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Diurnal Variation of Chemical Characteristics and Source Identification of Fine Particles in the Kaohsiung Harbor

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ABSTRACT

This study investigated the diurnal and monthly variation of fine particle ($PM_{2.5}$) concentrations and its chemical characteristics and source identification in the Kaohsiung Harbor. Three sites located in the harbor areas were selected for simultaneously sampling 12-h $PM_{2.5}$ in four months with consecutive seven days in each month. Water-soluble ions (WSIs), metallic elements, carbons, anhydrosugars, and organic acids in $PM_{2.5}$ were analyzed to characterize their chemical fingerprints and monthly variation. Field sampling and chemical analysis of $PM_{2.5}$ showed that significant diurnal and monthly variations of $PM_{2.5}$'s mass concentration and chemical composition were observed in the Kaohsiung Harbor. Prevailing wind direction highly influences the mass concentrations and chemical characteristics of $PM_{2.5}$ in the port areas. $PM_{2.5}$ was dominated by WSIs with the abundance of secondary inorganic aerosols (SIAs). Crustal elements dominated the metallic content of $PM_{2.5}$, but trace elements mainly originated from anthropogenic sources. The V/Ni ratios of $PM_{2.5}$ in the Kaohsiung Harbor were generally higher than 2.0. Organic carbon (OC) was superior to elemental carbon (EC) in $PM_{2.5}$ with the dominance of secondary OC (SOC). High concentration of levoglucosan (levo) was observed in spring due to nearby biomass burning. Additionally, high mass ratios of malonic and succinic acids (M/S) in $PM_{2.5}$ indicated the potential formation of SOAs. Results obtained from chemical mass balanced (CMB) receptor modeling showed that the major sources of $PM_{2.5}$ resolved in the Kaohsiung Harbor were mobile sources, ship emissions and oil-fired boilers, steel plants, secondary aerosols, sea salt spray, and fugitive dust. Primary $PM_{2.5}$ emitted from ship traffics accounted for 20.8% of $PM_{2.5}$.

Keywords: Fine particles, Harbor area, Diurnal variation, Chemical characteristics, Potential sources

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1 INTRODUCTION

Emissions from marine vessels contribute considerable quantity of air pollutants to the atmosphere, which could deteriorate air quality in local, regional, and even global levels (Aksoyoglu *et al.*, 2016). Particularly in the port and coastal areas, fine particles emitted from ships and heavy trucks might significantly influence the ambient air quality of the port area and neighboring metropolitan region, which could cause detrimental effects on human health and ecosystem (Wang *et al.*, 2007). Recently, environmental issues regarding the formation and adverse effects of marine aerosol particles have been focused on precisely quantifying the amount of emissions from marine vessels (Isakson *et al.*, 2001). Unfortunately, emissions from ships are dramatically increasing globally while many efforts have been aimed at decreasing the emissions from land-based sources (Corbett and Fischbeck, 1997).

Sea harbors play an important role for cross-continent cargo transport worldwide. In particular, ship traffics represent a comprehensive indicator for world economic development (Brandt *et al.*, 2013). However, they might also have negative impacts on atmospheric air quality, global warming, and global radiation balance as well (Brandt *et al.*, 2013). Exhausts from ships/vessels are mostly emitted while cruising at open waters and berthed in the harbors (Winnes *et al.*, 2015). Nevertheless, due to the closeness of harbors to the densely populated metropolitan areas, ship emissions from the port areas could be of great significance as potential air pollution sources which might cause detrimental effects on human health mainly depending upon the concentrations of air pollutants near the vulnerable receptors (Liu *et al.*, 2016).

A sea-land breeze is a local air circulation that occurs at the coastal regions due to a thermal contrast between sea and land (Tsai *et al.*, 2011). The recirculation of air pollutants associated with sea-land breezes and the thermal internal boundary layer (TIBL) is often recognized as the cause of consistent air pollution problems in the coastal areas (Miller, 2003). Influenced by sea-land breeze circulation, air pollutants transported by seaward return airflow can be recirculated landward, resulting in the accumulation of air pollutants in the coastal areas (Tsai *et al.*, 2011; Xu and Zhang, 2020). Previous studies reported that the occurrence of sea-land breeze circulation can easily lead to poor air quality in the coastal area (Ding *et al.*, 2004; Fung, 2005; Li *et al.*, 2020). Thus, air pollutants emitted from the harbor areas could be affected by the sea-land breezes, causing poor ambient air quality in the harbor areas as well as the neighboring metropolitan areas.

On-ocean shipping is regarded as an essential source of air pollutants including sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs), greenhouse gases (GHGs), and particulate matter (PM) (Corbett and Fischbeck, 1997). Air pollutants emitted from vessels can be blown leeward over hundreds and thousands of kilometers away from the coastline, which could significantly influence the downwind marine air quality. Ship emissions have become one of the rapid-growing mobile sources due to the significant increase of global shipping traffics. Previous study predicted that ship emissions could contribute approximately 17% of global CO_2 emissions in 2050 (Cames *et al.*, 2015). Additionally, shipping emissions in East Asia have resulted in 14,500–37,500 premature deaths in 2013 (Corbett *et al.*, 2007; Liu *et al.*, 2016). In the eastern Asian countries, especially in the megacities, industrial sources, transportation exhausts, and anthropogenic emissions remain a significant concern due to high emissions of air pollutants, which overall contribute 18–28% of total $PM_{2.5}$ emissions (Fu and Chen, 2017; Liu *et al.*, 2017). The ship emissions of $PM_{2.5}$ depend on their physical and chemical properties in a complex way. The carbonaceous particle, including organic carbon (OC) and elemental carbon (EC), is considered as the dominate composition, and might cause visibility impairment and monument discoloration. Several heavy metals, such as Cr, V, Ni, Cd, Pb and others, emission from the large implements and container trucks. These species could be as indicator for harbor emission. Therefore, it is required to investigate the effects of shipping emissions on local and regional air quality. The influences of ship transportation on the coastal and offshore air quality might differ in various geological regions due to major crucial factors including ship traffics, meteorological condition, and topographic terrain. For instance, the increase of ambient $PM_{2.5}$ concentrations in the offshore marine air is highly correlated to ship emissions in several European countries (Aksoyoglu *et al.*, 2016; Marelle *et al.*, 2016). In China, although high concentrations of air pollutants result mainly from the formation of SIAs (i.e., sulfate, nitrate, and ammonium) emitted from anthropogenic sources, another contributor might be ship emissions in the coastal cities (Lang *et al.*, 2017; Lv *et al.*, 2018).

Reducing emissions from land sources such as anthropogenic emissions and vehicular exhausts can be achieved by domestic legislation. However, controlling tail exhausts from ships is an important issue regarding international marine conventions. International Maritime Organization (IMO) is devoted to protect the marine environment by reducing air pollutants emitted from on-ocean ships. The International Convention for the Prevention of Marine Pollution (MARPOL) has been published in Ships Annex VI (Julian, 2000), in which four specific maritime regions are divided as Emission Control Areas (ECAs). The restrictions of ship emissions from 2009 to 2011 have significantly reduced the ambient concentration of SO_2 in the northern ECA of Europe. Moreover, sulfur emissions in the ECAs near Europe have increased during the past few years although land-based emissions have gradually decreased (Johansson *et al.*, 2013). According to the Environment

Agency of Europe (EAE), NO_x emissions from international marine transport in Europe increased and could be equivalent to land-based NO_x sources by 2020 (Aksoyoglu *et al.*, 2016).

Accordingly, it would be crucial to characterize the impacts of shipping emissions on ambient air quality in the coastal regions. This study aims to investigate the diurnal and monthly variation and the spatial distribution of $PM_{2.5}$ level, and characterize the chemical fingerprints of $PM_{2.5}$ in the Kaohsiung Harbor. Source identification and apportionment of $PM_{2.5}$ at the port sites were further resolved with CMB receptor modeling.

2 METHODOLOGIES

2.1 Sampling Protocol

In this study, the field sampling of $PM_{2.5}$ was carried out at the port area in the Kaohsiung Harbor (KH) (22°36′47″N, 120°16′40″E) where is the largest international seaport located at the southwestern coast of Taiwan Island. The shipping lines departing from the Kaohsiung Harbor navigated to all continents through the Taiwan Strait, the Bashi Channel, and the South China Sea, connecting to the world's major trade routes. In addition, the Kaohsiung Harbor is close to several sizable stationary sources such as petroleum refinery plants, oil- and coal-fired power plants, iron works, and shipyards. Additionally, there are several special industrial complexes for energy and resources recovery, shipbuilding yards, and semi-conductor manufactories. The Kaohsiung Harbor has the largest throughput in Taiwan and ranks the 16th largest harbor in the world.

Fine particles ($PM_{2.5}$) were simultaneously collected at three selected port sites in the Kaohsiung Harbor spatially distributed from north to south. Fig. 1 illustrates the locations of three port sites for sampling $PM_{2.5}$ at the Kaohsiung Harbor. Amongst the three $PM_{2.5}$ sampling sites, Site CH is located at the Chi-ho fishery checkpoint nearby the Port Entrance I at the northwestern end of the Kaohsiung Harbor, where has a ferry station cruising from the Qi-jin Island to the Gu-shan District in the Kaohsiung City. Site CH is located at the main route of fishing boats cruising inbound and outbound the northern entrance (i.e., Port Entrance I) of the Kaohsiung Harbor.

Site ZT is located at the Zhung-tao police station in the Commercial Port Zone at the central part of the Kaohsiung Harbor (see Fig. 1), where has several large bulk carrier terminals. In addition, there is another median-size container terminal adjacent to the Kaohsiung Export and Processing Zone (KEPZ). Since the Commercial Port Zone has bulk cargo terminals of old-style facilities, only medium tonnage (i.e., 20,000–50,000 tons) cargo ships are berthed. Therefore,

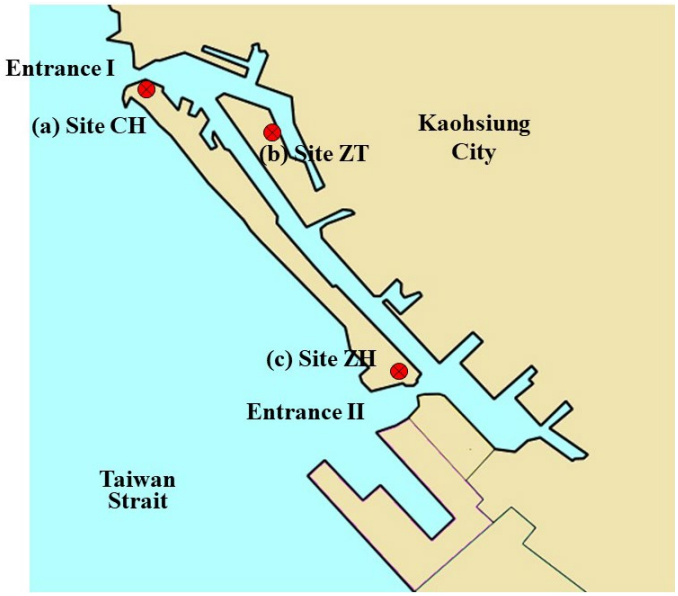

Fig. 1. Location of three $PM_{2.5}$ sampling sites selected for collecting $PM_{2.5}$ at the Kaohsiung Harbor (a) Chi-ho security checkpoint (CH), (b) Zhung-tao commercial port area, and (c) Zhung-he security checkpoint (ZH).

the bulk cargo vessels account for the most significant proportion of ships in the Commercial Port Zone.

Site ZH is located at the Zhung-he fishery security checkpoint adjacent to the Port Entrance II at the southwestern end of the Kaohsiung Harbor. The Port Entrance II is the main container entrance where is close to the third through fifth container terminals and the Phase-I Kaohsiung Intercontinental Container Center. The Port Entrance II is the secondary fairway for 100,000-ton vessels entering and exiting the Kaohsiung Harbor with a central channel width of 183 m and a water depth of 17.5 m, and is the primary channel for large on-ocean cargo ships and large container vessels. The container terminals nearby the Port Entrance II accommodate the berthing of various types of container vessels, and all adopt newly built-up modern container loading and unloading equipment. Moreover, the Port Entrance II is also close to an industrial complex, the Lin-hai Industrial Park, which is adjacent to several sizable industrial sources such as petroleum refinery plants, petrochemical plants, steel plants, and oil- and coal-fired power plants.

2.2 Sampling Methods

In this study, a $PM_{2.5}$ sampler (BGI, PQ-200) was applied to collect $PM_{2.5}$ at each sampling site. The $PM_{2.5}$ sampler was conducted in the volumetric flow rate of 16.67 L min^{-1} during the periods from February to November in 2020. Quartz fibrous filters (Advantec, PD-47A) of 47 mm diameter were used in the $PM_{2.5}$ sampler to collect 12-hr $PM_{2.5}$ samples for consecutive seven days in each month. Diurnal sampling of $PM_{2.5}$ was conducted at each sampling site in the daytime (08:00–20:00) and at nighttime (20:00–08:00). A total of 168 $PM_{2.5}$ samples were collected for exploring the diurnal variation of $PM_{2.5}$ concentration and its chemical fingerprints.

After sampling, each $PM_{2.5}$ filter was moved from the sampler with caution and placed in a petri dish which was then transported back to the Air Pollution Laboratory at the Institute of Environmental Engineering of National Sun Yat-sen University within two hours and conditioned at a constant temperature (T) of 20–25°C and a relative humidity (RH) of 40 ± 5% for 48 hours or longer. After conditioning, the $PM_{2.5}$ filters were weighted before and after sampling by an analytical microbalance (Sartorius, MSA6.6S) with the precision of 1.0 μg to precisely measure the masses of $PM_{2.5}$ filters before and after sampling and obtain the mass of particulate matter less than 2.5 μm over the filter which was then divided by the total volume of sampling air to further determine the mass concentrations of $PM_{2.5}$.

2.3 Chemical Analytical Methods

After conditioning and weighing, each $PM_{2.5}$ filter was then divided into four identical portions for further analysis of chemical composition in $PM_{2.5}$. The chemical analytical methods of water-soluble ions, metallic elements, carbonaceous content, anhydrosugars, and organic acids are available everywhere and described in the Supporting Information.

2.4 Quality Assurance and Quality Control (QA/QC)

The quality assurance and quality control (QA/QC) for both sampling and chemical analysis of $PM_{2.5}$ were conducted to ensure the accuracy of mass concentration and chemical analysis of $PM_{2.5}$ for this study. Prior to conducting $PM_{2.5}$ sampling, the air flowrate of each $PM_{2.5}$ sampler was calibrated with a film flowmeter. After sampling $PM_{2.5}$, a petri dish (Advantec; PD-47A) was used to fully preserve each $PM_{2.5}$ filter, which was temporarily stored in the environment of 4°C and then transported back to the Air Pollution Laboratory at National Sun Yet-Sen University for further conditioning, weighing, and chemical analysis within two weeks. The sampling and analytical procedure was similar to previous studies (Bagtasa and Yuan, 2020; Chang *et al.*, 2018; Hung *et al.*, 2018). Both field blank and transportation blank were further undertaken during the periods of $PM_{2.5}$ sampling, while reagent blank and filter blank were conducted for further analysis of chemical species in $PM_{2.5}$. The determination coefficient (R^2) of the calibration curve for each chemical species was required to be higher than 0.995. Background contamination was monitored by operational blanks (i.e., unexposed filters), which were proceeded simultaneously with field sampling. At least 10% of the samples were analyzed by spiking with a known amount of metallic and ionic species to determine their recovery efficiencies.

2.5 Neutralization Ratio (NR)

Neutralization ratio (NR) has been widely used to represent the aerosol acidity determined by secondary ionic species of NO_3^-, nss-SO_4^{2-}, and NH_4^+, which were firstly evaluated to analyze the acidity of $PM_{2.5}$. The definition of NR is described in the Supporting Information.

2.6 Enrichment Factor (EF)

Enrichment factor (EF) has been widely applied to differentiate the crustal and anthropogenic sources by using a predominant crustal element as the reference element. The principle of EF is described in the Supporting Information.

2.7 Chemical Mass Balanced (CMB) Receptor Modelling

The chemical mass balanced (CMB) receptor model was applied to resolve the source apportionment of $PM_{2.5}$ sampled at the three port sites in the Kaohsiung Harbor. The CMB receptor model has been widely applied to identify the potential sources and their contributions based on the principle of mass conservation (Gordon, 1988; Watson and Chow, 2007; Xu *et al.*, 2021). The principle of CMB receptor model is described in the Supporting Information.

3 RESULTS AND DISCUSSION

3.1 Diurnal Variation of $PM_{2.5}$ Concentration

This study conducted the simultaneous sampling of $PM_{2.5}$ at three port sites in the Kaohsiung Harbor and also investigated its diurnal and monthly variation. The diurnal and monthly variations of wind direction and $PM_{2.5}$ concentration during the sampling periods from February to November in 2020 were obtained from the ambient air quality monitoring station of the Kaohsiung Environmental Protection Bureau (KEPB) as illustrated in Fig. 2. The results showed that the prevailing winds were mainly blown from the west and the northwest in the daytime and from the east and the northeast at nighttime, respectively, at the three port sites in February, July, and November (see Fig. S1). In terms of monthly variation, the prevailing wind came mainly from the west in May, which blew air pollutants from the port area to the urban area. Particularly, the diurnal variations of wind directions in July and November were mainly influenced by the sea-land breeze. As illustrated in Fig. 2, a background $PM_{2.5}$ concentration level of 5.6 μg m^{-3} in the Kaohsiung Harbor was consistently observed in May and July.

Fig. S2. It showed that high concentrations of $PM_{2.5}$ observed in February mainly came from

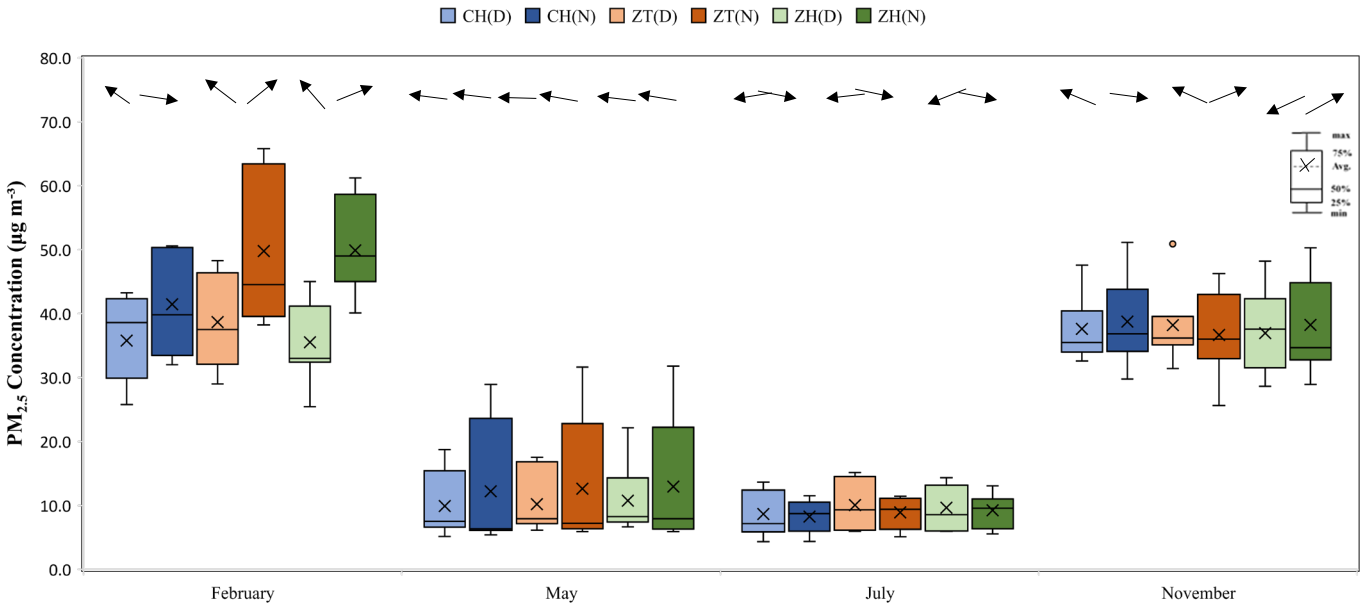

Fig. 2. Monthly and diurnal variation of $PM_{2.5}$ concentration at the Kaohsiung Harbor during the sampling periods.

Table 1. Monthly and diurnal variation of $PM_{2.5}$ concentrations at the Kaohsiung Harbor during the sampling periods.

Sampling Dates	Site CH (Chi-ho Checkpoint near Port Entrance I)			Site ZT (Kaohsiung Export and Processing Zone near Central Port Zone)			Site ZH (Zhung-he Checkpoint near Port Entrance II)		
	Day	Night	Mean	Day	Night	Mean	Day	Night	Mean
Feb. 18–24, 2020	35.8 ± 6.5	41.5 ± 7.0	38.6 ± 7.3	38.7 ± 6.6	49.8 ± 10.4	44.2 ± 10.3	35.5 ± 6.0	49.9 ± 7.0	42.7 ± 9.7
May 07–12, 2020	9.9 ± 5.1	12.2 ± 9.4	11.1 ± 7.3	10.2 ± 4.7	12.6 ± 10.0	11.4 ± 7.6	10.8 ± 5.4	12.9 ± 9.6	11.9 ± 7.6
July 21–27, 2020	8.7 ± 3.2	8.2 ± 2.3	8.4 ± 2.8	10.1 ± 3.5	8.9 ± 2.2	9.5 ± 3.0	9.6 ± 3.2	9.3 ± 2.4	9.5 ± 2.8
Nov. 04–12, 2020	37.6 ± 4.8	38.8 ± 6.5	38.2 ± 5.8	38.2 ± 5.7	36.7 ± 6.4	37.4 ± 6.1	36.9 ± 6.3	38.2 ± 7.3	37.6 ± 6.8
All Year	24.1 ± 15.6			25.6 ± 17.0			25.4 ± 16.5		

the northwest driven by ANMs via LRT. Unlike February, other three months (May, July, and November) were dominated by the sea-land breeze. A significant diurnal variation of $PM_{2.5}$ concentration was observed in the Kaohsiung Harbor during the $PM_{2.5}$ sampling periods. Overall, $PM_{2.5}$ came mostly from ship emissions cruised in the outer seas and in the port area in the daytime. However, $PM_{2.5}$ came mainly from industrial complex and neighboring metropolitan area at nighttime.

The diurnal, monthly, and yearly averaged $PM_{2.5}$ concentration at the three port sites in the Kaohsiung Harbor are summarized in Table 1. It clearly showed that a consistent trend of monthly averaged $PM_{2.5}$ concentration was observed in this study. The monthly average $PM_{2.5}$ concentrations at the port sites were in the order as: February (43.3 ± 11.8 μg m^{-3}) > November (37.9 ± 2.8 μg m^{-3}) > May (11.4 ± 7.2 μg m^{-3}) > July (9.1 ± 2.8 μg m^{-3}). Overall, the concentration of $PM_{2.5}$ followed a consistent monthly variation trend at the port sites in the Kaohsiung Harbor. The $PM_{2.5}$ concentrations higher than 35 μg m^{-3} were observed mainly in February and November, while a relatively lower concentration commonly occurred in May and July in the Kaohsiung Harbor. In addition, although the concentrations in May and July nearly approached the yearly standard of 15 μg m^{-3} by Taiwan Environmental Protection Administration (TWEPA) and standard of 10 μg m^{-3} ruled by WHO.

Fig. 2 further illustrates the diurnal variation of ambient $PM_{2.5}$ concentrations at the port sites in the Kaohsiung Harbor. It showed that the ambient concentrations of $PM_{2.5}$ at nighttime were generally higher than those in the daytime at all port sites in February, May, and November. The mass concentrations of $PM_{2.5}$ were similar both in the daytime and at nighttime in July at the port sites. The mass ratios of daytime and nighttime $PM_{2.5}$ concentrations (D/N) ranged from 0.6 to 2.1. The frequency of sampling days for D/N > 1.0 was 38.1%, while that for D/N < 1.0 was 61.9%. Interestingly, the concentrations of $PM_{2.5}$ at nighttime were commonly higher than those in the daytime at the Kaohsiung Harbor. Air pollutants in the Kaohsiung metropolitan area were blown to the port area by the land breeze at nighttime, which can be thus accumulated in the port area.

3.2 Diurnal Variation of Chemical Composition in $PM_{2.5}$

The chemical composition of $PM_{2.5}$ sampled in the daytime and at nighttime was further analyzed to resolve the diurnal variation of chemical composition of $PM_{2.5}$ in the Kaohsiung Harbor. The concentrations of water-soluble ions (WSIs) in $PM_{2.5}$ at the port sites in the Kaohsiung Harbor in four months are illustrated in Fig. 3. The average percentages of WSI_S in $PM_{2.5}$ ($WSI_S/PM_{2.5}$ ratio) at Sites CH, ZT, and ZH were in the range of 49.1%–55.5%, 46.8%–55.6%, and 48.2%–61.9%, respectively. The main WSIs in $PM_{2.5}$ included SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, and Na^+, representing SIAs formed by atmospheric chemical reactions and sea salts emitted from oceanic spray, respectively. Additionally, the concentrations of WSIs at each sampling site in February and November were far higher than those in May and July (see Fig. 3), which closely followed the monthly variation trend of $PM_{2.5}$ concentration.

In this study, the mass ratios of SIAs in WSIs (SIAs/WSIs ratio) in $PM_{2.5}$ at the port sites in the Kaohsiung Harbor ranged from 65.4% to 86.6%. Moreover, the monthly SIAs/WSI ratios in the Kaohsiung Harbor were in the order as: November (80.4%) > February (80.9%) > May (73.6%) > July (71.8%). The diurnal variation of SIAs showed that daytime SIA concentrations were commonly higher than those at nighttime during the $PM_{2.5}$ sampling periods, which concurred with the diurnal

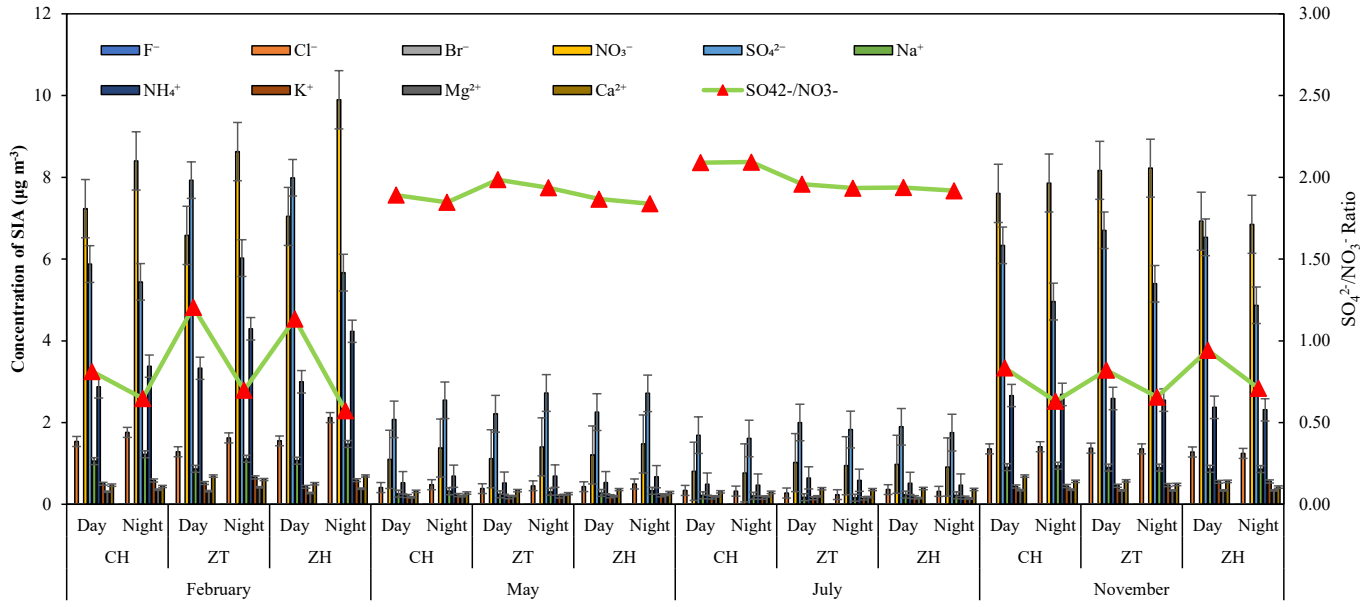

Fig. 3. Monthly and diurnal variation of water-soluble ions in $PM_{2.5}$ at the Kaohsiung Harbor during the sampling periods.

variation trend of $PM_{2.5}$ concentration. For the three $PM_{2.5}$ sampling sites, the mass concentrations of SO_4^{2-} at nighttime were commonly lower than those in the daytime. Moreover, the spatial distribution of NO_3^- and NH_4^+ concentrations showed no obvious difference in the Kaohsiung Harbor. The concentrations of NO_3^- in $PM_{2.5}$ at the port sites were lower while compared to previous researches (Tian *et al.*, 2013; Xu *et al.*, 2018; Zhang *et al.*, 2014), even though the potential underestimation of nitrate due to fast vaporization of nitrate. This might be attributed to the environmental condition suitable for nitrate generation in the coastal areas (Liu *et al.*, 2016). The molar ratios of SO_4^{2-}/NO_3^- at nighttime were commonly lower than those in the daytime in February and November (see Fig. 3). It was probably resulted from the prevalence of vehicular exhausts and ship activities in the port area in the daytime. Moreover, the concentrations of crustal ions mainly denoted by Ca^{2+} in $PM_{2.5}$ collected in the daytime were slightly higher than those at nighttime. Previous researches reported that the major sources of crustal matter in $PM_{2.5}$ were paved/unpaved road dust and soil dust emitted from storage piles and construction sites (Liu *et al.*, 2016; Xue *et al.*, 2010). Higher Ca^{2+} content in $PM_{2.5}$ in the daytime than those at nighttime were commonly observed, showing that anthropogenic activities relevant to fugitive dust and road traffics in the daytime were mostly higher than those at nighttime in the Kaohsiung Harbor. Large amounts of SO_2, NO_x, organic matter (OM), and particulate matter (PM) could be exhausted from ship emissions, which can then convert to sulfate, nitrate, and second organic aerosols (SOAs) via atmospheric chemical reactions.

Fig. 4 depicts the diurnal and monthly variations of metallic elements in $PM_{2.5}$ at the port area in the Kaohsiung Harbor during the $PM_{2.5}$ sampling periods. As illustrated in Fig. 4, the monthly variations of metallic elements and $PM_{2.5}$ concentrations were quite similar at the port sites, and both showed the consistent descending order as: February > November > May > July. In terms of diurnal variation, the metallic elements accounted for 12.7% and 12.3% of $PM_{2.5}$ in the Kaohsiung Harbor in the daytime and at nighttime, respectively. Overall, crustal elements (e.g., Mg, Al, Ca, Fe, and K) predominated the metallic content in $PM_{2.5}$, accounting for 82.9%–90.1% and 81.6%–89.7% of metallic content in the daytime and at nighttime, respectively. Previous literature reported that vanadium (V) and nickel (Ni) are two indicatory metals typically associated with the combustion of heavy fuel oil (HFO) (Almeida *et al.*, 2017; Harrison and Williams, 1996). Atmospheric V is considered being emitted from oil-fired boilers (Pacyna, 1984), while Pb and Zn both are correlated with shipping emissions (Viana *et al.*, 2009).

The correlation of V with major chemical species (Ni, Zn, Pb, NH_4^+, NO_3^-, and SO_4^{2-}) in $PM_{2.5}$ relevant to the shipping emissions was further analyzed to investigate the influences of shipping emissions to $PM_{2.5}$ in the port area as summarized in Table 2. It showed that the correlation

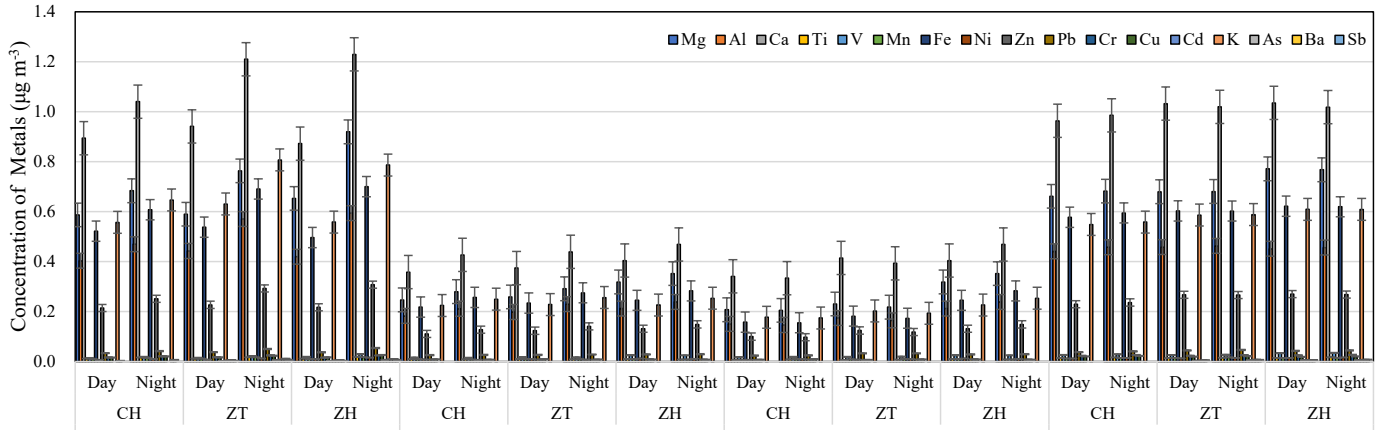

Fig. 4. Monthly and diurnal variation of metallic elements in $PM_{2.5}$ at the Kaohsiung Harbor during the sampling periods.

Table 2. Correlation coefficients of vanadium with major chemical species in $PM_{2.5}$ in the Kaohsiung Harbor during the sampling periods.

Daytime	Ni	Pb	Zn	SO_4^{2-}	NO_3^-	NH_4^+
V	0.84	0.59	0.48	0.32	0.05	0.16
Nighttime	Ni	Pb	Zn	SO_4^{2-}	NO_3^-	NH_4^+
V	0.88	0.70	0.68	0.50	0.67	0.50

coefficients of chemical species in $PM_{2.5}$ sampled at nighttime were commonly higher than those in the daytime. It is mainly attributed to the fact that more anthropogenic activities occurred in the daytime while compared to those at nighttime. Unfortunately, it was difficult to accurately differentiate shipping emissions from other local sources since SO_4^{2-} and NO_3^- are mainly originated from fuel burning sources in the industrial complex and the port area as well.

As aforementioned, V is emitted mainly from ship emissions, while Ni might have other sources except ship emissions. Previous research reported that the contribution of ship emissions to primary $PM_{2.5}$ could be evaluated by considering V as a valuable marker for fuel combustion in the ship engines. The contribution of ship emissions to $PM_{2.5}$ in the Kaohsiung Harbor could be estimated by Eq. (1) (Mamoudou *et al.*, 2018).

$$PM_a = \langle r \rangle \times V_a / F_{(V.HFO)} \quad (1)$$

where PM_a is the estimated primary $PM_{2.5}$ concentration (μg m^{-3}); <r> is the average ratio of $PM_{2.5}$ to the normalized V emitted (per ppm) based on the heavy fuel oil (HFO) burning experiments for ship engines; V_a is the in-situ ambient concentration of V in $PM_{2.5}$ (μg m^{-3}); <FV, HFO> is the average V content (ppm) of HFO used by vessels (Saraga *et al.*, 2019). In this study, <r> was set as 8205.8 ppm obtained from the experiments conducted by Agrawal *et al.* (2020), and <FV, HFO> was set as 93 ppm for the average V content of HFO.

The results indicated that, in the Kaohsiung Harbor, the concentrations of primary $PM_{2.5}$ contributed from ship emissions in the daytime and at nighttime were in the range of 1.26–2.94 and 1.38–3.08 μg m^{-3} with the average concentrations of 1.88 and 2.08 μg m^{-3}, respectively. It showed that the contributions of ship emissions to $PM_{2.5}$ at nighttime were slightly higher than those in the daytime owing to low wind speed at nighttime, resulting in unfavorable dispersion of $PM_{2.5}$ in the atmosphere at the port area. Additionally, most of ships cruised inbound and outbound the seaport in the daytime and berthed at the terminals mostly at nighttime. Overall, primary $PM_{2.5}$ contributed from ship traffics accounted for 20.8% of $PM_{2.5}$ in May and July, which were considerably higher than those of 5.6% in February and November (see Fig. 5). It was mainly attributed to the fact that polluted air masses were transported northerly from northeastern Asian countries by the ANMs frequently occurred in winter and spring, resulting in a higher contribution of LRT and a lower contribution of ship emissions to $PM_{2.5}$. Oppositely, the contribution

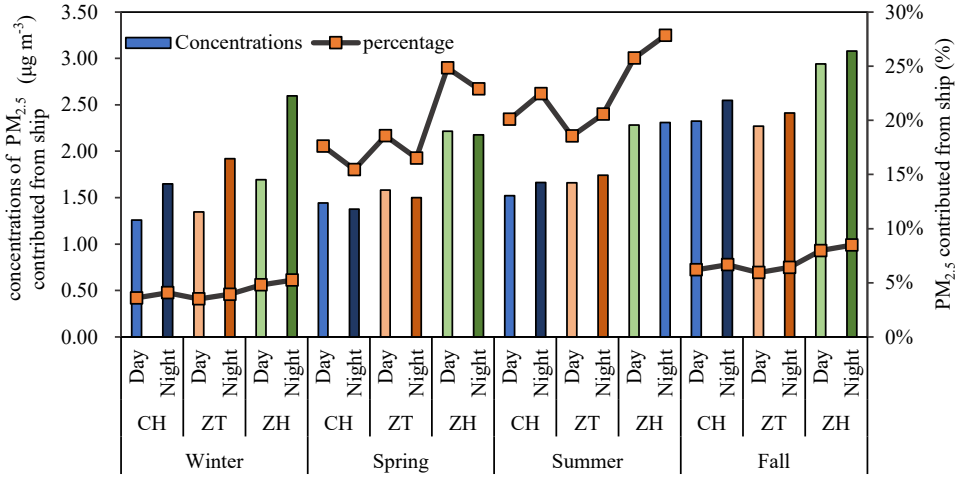

Fig. 5. Diurnal variation of contribution estimate to $PM_{2.5}$ from ship emissions at the Kaohsiung Harbor.

of northerly LRT to $PM_{2.5}$ is strongly suppressed in summer and fall, which caused high contributions of ship emissions to $PM_{2.5}$ in May and July.

The diurnal and monthly variations of carbonaceous content in $PM_{2.5}$ at theport area in the Kaohsiung Harbor during the $PM_{2.5}$ sampling periods are illustrated in Fig. 6. It showed that the carbonaceous content including OC and EC accounted for 12.6–33.0% of $PM_{2.5}$ in the Kaohsiung Harbor. The concentrations of OC were consistently higher than those of EC at the port areas in four months. Previous literature reported that EC has a molecular structure similar to pure graphite which is primarily originated from incomplete combustion (Long *et al.*, 2013). Interestingly, almost constant EC concentration levels of 0.86 and 2.03 μg m^{-3} with relative low variation were observed in the warm and cold months, respectively, in the Kaohsiung Harbor (see Fig. 6). Moreover, OC generally has much more complicated types of sources than EC, which consists of primary organic carbon (POC) and secondary organic carbon (SOC). Amongst the two types of OC, POC is mainly emitted from industrial boilers, cooking emissions, vehicular exhausts, coal/oil burning, forest fires, and tobacco burning. SOC is chemically converted from POC emitted from the primary sources of OC through atmospheric chemical reactions (Xu *et al.*, 2015).

The average concentrations of OC and EC in $PM_{2.5}$ were 2.8 and 1.4 μg m^{-3}, respectively, in the Kaohsiung Harbor during the $PM_{2.5}$ sampling period, implying that organic carbonaceous matter was consistently enriched in $PM_{2.5}$ rather than elemental carbonaceous matter. Particularly, the diurnal average concentrations of OC and EC were obviously different in February and July. In February. the concentrations of OC and EC at nighttime were higher than those in the daytime ($p < 0.05$), while an opposite trend was observed in July ($p < 0.05$). It was mainly attributed to high atmospheric stability owing to low temperature and low wind speed at nighttime in February. Additionally, a large amount of $PM_{2.5}$ in the polluted air masses could be transported northerly to the Kaohsiung Harbor by ANMs in February. Oppositely, anthropogenic activities including industrial emissions and ship/vehicular exhausts in the port area were considerably presented in the daytime in July.

Anhydrosugars including three major isometrics of levoglucosan (levo), mannosan, and galactosan are commonly formed from biomass burning, which can be used as a valuable biomarker of biomass burning (Engling *et al.*, 2014; Simoneit, 2002). Amongst the three anhydrosugars, only levo was detectable, while mannosan and galactosan were not detected in $PM_{2.5}$ (i.e., below the method detection limits (MDL)) sampled in the Kaohsiung Harbor. Fig. 7 illustrates the diurnal and monthly variation of levo concentration in $PM_{2.5}$ at the Kaohsiung Harbor. Levo comprised of 0.06–0.55% of $PM_{2.5}$ by mass with an average concentration of 45.8 μg m^{-3}. In terms of diurnal variation, the average concentration of levo in the daytime (40.9 μg m^{-3}) was obviously lower than that at nighttime (49.0 μg m^{-3}), implying less biomass burning activities in the port area and neighboring metropolitan areas at nighttime. Moreover, levo is hardly degraded through atmospheric chemical reactions, thus, it can be transported from Asian continents (e.g., mainland

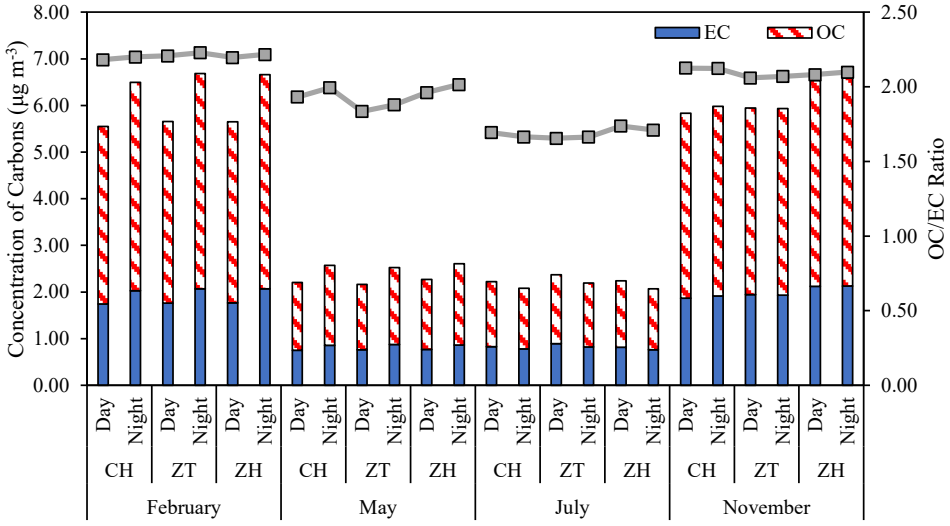

Fig. 6. Monthly and diurnal variation of carbonaceous content and OC/EC ratio of $PM_{2.5}$ at the Kaohsiung Harbor during the sampling periods.

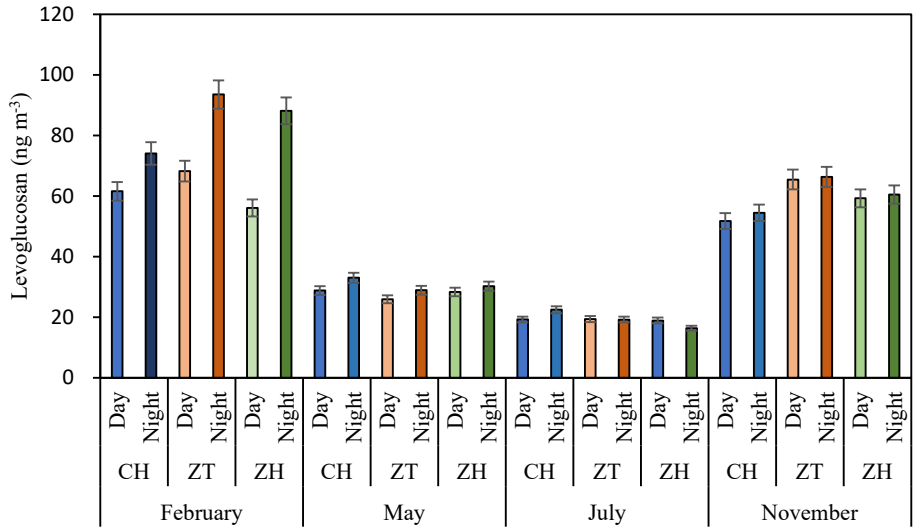

Fig. 7. Monthly and diurnal variation of levoglucosan concentration in $PM_{2.5}$ at the Kaohsiung Harbors.

China, Indochina Peninsula, and Southeast Asia) to the remote leeward lands or seas via LRT (Sanz Rodriguez *et al.*, 2020).

The diurnal and monthly variations of organic acids in $PM_{2.5}$ at the port area in the Kaohsiung Harbor are illustrated in Fig. 8. In this study, organic acids detected in $PM_{2.5}$ included oxalic (C2), malonic (C3), and succinic (C4) acids. It showed that the concentrations of organic acids in $PM_{2.5}$ at nighttime were obviously higher than those in the daytime during the $PM_{2.5}$ sampling periods (Fig. 8). Oxalic acid was the most abundant organic acid in $PM_{2.5}$, and followed by malonic and succinic acids. It was mainly attributed to the fact that oxalic, malonic, and succinic acids were mainly originated from vehicular exhausts with the highest emission rates noteworthy from gasoline engines. Malonic acid is chemically formed in the atmosphere through atmospheric photochemical reactions of organic precursors released from fossil fuel combustion and biomass burning (Kawamura and Bikkina, 2016).

3.3 Chemical Significance of $PM_{2.5}$

The chemical significance of $PM_{2.5}$ and the index of representative chemical species are further

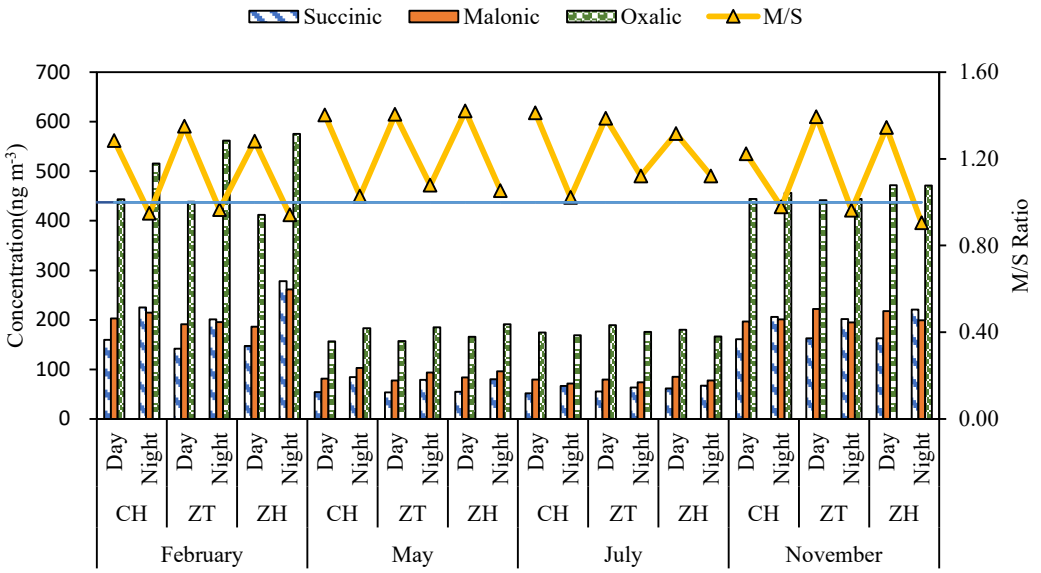

Fig. 8. Monthly and diurnal variation of organic acids and M/S ratio of $PM_{2.5}$ at the Kaohsiung Harbors.

investigated in this section. First of all, this study applied the equivalent concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ to calculate NR which can be used to determine whether $PM_{2.5}$ was acidic or basic particle. The definition of NR is described in the Supporting Information. In addition to secondary sulfate (SO_4^{2-}) produced by atmospheric chemical reactions, other potential sources of SO_4^{2-} in $PM_{2.5}$ were contributed from the oceans. Thus, it is necessary to use non-sea salt sulfate (nss-SO_4^{2-}) instead of gross SO_4^{2-} to calculate the NR of $PM_{2.5}$ (Wang *et al.*, 2019).

As depicted in Fig. 9, the monthly variation of NR for $PM_{2.5}$ during the $PM_{2.5}$ sampling periods was in the order as: February (0.8) > July (0.6) > May (0.6) > November (0.4). In terms of the diurnal variation of NR, the NR values for daytime and nighttime $PM_{2.5}$ in the cold months (February and September) were more diverse than those in the warm months (May and July). All NR values less than unity showed that NH_4^+ cannot solely neutralize the excess nss-SO_4^{2-} and NO_3^-, indicating that $PM_{2.5}$ was recognized as acidic particles in the Kaohsiung Harbor, which concurred with previous studies conducted in several harbor areas (Genga *et al.*, 2017; Tseng *et al.*, 2021). In February, relatively low air temperature favored the conversion of both NH_3(g) and HNO_3(g) to form NH_4NO_3(s) via atmospheric chemical reactions, while reversible reactions commonly occurred in contrast with ambient air temperature near 25–33°C in other three months (see Table S1). Due to poor atmospheric dispersion condition in February, nss-SO_4^{2-} and NO_3^- emitted from the port areas tended to be accumulated in the Kao-ping Air Quality Zone (KPAQZ), thus resulting in higher NR values than other three months.

Moreover, the molar ratio of V and Ni (V/Ni ratio) has been used as a valuable indicator to identify the extent of ship emissions (Isakson *et al.*, 2001). Fig. 10 depicts the diurnal and monthly variations of V/Ni in $PM_{2.5}$ in the Kaohsiung Harbor. As illustrated in Fig. 10, the concentrations of V and Ni had similar variation trend both in the daytime and at nighttime with high correlation coefficients (r) of 0.84 and 0.89, respectively. However, this study revealed relatively low r values in winter and high r values in May and July, since wind speeds were relatively low in May and July, which was suitable for coastal and offshore boating activities. Particularly, the tourism ferry shipping was much active in summer while compared to other three months, resulting in high concentrations of V and Ni in ambient $PM_{2.5}$. Oppositely, strong winds commonly occurred in February were often blown northerly to the Kaohsiung Harbor which are dull months for tourism ferry shipping, thus leading to low concentrations of V and Ni in $PM_{2.5}$.

Previous research reported that, as the V/Ni ratio in PM was higher than 1.5, it is considered being primarily influenced by ship emissions (Mazzei *et al.*, 2008). Other literature also reported that the mean value of V/Ni ratio is 1.9 for $PM_{2.5}$ emitted from the combustion of heavy fuel oil (Viana *et al.*, 2008). In this study, the annual averaged V/Ni ratios in the daytime and at nighttime

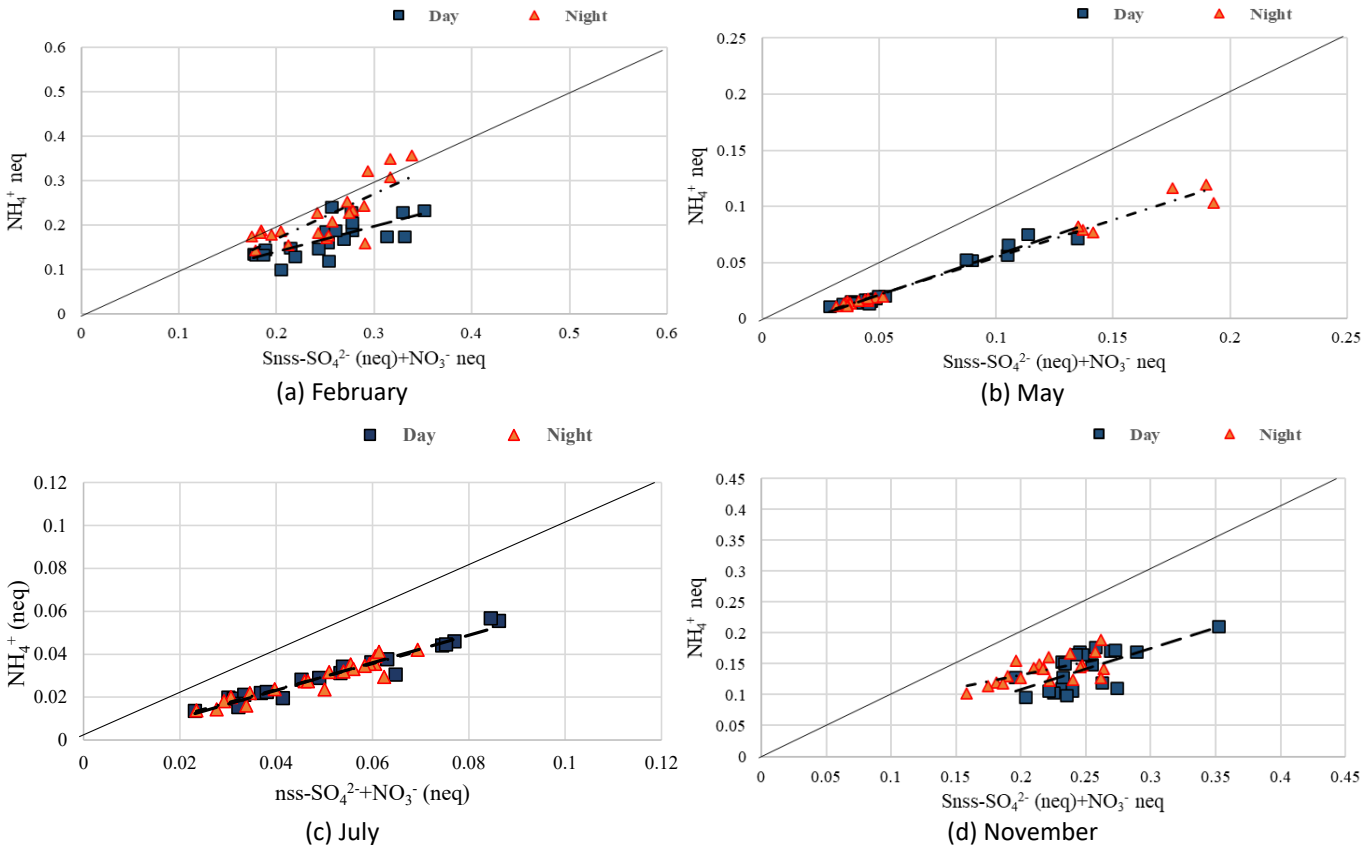

Fig. 9. Plot of NH_4^+ verse nss-SO_4^{2-} + NO_3^- in $PM_{2.5}$ at the Kaohsiung Harbor during the $PM_{2.5}$ sampling periods.

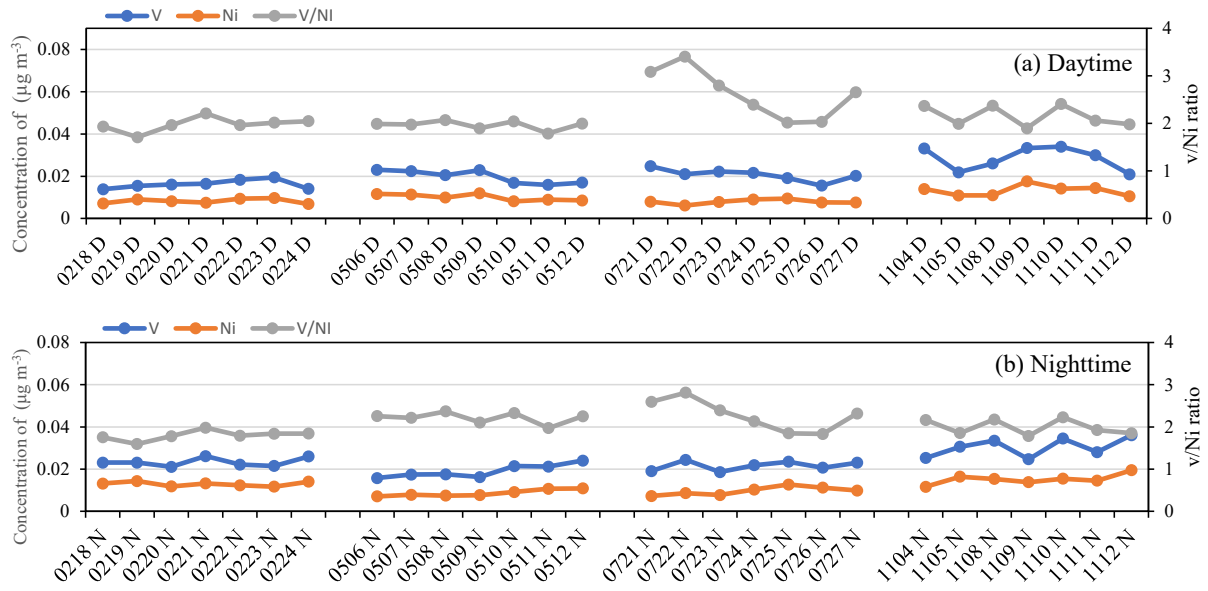

Fig. 10. Monthly and diurnal variations of V and Ni concentrations and V/Ni ratio at Kaohsiung Harbor.

were 2.2 and 2.1, respectively, in the Kaohsiung Harbor, indicating that $PM_{2.5}$ in the Kaohsiung Harbor was highly influenced by ship emissions. Moreover, an obvious trend of higher V/Ni ratios in July and lower V/Ni ratios in February was observed. Overall, the V/Ni ratios of $PM_{2.5}$ in the Kaohsiung Harbor were generally higher than 2.0, but lower than Shanghai Harbor (Zhao *et al.*, 2013).

Fig. S3 illustrates the enrichment factors of metallic elements in the Kaohsiung Harbor during the $PM_{2.5}$ sampling periods. However, there were no significant differences of metallic elements

Table 3. Correlation of levoglucosan, organic carbon, and potassium ion in $PM_{2.5}$ in the Kaohsiung Harbor during the sampling periods.

Months	Daytime		Nighttime	
	Levo vs. K^+	Levo vs. OC	Levo vs. K^+	Levo vs. OC
February	0.92	0.13	0.77	0.99
May	0.91	0.11	0.81	0.78
July	0.14	0.08	0.03	0.39
November	0.21	0.12	0.19	0.11

in $PM_{2.5}$ sampled in the daytime and at nighttime. It showed that K, Ca, Al, and Mg came mainly from crust and oceanic spray. In particular, the EF values of trace elements (Ni, V, Cr, and Zn) were obviously higher than 10 in the Kaohsiung Harbor, indicating that they were highly influenced by $PM_{2.5}$ emitted from ships/vessels berthed on the terminals and cruised inside and outside the Kaohsiung Harbor in daytime and nighttime.

The correlations of levo with OC and K^+ in $PM_{2.5}$ were further explored to identify the potential sources of biomass burning as shown in Table 3. It showed that levo was strongly correlated with OC in $PM_{2.5}$ at nighttime in February (r = 0.99) and May (r = 0.78). A strong correlation (r = 0.77–0.99) between levo and K^+ in $PM_{2.5}$ was observed for $PM_{2.5}$, further implying that $PM_{2.5}$ was originated from biomass burning., Particularly, OC was contributed from ship emissions in the daytime in the port areas, resulting in relatively high correlation of OC with levo.

Another important factor was the mass ratio of OC and EC (OC/EC ratio) which is often used as an indicator to evaluate the formation of SOAs (Feng *et al.*, 2007; Wu and Yu, 2016). It is worth noting that the concentrations of OC in $PM_{2.5}$ were obviously higher than those of EC. The monthly variation of OC/EC ratios for $PM_{2.5}$ in the Kaohsiung Harbor are illustrated in Fig. 6. The OC/EC ratios were generally higher than 2.0 in February and November, showing the potential formation of SOAs in the atmosphere during the periods of ANMs. High OC/EC ratios in spring and winter suggested that $PM_{2.5}$ at the port area in the Kaohsiung Harbor were significantly influenced by long-range transported SOAs in $PM_{2.5}$ blown from ACOs (Wang *et al.*, 2015; Yuan *et al.*, 2020).

Fig. 8 illustrates the mass ratios of malonic acid and succinic acid (M/S ratio) in $PM_{2.5}$ in the Kaohsiung Harbor. The M/S ratio has been commonly used as a valuable index to evaluate the importance of their sources in the atmosphere since malonic acid is a major product of succinic acid in the atmospheric photochemical reactions (Yao *et al.*, 2002). The M/S ratio has been reported as 0.3–0.8 for local anthropogenic sources, and mostly higher than 1.0 for SOAs which are small-sized and long-lived in the atmosphere, and could be produced from the intensified photochemical reactions (Aggarwal andd Kawamura, 2008; Hallquist *et al.*, 2009). The significance of atmospheric photochemical process for the formation of organic acids can be ascertained by the mass ratio of malonic to succinic acid (M/S) (Kawamura and Sakaguchi, 1999).

Moreover, the mass ratios of M/S were greater than unity for photochemically aged aerosols, whereas it is lower than unity for vehicular emissions (i.e., primarily originated) (Kawamura and Kaplan, 1987). This study revealed an obvious variation trend of M/S ratio in the Kaohsiung Harbor (see Fig. 8). The M/S ratios of $PM_{2.5}$ in the daytime were mostly higher than those at nighttime, showing that organic matter (OM) in $PM_{2.5}$ was mainly due to the heterogeneous photochemical reactions caused by solar radiation producing more SOAs. On the contrary, low temperature and no solar radiation at nighttime would cause much weak atmospheric photochemical reaction, thus resulting in low M/S ratios mainly correlated to vehicular and/or ship emissions.

3.4 Source Apportionment of $PM_{2.5}$

The source apportionment of daily $PM_{2.5}$ sampled at the port sites in the Kaohsiung Harbor was further resolved by chemical mass balanced (CMB) receptor model. The overall resolved mass percentages of potential contributors to $PM_{2.5}$ were in the range of 91.1%–97.3% (see Fig. 11). It showed that the highest and the lowest monthly resolved contribution percentages to $PM_{2.5}$ were in February and July, respectively. The highest contribution percentage to $PM_{2.5}$ in February was mainly attributed to the fact that the poorest ambient air quality was commonly observed in late winter due to the superimposition effect of LRT and local emissions. As illustrated in Fig. 11, the

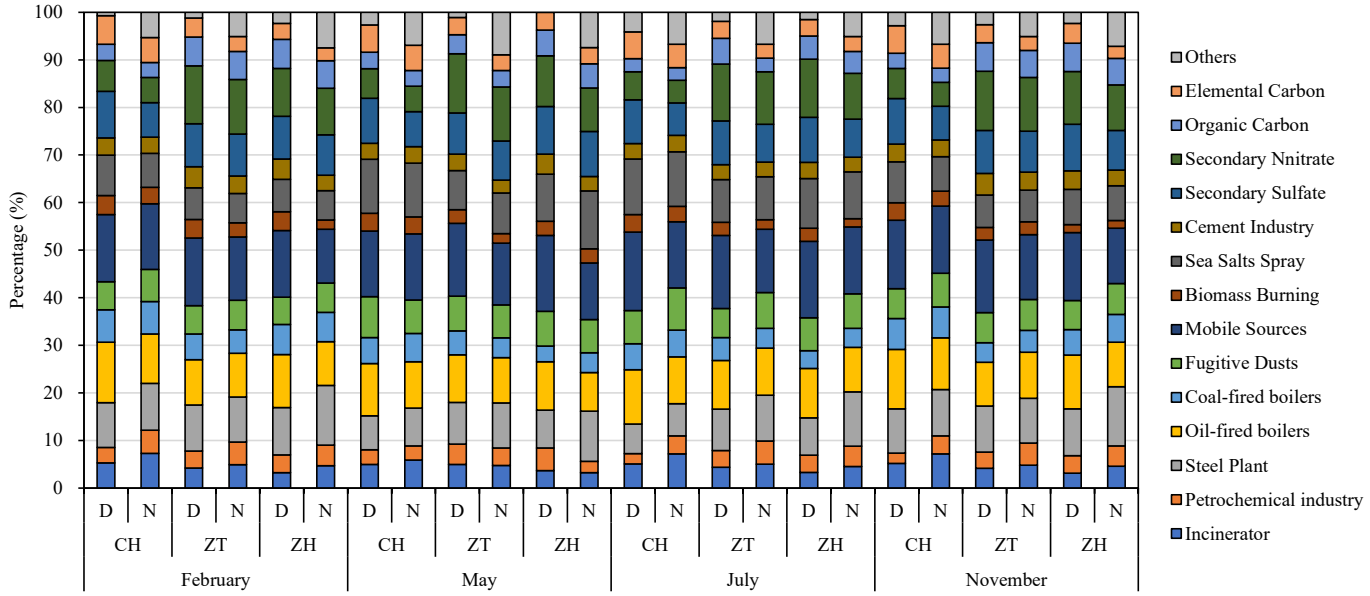

Fig. 11. Source apportionment of $PM_{2.5}$ at the Kaohsiung Harbor resolved by CMB receptor model.

contribution percentages to $PM_{2.5}$ at the three port sites was mobile sources (11.3%–16.5%), and followed by ship emissions and oil-fired boilers (8.1%–12.5%), steel plants (6.2%–12.6%), secondary nitrate (4.8%–12.4%), secondary sulfate (6.8%–10.0%), sea salt spray (6.2%–12.2%), fugitive dust (5.7%–8.9%), coal-fired boilers (3.3%–6.8%), incinerators (3.1%–7.3%), organic carbon (2.7%–6.1%), elemental carbon (2.5%–5.8%), petrochemical plants (2.2%–4.9%), cement plants (2.7%–4.5%), and biomass burning (1.6%–4.0%), respectively.

We further resolved the diurnal variation of source apportionment for 12-hr $PM_{2.5}$ in the Kaohsiung Harbor. As illustrated in Fig. S5(a), the averaged source contributor to $PM_{2.5}$ solely in the daytime was also mobile sources (14.7%), and followed by ship emissions and oil-fired boiler (10.8%), secondary nitrate (9.8%), secondary sulfate (9.4%), steel plants (8.7%), sea salt spray (8.8%), fugitive dust (6.6%), coal-fired boiler (5.1%), organic carbon (4.7%), elemental carbon (4.4%), incinerators (4.3%), petrochemical plants (4.0%), cement plants (3.8%), and biomass burning (3.2%).

As illustrated in Fig. S5(b), the averaged contributor to $PM_{2.5}$ solely at nighttime was mobile sources (13.1%), and followed by steel plants (10.0%), ship emissions and oil-fired boiler (9.6%), secondary nitrate (8.6%), sea salt spray (8.6%), secondary sulfate (8.0%), fugitive dust (7.0%), incinerators (5.3%), coal-fired boilers (5.2%), organic carbon (4.3%), elemental carbon (3.7%), cement plants (3.3%), petrochemical plants (3.2%), and biomass burning (2.6%).

Overall, the contribution percentages of mobile sources, ship emissions and oil-fired boilers, steel plants, cement plants, petrochemical plants, sea salt spray, and secondary aerosols in the daytime were always higher than those at nighttime (see Tables S2–S3). It was mainly attributed to the fact that anthropogenic activities densely and frequently occurred in the port area during the daytime sampling periods. Under the influence of the sea breeze in the daytime, the contribution of sea salt spray is also higher than those at nighttime. Oppositely, the contributions of fugitive dust and incinerators at nighttime were higher than those in the daytime. It was mainly because strong land breeze blew fugitive road dust and incineration particles from nearby metropolitan area to the Kaohsiung Harbor at nighttime. Moreover, compared to Site ZH, the contribution percentages of sea salt spray were commonly higher at Sites CH and ZH where are close to the port entrances I & II due to the influences of sea breeze blown from outer seas to the port area in the daytime, resulting in higher resolution percentages to $PM_{2.5}$ in the daytime than those at nighttime.

4 CONCLUSIONS

This study explored the chemical fingerprints, diurnal and monthly variation, and source apportionment of $PM_{2.5}$ in the Kaohsiung Harbor. A diurnal variation of $PM_{2.5}$ concentrations was

commonly observed in the port area, depicting that nighttime $PM_{2.5}$ concentrations (32.5 ± 16.9 μg m^{-3}) were higher than those in the daytime (28.2 ± 13.9 μg m^{-3}) in four months except July. Similarly, the concentrations of SIAs in $PM_{2.5}$ at nighttime (10.5 ± 6.7 μg m^{-3}) were also higher than those in the daytime (10.3 ± 6.7 μg m^{-3}). It was mainly attributed from the prevalence of vehicular exhausts and high ship traffics in the daytime. Moreover, the concentrations of V and Ni were highly correlated with high correlation coefficients (r) of 0.84 and 0.89 in the daytime and at nighttime, respectively, depicting significant contribution of ship emissions to the port $PM_{2.5}$. The amounts of primary $PM_{2.5}$ contributed from ship emissions were in the ranges of 1.3–2.9 and 1.4–3.1 μg m^{-3} in the daytime and at nighttime, respectively. The concentrations of TC (= OC + EC) at nighttime (4.4 ± 2.0 μg m^{-3}) were always higher than those in the daytime (4.1 ± 1.8 μg m^{-3}) in February ($p < 0.05$), while an opposite trend was observed in July ($p < 0.05$). It was mainly due to stable atmospheric condition at nighttime and northerly prevailing winds which transported polluted air masses to the Kaohsiung Harbor by ANMs via LRT. In May and July, anthropogenic emissions and vehicular exhausts were more significant in the daytime. The concentrations of levo in the daytime (27.7 ± 1.8 ng m^{-3}) were lower than those at nighttime, (30.7 ± 1.5 ng m^{-3}) notably owing to low air temperature at nighttime. High M/S ratios in the daytime showed that organic matter (OM) in $PM_{2.5}$ was mainly attributed to the formation of SOAs by atmospheric chemical reactions. On the contrary, low temperature and no solar radiation at nighttime caused much weak atmospheric chemical reactions, resulting in low M/S ratios mainly correlated to vehicular/ship emissions. The diurnal variation of $PM_{2.5}$ concentrations and its chemical composition was highly influenced by sea-land breeze. Both primary and secondary $PM_{2.5}$ can be blown from the metropolitan area to the port area by land breeze at nighttime and vice versa by sea breeze in the daytime. Under the condition of low wind speeds at nighttime, the effects of sea-land breeze caused the accumulation of $PM_{2.5}$ in the between of harbor and urban areas, resulting in high concentrations of $PM_{2.5}$ in the Kaohsiung Harbor and neighboring metropolitan area. The major sources of $PM_{2.5}$ in the port area were mobile sources (11.3%–16.5%), ship emissions and oil-fired boilers (8.1%–12.5%), steel plants (6.2%–12.6%), secondary aerosols (4.8%–12.4%), sea salt spray (6.2%–12.2%), and fugitive dust (5.7%–8.9%).

According to the research results, the air quality of the Kaohsiung Harbor at night is poor, especially in February and November. Therefore, it is suggested that the environmental protection agency should strengthen the port area inspection, oil sampling inspection, and street-cleaning at night.

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SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.220100

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