to increase from summer to spring at both sites mainly because the concentrations of acidic gases (e.g., SO₂ and NO_x) were raised up, resulting in chemical reactions between the chloride in PM_{2.5} and acidic gases in the atmosphere to form Na₂SO₄, NaNO₃, and HCl, and HCl was then evaporated from PM_{2.5} to the atmosphere.

Since both sampling sites are located along the coastline, the effect of sea salts could not be neglected to determine the neutralization rate (NR). The corrected formula is used to determine NR as follows (Solomon and Moyers, 1984):

$$\text{Neutralization ratio (NR)} = \frac{[\text{NH}_4^+]}{[\text{nss-SO}_4^{2-}] + [\text{NO}_3^-]} \quad (3)$$

where:

[NH₄⁺]: the equivalent concentration of NH₄⁺ (neq m⁻³);

[nss-SO₄²⁻]: the equivalent concentration of non-sea salt SO₄²⁻ (neq m⁻³);

[NO₃⁻]: the equivalent concentration of NO₃⁻ (neq m⁻³).

Previous literature reported that, when NR < 1, the pH values of fine particles below 7.0 present as acidic particles since the equivalent concentrations of NH₄⁺ is not enough

for neutralizing SO₄²⁻ and NO₃⁻. On the contrary, when NR > 1, the pH value of fine particles above 7.0 present as alkaline particles, and when NR = 1, the pH value of fine particles equivalent to 7.0 present as neutral particles. Calculated by Eq. (4), the NRs of PM_{2.5} sampled at both sites were far below unity, indicating that PM_{2.5} particles were always acidic. This phenomenon was probably attributed to the fact that the upwind acidic particulates carried by cross-boundary transport were blown to the downwind regions and thus reduced the pH value of PM_{2.5}. In addition to NH₄⁺, the cations of Na⁺, Ca²⁺, and Mg²⁺ could also played important roles for neutralizing the residual acidity of PM_{2.5}. If the equivalent concentrations of cations were high enough to neutralize nss-SO₄²⁻ and NO₃⁻, the NR values would be close to unity. This study revealed that excess nss-SO₄²⁻ and NO₃⁻ in PM_{2.5} were observed for NH₄⁺ neutralization, but can be further neutralized by Na⁺, Ca²⁺, and Mg²⁺ at both sites as illustrated in Figs. 4 and 5.

The metallic contents of PM_{2.5} are depicted in Fig. 6. It showed that the trend of metallic element concentration was in accordance with the PM_{2.5} concentrations to some extent. Among the metallic elements, crustal elements (i.e., K, Mg, and Ca) had relatively stable concentration level, while other trace metals had relatively lower concentrations. Moreover, the concentrations of metallic elements emitted from anthropogenic sources such as Cr, Ni, As, Cd, Cu, and V in PM_{2.5} in summer were generally lower than those in other three seasons, and then increased gradually as the northeastern monsoons dominated the prevailing winds in fall, winter, and spring. The increases of trace metal concentrations would be attributed to higher atmospheric stability which thus hinder the dispersion of PM_{2.5} in the atmosphere. As a result, the contribution of metallic elements to PM_{2.5} varied with seasons at Checheng and Laoag. Comparing with the

Fig. 3. Seasonal variation of chloride deficit and $[\text{Cl}^-]/[\text{Na}^+]$ for $\text{PM}_{2.5}$ at Checheng and Laoag.

Fig. 4. Neutralization of $[\text{NH}_4^+]$ with $[\text{nss-SO}_4^{2-}] + [\text{NO}_3^-]$ for $\text{PM}_{2.5}$ at Checheng and Laoag.

Fig. 5. Neutralization of $[\text{NH}_4^+] + [\text{Na}^+] + [\text{Mg}^{2+}] + [\text{Ca}^{2+}]$ with $[\text{nss-SO}_4^{2-}] + [\text{NO}_3^-]$ for $\text{PM}_{2.5}$ at Checheng and Laoag.

Fig. 6. Seasonal variation of metallic element concentration of $PM_{2.5}$ at (a) Checheng and (b) Laoag in different seasons.

fingerprints of metallic contents of $PM_{2.5}$ in different seasons at Checheng and Laoag, the seasonal variation of metallic elements was quite similar between $PM_{2.5}$ sampled at both sites. It suggested that the chemical composition of $PM_{2.5}$ at southern Taiwan and northern Philippines might be correlated with each other. The enrichment factor (EF) results showed that the EFs of Mg, K, Ca and Al were constantly lower than 10 at Checheng and Laoag in all seasons, indicating that these metals were originated from crustal materials. On the contrary, the EFs of Cr, Ni, Cu and Pb were however higher than 10 at Checheng and Laoag in all seasons, particularly in winter and spring, implying that these metals were highly potentially contributed from anthropogenic sources.

Seasonal variation of carbonaceous content in $PM_{2.5}$ is depicted in Fig. 7. It illustrated that the concentrations of OC were always higher than those of EC at both sites. Since EC was mainly contributed from atmospheric inert carbonaceous materials, diesel engines, fuel burning, and industrial emissions, thus the concentrations of EC in $PM_{2.5}$ sampled at both sites were relatively low. The concentrations of OC at Laoag were always higher than those at Checheng. Organic carbon emitted from anthropogenic sources in the neighboring upwind countries (e.g., China, Korea, and Japan) could be transported northerly by northeastern monsoons to Checheng, resulting in a significant increase of TC concentrations with the order of spring > fall > winter > summer. While, the concentrations of TC in $PM_{2.5}$ at Laoag varied with season and were ordered as spring > winter > summer > fall, due to the effects of monsoons in different seasons. In fall, clean marine air transported easterly toward Laoag was mainly originated from the West Pacific Ocean. In summer, the main sources of TC were anthropogenic sources in central and southern Philippines. In winter and

spring, the prevailing winds varied gradually from southern to northern monsoons which could carry polluted air masses to the downwind regions such as Taiwan and the Philippines. Additionally, occasional burning of biomass (e.g., agricultural debris) in the field surrounding the Laoag site might contribute high concentration of OC in $PM_{2.5}$.

Anhydrosugars including levoglucosan, mannosan, and galactose are the most effective organic tracers for biomass burning aerosols in the atmosphere. In the present study, levoglucosan was the only anhydrosugar been detected, while mannosan and galactose were not detectable for all $PM_{2.5}$ samples. We found that the concentrations of levoglucosan in $PM_{2.5}$ at Laoag were always higher than those at Checheng (see Fig. 8), concurring with the spatial distribution trend of OC observed at Laoag and Checheng. The highest average levoglucosan concentration of 19.15 ng m^{-3} was found in winter and spring at Laoag since it is located far away from densely populated areas and is predominantly influenced by the northeastern monsoons. Additionally, high concentrations of levoglucosan in $PM_{2.5}$ at Laoag might be attributed to the abundant large-scale biomass burning in the field.

Since K^+ and OC have been used as the indicators of biomass burning (Simoneit *et al.*, 2002), a positive correlation of K^+ and OC with levoglucosan in $PM_{2.5}$ was observed at Checheng and Laoag during the sampling periods (see Fig. 9). The linearity of the correlation (K^+ vs. levoglucosan and OC vs. levoglucosan) at Laoag was somewhat better than that at Checheng. Additionally, the correlation between OC and levoglucosan in $PM_{2.5}$ was similar to that between K^+ and levoglucosan, confirming that levoglucosan, K^+ , and OC can be indicators of biomass burning. Overall, the linear correlation of two indicator pairs at Laoag was superior to those at Checheng.

Fig. 7. Seasonal variation of carbonaceous content of $\text{PM}_{2.5}$ at Checheng and Laoag.

Fig. 8. Seasonal variation of levoglucosan concentration of $\text{PM}_{2.5}$ at Checheng and Laoag.

Clustered Transport Routes of $\text{PM}_{2.5}$

Fig. 10 illustrates the clustered routes of air masses transported toward Checheng and Laoag during the $\text{PM}_{2.5}$ sampling periods. Tables 3 and 4 summarize the transport routes of air masses and their $\text{PM}_{2.5}$ concentrations and frequencies at Checheng and Laoag in all seasons. The transport of air mass toward Checheng can be clustered into seven sub-routes, while the transport of air masses arriving at Laoag can be clustered into eight sub-routes. Top two $\text{PM}_{2.5}$ concentrations of 13.2 ± 6.5 and $11.4 \pm 7.0 \mu\text{g m}^{-3}$ at Checheng were identified to transport from Central and North China, Korean Peninsula, and the Japanese islands in winter and spring, respectively. While, top two $\text{PM}_{2.5}$ concentrations of 20.2 ± 13.5 and $23.2 \pm 7.6 \mu\text{g m}^{-3}$ at Laoag were transported from Central China and southern Korea in winter and spring, respectively. The results showed that high concentrations of $\text{PM}_{2.5}$ came mainly from the neighboring northeastern Asian countries of China, Korea, and Japan. Previous literature reported that high concentrations of $\text{PM}_{2.5}$ occurred in spring was mainly due to the burning of fossil fuels (e.g., coal and oil) (Chang *et al.*, 2011). Additionally, wood burning for space heating in cold seasons is another non-negligible source for emitting $\text{PM}_{2.5}$, which can be transported by the northerly monsoons through long-range transport toward the downwind regions.

Overall, the main transport routes toward Checheng came from northeastern Asia (i.e. North China, Korean Peninsula,

and the Japanese islands, noted as *N*, *NEE*, and *CC*) in winter and spring, while those came from South China Sea (noted as *S* and *SW*) mainly occurred in summer. The concentrations of $\text{PM}_{2.5}$ in the southerly air masses were much lower than those in the northerly air masses. The main transport route toward Laoag came from the West Pacific Ocean (*SEE*) in fall. High concentrations of $\text{PM}_{2.5}$ in air masses came mainly from North China passing through the coastal regions of Southeast China toward Laoag in winter and spring.

Correlation Analysis for Mass Concentration and Chemical Composition of $\text{PM}_{2.5}$ at Checheng and Laoag

In order to inter-compare the correlation between the atmospheric $\text{PM}_{2.5}$ at Checheng and Laoag, a paired *t*-test was further employed for this study. It showed that the *p*-values of $\text{PM}_{2.5}$'s mass concentration and chemical composition between Checheng and Laoag were 0.001 and 0.018 ($p < 0.05$), respectively (see Table 5), indicating a significant correlation between atmospheric $\text{PM}_{2.5}$ at Checheng and Laoag. As shown in Table 5, the *p*-values of $\text{PM}_{2.5}$ concentration in summer, fall, winter, and spring were 0.042, 0.631, 0.009, and 0.028, respectively, indicating that the correlation between the concentrations of $\text{PM}_{2.5}$ at Checheng and Laoag were significant in summer, winter, and spring, but insignificant in fall. In summer, air masses were blown from South China Sea and Indochinese Peninsula, resulting in significant correlation between upwind site (Laoag) and

Fig. 9. Correlation of (a) K^+ versus levoglucosan and (b) OC versus levoglucosan in $PM_{2.5}$ at Checheng and Laoag.

downwind site (Checheng). Moreover, the mass concentrations of $PM_{2.5}$ at Laoag were consistently higher than those at Checheng (Table 1), suggesting that $PM_{2.5}$ blown from Laoag could influence the mass concentrations and chemical composition of $PM_{2.5}$ at Checheng. On the contrary, in the seasons of winter and spring, northeastern monsoons could blow $PM_{2.5}$ from the north to the south. High concentrations of $PM_{2.5}$ mainly blown from North China, Korean Peninsula, and the Japanese islands turned clockwise across East China Sea and arrived at Checheng and Laoag. Insignificant correlation in fall was probably attributed to the fact that clean air masses were blown from the West Pacific Ocean toward Laoag, but Checheng was mainly influenced by northeastern monsoons blown from Northeast Asian countries. As a result, different sources of air masses resulted in insignificant correlation between the concentrations of $PM_{2.5}$ at Checheng and Laoag.

Furthermore, this study employed the paired *t*-test on the chemical composition of $PM_{2.5}$ at Checheng and Laoag. The *p*-values of $PM_{2.5}$'s chemical composition were 0.007, 0.006, and 0.009 (< 0.05) in summer, winter, and spring, respectively (Table 5). According to the chemical composition of $PM_{2.5}$, a significant correlation of $PM_{2.5}$ at Checheng and Laoag was observed during these three seasons. In summer, clean air masses were blown from South China Sea, thus

both Checheng and Laoag were influenced by marine air. High $PM_{2.5}$ concentrations at Checheng and Laoag in winter and spring came mainly from North China, Korean Peninsula, and the Japanese islands. Polluted air masses passed the southern tip of Taiwan (Checheng) to northern Philippines (Laoag) by long-range transport. However, the *p*-value of $PM_{2.5}$'s chemical composition in fall was 0.076 ($p > 0.05$, insignificant correlation) (Table 5). In the season of fall, air masses were blown from the West Pacific Ocean toward Laoag, but Checheng was highly influenced by northerly winds due to the effect of northeastern monsoons, thus resulting in insignificant correlation between the chemical composition of $PM_{2.5}$ at Checheng and Laoag.

Correlation Analysis for Mass Concentration and Chemical Composition of $PM_{2.5}$ between Northerly and Southerly Transport Routes

In addition to employ the seasonal *p*-values of $PM_{2.5}$'s mass concentration and chemical composition at Checheng and Laoag, we further innovatively clustered the transport routes of air masses into two major groups, namely *northerly* and *southerly trajectories*. It showed that the *p*-values for these two clustered transport routes (see Table 5) were always lower than 0.05, indicating that $PM_{2.5}$ sampled at southern Taiwan (Checheng) and northern Philippines

(Laoag) highly correlated with each other for both $PM_{2.5}$'s mass concentration and chemical composition.

To further clarify the transport of $PM_{2.5}$ toward Checheng and Laoag, we figured out three air trajectories passing

through both Checheng and Laoag during the sampling periods. Two trajectories (noted as *S*) transported along the western coastline of Luzon across the Bashi Channel toward Checheng on August 23, 2015, and January 30, 2016.

(A) Central China; (B) Northern China; (C) South Korea; (D) Southern Japan; (E) West Pacific Ocean; (F) West Philippines; (G) South China Sea; (H) West Taiwan

Fig. 10. Clustered routes of air masses transported toward (a) Checheng and (b) Laoag during the $PM_{2.5}$ sampling periods.

Table 3. $PM_{2.5}$ concentrations and frequencies of clustered transport routes toward Checheng.

Transportation routes		CC	N	NNE	ENE	ESE	S	SW
Annual	$PM_{2.5}$	13.2	11.4	8.9	10.0	6.9	6.0	6.2
	SD	6.5	7.0	4.4	10.2	3.7	3.0	1.3
	Frequency	9.6%	36.5%	5.8%	3.9%	21.1%	3.9%	19.2%
Summer	$PM_{2.5}$	-	-	-	-	4.0	8.1	6.2
	SD	-	-	-	-	0.00	0.00	1.3
	Frequency	-	-	-	-	8.3%	8.4%	83.3%
Fall	$PM_{2.5}$	9.6	10.3	-	-	6.6	-	-
	SD	1.1	1.9	-	-	3.4	-	-
	Frequency	14.3%	21.4%	-	-	64.3%	-	-
Winter	$PM_{2.5}$	11.2	6.2	4.1	3.4	-	3.9	-
	SD	2.7	2.4	0.0	0.0	-	0.0	-
	Frequency	14.3%	64.3%	7.1%	7.2%	-	7.1%	-
Spring	$PM_{2.5}$	24.5	18.6	12.4	17.8	11.3	-	-
	SD	0.0	6.2	2.2	0.0	0.0	-	-
	Frequency	8.4%	58.3%	16.7%	8.3%	8.3%	-	-

Unit of $PM_{2.5}$: $\mu g m^{-3}$; SD: standard deviation; CC: central China; N: north; NNE: north-northeast; ENE: east-northeast; ESE: east-southeast; S: south; SW: southwest.

Table 4. PM_{2.5} concentrations and frequencies of clustered transportation routes toward Laoag.

Transportation routes		CC	N	NNE	ENE	ESE	S	SW	TW
Annual	PM _{2.5}	20.2	18.6	23.2	18.9	9.3	17.6	10.1	13.3
	SD	13.5	7.7	7.6	6.3	3.3	4.5	3.2	0.0
	Frequency	6.5%	21.7%	8.7%	6.5%	41.1%	4.6%	8.7%	2.2%
Summer	PM _{2.5}	-	-	-	-	7.5	17.6	10.1	-
	SD	-	-	-	-	0.00	4.5	3.2	-
	Frequency	-	-	-	-	14.3%	28.6%	57.1%	-
Fall	PM _{2.5}	-	-	-	-	8.4	-	-	-
	SD	-	-	-	-	2.3	-	-	-
	Frequency	-	-	-	-	100%	-	-	-
Winter	PM _{2.5}	20.2	14.1	16.8	-	8.6	-	-	13.3
	SD	13.5	6.5	3.5	-	0.2	-	-	0.00
	Frequency	23.1	30.8%	15.4%	-	23.1%	-	-	7.6%
Spring	PM _{2.5}	-	21.6	29.6	19.0	17.0	-	-	-
	SD	-	7.3	3.4	6.3	2.9	-	-	-
	Frequency	-	46.2%	15.4%	23.1%	15.3%	-	-	-

Unit of PM_{2.5}: $\mu\text{g m}^{-3}$; SD: standard deviation; CC: central China; N: north; NNE: north-northeast; ENE: east-northeast; ESE: east-southeast; S: south; SW: southwest; TW: Taiwan.

Table 5. The p-values for the mass concentration and chemical composition of PM_{2.5} at Checheng and Laoag for the paired *t*-test in different seasons and transport routes.

Seasons & routes	p-values	
	PM _{2.5} concentration	Chemical composition
Annual	0.001	0.018
Summer	0.042	0.007
Fall	0.631	0.076
Winter	0.009	0.006
Spring	0.028	0.009
Northerly routes	0.001	0.009
Southerly routes	0.033	0.007
S and TW routes	-	0.030

–: Data number is not enough for employing the paired *t*-test analysis.

Another trajectory (noted as *TW*) moved along the western coastline of Taiwan across the Bashi Channel toward Laoag on January 22, 2016. The chemical composition of PM_{2.5} for the above two trajectories was also employed for the paired *t*-test. It showed that the p-value was 0.030 ($p < 0.05$), indicating a considerable degree of correlation for atmospheric PM_{2.5} between southern Taiwan (Checheng) and northern Philippines (Laoag) (Table 5). The above three cases observed in this study proved that air masses containing PM_{2.5} could be transported back and forth between southern Taiwan and northern Philippines.

Identification and Apportionment of PM_{2.5} Sources

In this study, the source identification and apportionment of PM_{2.5} sampled at Checheng and Laoag was determined by PCA and CMB receptor model. Prior to conducting the source apportionment of PM_{2.5} using CMB receptor modeling, the source identification of PM_{2.5} was performed by using PCA. Results obtained from PCA showed that the major loading factors of PM_{2.5} at Checheng included crustal materials, oceanic spray, vehicular exhausts, biomass burning, and industrial processes (see Table 6). At Laoag, the major loading factors of PM_{2.5} included crustal materials, vehicular

exhausts, mixing anthropogenic sources, oceanic spray, and biomass burning. The major sources identified by PCA in this study were quite similar, indicating both remote sites had similar sources of PM_{2.5} mainly transported from long-range cross-boundary transport.

Moreover, the source apportionment of PM_{2.5} was further resolved by CMB receptor model. The resolved source types of PM_{2.5} at Checheng and Laoag included soil dust, oceanic spray, vehicular exhausts, and secondary aerosols (see Table 7). During the southeastern monsoon periods, clean air masses transported mainly from South China Sea, resulting in pretty similar source apportionment of PM_{2.5} at Checheng and Laoag. During the northeastern monsoon periods, the transport routes came mostly from Central and North China, Korean Peninsula, and the Japanese islands. Polluted air masses containing PM_{2.5} passed through major industrial complex regions along the southeastern coastal areas of China. As a result, industrial boilers and waste incinerators contributed more PM_{2.5} to the atmosphere since fall. The results showed that the source types of PM_{2.5} became more complicated in winter and spring. Particularly, the contribution percentages of industrial processes increased dramatically. The highest contribution of biomass burning

Table 6. Seasonal variation of principle component analysis for PM_{2.5}.

Summer				
CC			LO	
	Chemical Components	Variation	Chemical Components	Variation
PC1	NH ₄ ⁺ , Mg, K, Ca, Cr, Mn, Fe, Zn, Al, Pb, Ni, Ti	48.8%	NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Mg ⁺ , Ca ⁺ , OC, K, Ni	45.3%
PC2	Na ⁺ , Cl ⁻	13.5%	Mg, Ca, Fe, Zn, Al, Cd, Ti	33.5%
PC3	K ⁺ , OC	12.5%	EC, Mn, Pb	13.2%
PC4	EC	7.3%	Cl ⁻ , Na ⁺	8.0%
Fall				
CC			LO	
	Chemical Components	Variation	Chemical Components	Variation
PC1	NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ , K ⁺ , Cl ⁻ , Na ⁺ , Mn, Al, EC, OC, Pb, Ni	43.5%	Cl ⁻ , SO ₄ ²⁻ , Na ⁺ , NH ₄ ⁺ , K ⁺ , NO ₃ ⁻ , Mg ⁺ , Ca ²⁺	39.1%
PC2	Mg, Cd	15.0%	Zn, Ni, Ti	16.3%
PC3	Mg ⁺ , Ca	12.1%	EC, Mg, K, Pb, Cd	11.8%
PC4	Zn	6.6%	Fe	10.3%
Winter				
CC			LO	
	Chemical Components	Variation	Chemical Components	Variation
PC1	EC, Mg, Cr, Mn, Fe, Al, Cd, Pb, Ni, Ti	41.8%	NO ₃ ⁻ , NH ₄ ⁺ , Mn, Fe, Zn, Al	50.4%
PC2	Cl ⁻ , SO ₄ ²⁻ , Na ⁺ , NH ₄ ⁺ , K ⁺ , NO ₃ ⁻	30.5%	Cl ⁻ , Na ⁺ , Mg ²⁺	16.3%
PC3	OC	10.2%	K, Zn	11.6%
PC4	Zn	6.8%	Mn, Cr, Cd, Ti	7.4%
Spring				
CC			LO	
	Chemical Components	Variation	Chemical Components	Variation
PC1	Cl ⁻ , NH ₄ ⁺ , Na ⁺ , NO ₃ ⁻ , SO ₄ ²⁻ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Cr, Fe, Al, EC, Ni, Ti	28.5%	Cl ⁻ , SO ₄ ²⁻ , Na ⁺ , NH ₄ ⁺ , NO ₃ ⁻ , Zn, Cd, Cr, Mg, Fe, Ni, Ca	49.4%
PC2	K, OC	17.2%	OC, EC, K ⁺	9.4%
PC3	Pb	12.8%	Mg ²⁺ , Pb	8.3%
PC4	Cd	12.3%	Mn	6.4%

Table 7. Source apportionment of PM_{2.5} at Checheng and Laoag.

Sampling Sites	Checheng				Laoag			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring
Incinerators	3.0%	3.7%	2.7%	2.8%	1.8%	6.6%	6.9%	6.0%
Petrochemical industries	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Steel plants	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Industrial boilers	2.5%	2.8%	2.2%	2.0%	1.3%	1.5%	1.0%	1.4%
Cement industries	0.0%	2.0%	1.2%	1.0%	1.2%	0.0%	1.1%	0.6%
Soil dusts	18.6%	18.5%	19.5%	22.6%	21.2%	12.5%	16.4%	16.6%
Vehicular exhausts	11.2%	14.4%	12.0%	13.5%	18.7%	11.4%	10.6%	11.7%
Biomass burning	6.1%	6.5%	7.5%	10.3%	4.1%	9.3%	11.9%	11.9%
Oceanic spray	18.0%	15.1%	17.2%	18.3%	18.8%	21.8%	22.7%	19.7%
Secondary sulfate	11.8%	10.9%	6.5%	11.0%	7.3%	4.0%	6.9%	7.2%
Secondary nitrate	7.5%	8.8%	5.4%	9.2%	13.4%	7.5%	7.5%	7.9%
Organic carbon	1.5%	1.7%	1.4%	2.1%	0.0%	7.8%	6.3%	6.5%
Elemental carbon	0.0%	1.2%	1.1%	1.1%	0.0%	4.4%	2.6%	2.6%
Others	19.7%	14.4%	23.2%	6.2%	12.3%	13.3%	6.4%	7.9%

was observed in spring in Checheng and Laoag, concurring with the swidden agricultural practices employed in Indochinese Peninsula (Fig. 11).

CONCLUSIONS

This study inter-correlated the mass concentrations and chemical compositions of the atmospheric PM_{2.5} between southern Taiwan (Checheng) and the northern Philippines (Laoag). Field sampling of the PM_{2.5} revealed that the maximum and minimum concentrations at both sites occurred during winter and summer, respectively. The high winter concentrations were mainly attributable to northeastern monsoons, which transported polluted air masses containing PM_{2.5} southerly toward southern Taiwan and the northern Philippines.

Chemical analysis showed that the PM_{2.5} compositions were dominated by water-soluble ions (WSIs), to which secondary inorganic aerosols (SIAs) contributed 34.1–76.0%. The concentration of trace elements emitted from anthropogenic sources, such as Cr, Ni, As, Cd, Cu, and V, increased dramatically from late fall till early spring, when northeasterly winds prevailed. More organic carbon (OC) than elemental carbon (EC) was found, with secondary OC (SOC) contributing approximately 23.9–38.9% to the former,

thus indicating the formation of secondary organic aerosols (SOAs). Moreover, the concentration of levoglucosan highly correlated with those of K⁺ and OC, confirming that these three substances are key indicators of biomass burning, and high levels of levoglucosan during spring suggested that wood combustion for heating was a significant source of PM_{2.5}. The PM_{2.5} in Checheng and Laoag also exhibited similar chemical compositions, indicating the possibility of transport between southern Taiwan and the northern Philippines.

The simulated backward trajectories demonstrated that high concentrations of PM_{2.5} were mainly caused by emissions from neighboring regions to the north, namely, North China, the Korean Peninsula, and Japan. The concentrations at Checheng and Laoag exhibited significant correlations during summer, winter, and spring but insignificant correlations during fall. Such similarities were also observed for the chemical compositions. Furthermore, the resolved source apportionment of PM_{2.5} at Checheng and Laoag, which identified soil dust, oceanic spray, vehicular exhaust, and secondary aerosols as factors, showed more complex results for winter and spring compared to summer and fall. Finally, the contribution of industrial sources increased gradually beginning with fall, and the contribution of biomass burning peaked during spring.

Fig. 11. The fire maps at Checheng and Laoag during sampling periods.

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