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

(Supporting Information)

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A. Chemical Analytical Methods

One quarter of the filter was used for analyzing the water-soluble ionic species in PM$_{2.5}$. Each quarter of the filter was put into a 50-ml PE bottle poured with 30 mL distilled deionized water (DI H$_2$O) with conductivity $> 18.2$ M$\Omega$ to dissolve ionic species of PM$_{2.5}$ with an ultrasonic vibrator (Branson, 5510) for 120 min. An ion chromatograph (IC) (Dionex, DX-120) was initially calibrated and used to analyze the concentrations of major anions ($F^-$, $Br^-$, $Cl^-$, $SO_4^{2-}$, and $NO_3^-$) with 1.8 mM Na$_2$CO$_3$/1.7 mM NaHCO$_3$ solution as an eluent. Another ion chromatograph (Dionex, ICS 1100) was then used to analyze the concentrations of major cations ($NH_4^+$, $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$) with 20 mM methane sulfonic acid as an eluent.

Another quarter of the quartz fibrous filter was used for analyzing the metallic content of PM$_{2.5}$. One quarter of each PM$_{2.5}$ filter was initially digested in a 20 mL mixed acid solution (HNO$_3$: HClO$_3$ = 3:7) at a temperature of 150–200°C for 120 min, and then diluted to 25 mL with distilled deionized water (DI H$_2$O). Seventeen metallic elements including Cr, Mn, Fe, Ni, Zn, Cd, Pb, Mg, K, Ca, Ti, Al, As, V, Cu, Ba, and Sb in PM$_{2.5}$ were then analyzed with an inductively coupled plasma/atomic emission spectrometry (ICP/AES) (Perkin Elmer, Optima 2000DV).

The carbonaceous content of PM$_{2.5}$ was measured with an elemental analyzer (EA) (Elementar, Vario EL III). One quarter of the quartz fibrous filter was further cut into two identical pieces; each piece is equivalent to one eighth of the filter. One of the two pieces was preheated in advance by hot nitrogen gas (340-345°C) for 30 min to expel organic carbon (OC) fraction, after which the amount of elemental carbon (EC) was then determined. Another piece was further analyzed without preheating, and the carbon content was thus characterized as total carbon (TC). Organic carbon
(OC) was then determined by extracting EC from TC.

Another quarter of the quartz fibrous filter was further analyzed for anhydrosugars (i.e. levoglucosan, mannosan, and galactosan) and organic acids (OAs) (i.e. oxalic acid, malonic acid, and succinic acid) in PM$_{2.5}$ with a high-performance ionic chromatograph (HPIC) (Dionex, ICS 5000$^+$$^+$). Each quarter filter was initially extracted by DI H$_2$O with conductivity $> 18.2$ M$\Omega$ in a PE bottle under ultrasonic vibration for 120 min with a prebaked quartz fibrous filter (0.3 $\mu$m pore size). Anhydrosugars were analyzed by using 200.0, 100.0, 18.0, and 5.0 mM NaOH as the eluents in a flow rate of 1.0 mL/min, while OAs were analyzed by using 25.0 mM H$_2$SO$_4$ and 5.0 mM NaOH as the eluents in a flow rate of 1.0 mL/min.

B. Neutralization Ratio (NR)

A comparison of ammonium concentrations to non-sea salt sulfate plus nitrate concentrations (NH$_4^+$/ (nss-SO$_4^{2-}$+NO$_3^-$)) in the unit of micro equivalents per cubic meter ($\mu$eq/m$^3$). The micro equivalent concentrations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ ($\mu$eq/m$^3$) were determined by dividing their mass concentration (µg/m$^3$) to its equivalent molecular weight (MW). The nss-SO$_4^{2-}$ is the excess sulfate that was calculated by subtracting the amount of SO$_4^{2-}$ in the seawater from that of SO$_4^{2-}$ in the atmosphere. We can then determine the nss-SO$_4^{2-}$ concentration by the equation of (nss-SO$_4^{2-}$ = SO$_4^{2-}$ − 0.251×Na$^+$).

C. Enrichment Factor (EF)

Enrichment factor (EF) has been widely used as an indicator to identify whether atmospheric aerosol particles are originated from natural or anthropogenic sources. EF is defined as the mass ratio of metallic elements to a reference element expressed by
Eq. (1) (Gorden, 1974).

\[ EF = \frac{(Tr_{PM}/Ref_{PM})}{(Tr_{crust}/Ref_{crust})} \]  

(1)

where \( Tr \) is the concentrations of metallic elements in PM\(_{2.5}\) emitted from the pollution sources; \( Ref \) is the concentration of a reference element in PM\(_{2.5}\) emitted from the crustal. Aluminum (Al) is one of the major crustal elements, which has been commonly used as the reference element in the previous studies (Li et al., 2016; Li et al., 2020). In this study, we herein used Al as the reference element to determine the EF values of the metallic elements in PM\(_{2.5}\).

Previous literature has set up the criteria of EF to differentiate whether the particulate matter (e.g. PM\(_{2.5}\) and PM\(_{10}\)) is originated from anthropogenic and/or natural sources (Zhou et al., 2014). As EF>10, it indicates that the metallic elements are mainly contributed by anthropogenic sources. As EF<1, it indicates that the metallic elements are originated mostly from the crust. As 1<EF<10, it indicates that the metallic elements may be contributed from the combination of crustal and anthropogenic sources (Ahmed et al., 2017).

D. Chemical Mass Balanced (CMB) Receptor Modelling

The CMB model was applied to resolve the potential sources of PM\(_{2.5}\) and their contributions by verifying several fit indices, such as \( \chi^2 \) (≤ 4.0), \( R^2 \) (≥0.8), the percentage of mass (80-120%), T statistics (≥2.0), and the degrees of freedom (>5). The residual and uncertainty ratios were required between -2.0 to 2.0, and their values should be as close as zero in order to obtain acceptable resolved results. The higher degrees of freedom are, the better resolution of CMB simulation could be. In this
study, the source apportionment of PM$_{2.5}$ was carried out by using CMB Version 8.0 developed by Desert Research Institute (DRI). Comprehensive knowledge of the physicochemical characteristics of PM$_{2.5}$ measured at both sources and receptors are required to identify the source types and quantify their contributions to PM$_{2.5}$ at each receptor site. The relationship between the mass concentrations of chemical species measured at the receptor site and those emitted from the potential sources can be presented by equation (2).

$$C_i = \sum_{j=1}^{P} \alpha_{ij} F_{ij} S_j$$  \hspace{1cm} (2)

where $C_i$ is the concentration of species i measured at the receptor site (µg/m$^3$); $\alpha_{ij}$ is the coefficient of species i generated or removed during the transport process; $F_{ij}$ is the mass fraction of species i in the chemical profile of the source j (%); $S_j$ is the mass concentration of all species at the receptor site assigned to the source j (µg/m$^3$).

E. 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 in 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 then temporarily stored in the environment of 4°C and 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 (Chang et al., 2018; Hung et al., 2018; Bagtasa and Yuan, 2020). Both field and transportation blanks were
further undertaken for the sampling of PM$_{2.5}$, while reagent and filter blanks were conducted for the chemical analysis of 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.
**Table Captions**

**Table S1.** Meteorological data measured at the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.

**Table S2.** Source apportionment of PM$_{2.5}$ at the Kaohsiung Harbor during the sampling periods of daytime resolved by CMB.

**Table S3.** Source apportionment of PM$_{2.5}$ at the Kaohsiung Harbor during the sampling periods of nighttime resolved by CMB.

**Table S4** The quality assure and quality control (QA/QC) of water-soluble ions and metallic elements in PM$_{2.5}$ at the two remote islands in the SCS.
| Months | Sampling Sites | Air Temperature (°C) | Relative Humidity (%) | Wind Speed (m/s) | Wind Direction |
|--------|----------------|----------------------|-----------------------|-----------------|----------------|
|        | QH             | Day: 21.52±2.3       | 62.55±6.4             | 3.13±0.7        | WNW            |
|        |                | Night: 18.34±3.5     | 77.4±1.7              | 1.38±0.6        | ESE            |
|        | ZD             | Day: 22.4±2.0        | 62.8±5.0              | 3.08±0.1        | WNW            |
|        |                | Night: 19.6±1.7      | 75.4±3.7              | 1.87±0.4        | ESE            |
|        | ZH             | Day: 22.1±0.7        | 62.9±5.1              | 3.15±0.2        | NW             |
|        |                | Night: 19.4±0.4      | 75.9±3.4              | 2.04±0.7        | ESE            |
|        | QH             | Day: 29.74±0.8       | 70.1±4.3              | 4.06±0.3        | WNW            |
|        |                | Night: 27.47±1.1     | 80.3±4.8              | 1.97±0.9        | W              |
|        | ZD             | Day: 30.1±1.4        | 71.5±6.7              | 3.80±1.0        | WNW            |
|        |                | Night: 28.8±1.3      | 79.9±6.2              | 1.90±0.4        | WNW            |
|        | ZH             | Day: 30.7±1.4        | 67.1±5.1              | 3.70±0.1        | WNW            |
|        |                | Night: 28.55±2.4     | 77.6±4.3              | 2.04±0.7        | WNW            |
|        | QH             | Day: 33.16±1.1       | 68.1±4.2              | 2.88±0.2        | W              |
|        |                | Night: 29.97±2.1     | 76.8±6.1              | 2.03±0.6        | ES             |
|        | ZD             | Day: 32.3±1.4        | 70.8±5.7              | 2.85±0.8        | WSW            |
|        |                | Night: 29.75±1.2     | 80.2±6.8              | 1.81±0.1        | ES             |
|        | ZH             | Day: 32.5±1.8        | 64.0±5.8              | 2.65±0.2        | SW             |
|        |                | Night: 29.7±2.7      | 74.7±7.8              | 1.74±0.4        | ESE            |
|        | QH             | Day: 25.6±1.0        | 72.8±5.6              | 2.58±0.7        | W              |
|        |                | Night: 22.28±1.8     | 79.63±7.5             | 0.87±0.2        | ESE            |
|        | ZD             | Day: 26.2±2.0        | 75.1±9.4              | 2.87±0.5        | W              |
|        |                | Night: 24.4±2.3      | 81.1±6.0              | 1.96±0.1        | ESE            |
|        | ZH             | Day: 25.9±2.6        | 70.9±8.1              | 2.16±0.6        | ES             |
|        |                | Night: 23.9±1.7      | 77.3±7.1              | 1.09±0.1        | SW             |
Table S2. Source apportionment of PM$_{2.5}$ in the Kaohsiung Harbor resolved by CMB receptor model in the daytime during the PM$_{2.5}$ sampling periods.

| Types of Sources (Daytime) | February | May | July | November |
|----------------------------|----------|-----|------|----------|
|                            | Concentration (μg m$^{-3}$) | Percentage (%) | Concentration (μg m$^{-3}$) | Percentage (%) | Concentration (μg m$^{-3}$) | Percentage (%) | Concentration (μg m$^{-3}$) | Percentage (%) |
| Incinerators                | 1.6±0.3  | 4.2±0.8 | 0.5±0.1 | 4.5±0.6 | 0.4±0.1 | 4.2±0.7 | 1.6±0.3 | 4.1±0.8 |
| Petrochemical industries    | 1.3±0.1  | 3.5±0.2 | 0.4±0.1 | 4.0±0.7 | 0.3±0.1 | 3.1±0.7 | 1.2±0.2 | 3.1±0.7 |
| Steel plants               | 3.6±0.2  | 9.7±0.2 | 0.7±0.1 | 8.0±0.7 | 0.7±0.3 | 7.6±1.0 | 3.6±0.1 | 9.6±0.2 |
| Oil-fired boilers          | 4.1±0.4  | 11.1±1.3 | 1.0±0.2 | 10.4±0.4 | 1.0±0.4 | 10.7±0.5 | 4.1±0.5 | 11.0±1.4 |
| Coal-fired boilers         | 2.3±0.1  | 6.2±0.6 | 0.5±0.1 | 4.6±0.9 | 0.4±0.1 | 4.7±0.7 | 2.0±0.4 | 4.5±1.0 |
| Fugitive Dusts             | 2.2±0.1  | 5.9±0.1 | 0.7±0.3 | 7.7±0.6 | 0.6±0.1 | 6.7±0.4 | 2.3±0.1 | 6.2±0.1 |
| Mobile Sources             | 5.2±0.2  | 14.1±0.1 | 1.5±0.6 | 15.0±0.9 | 1.5±0.6 | 16.0±0.5 | 5.5±0.2 | 14.7±0.4 |
| Biomass burning            | 1.4±0.1  | 4.0±0.1 | 0.3±0.1 | 3.2±0.4 | 0.3±0.1 | 3.1±0.5 | 1.0±0.3 | 2.7±0.8 |
| Sea Salts Spray            | 2.7±0.3  | 7.3±0.8 | 1.0±0.1 | 9.8±1.3 | 1.0±0.1 | 10.4±1.1 | 2.9±0.3 | 7.6±0.7 |
| Cement Industry            | 1.5±0.2  | 4.1±0.3 | 0.4±0.1 | 3.7±0.4 | 0.3±0.1 | 3.3±0.1 | 1.5±0.1 | 4.1±0.3 |
| Secondary sulfate          | 3.4±0.1  | 9.3±0.4 | 0.9±0.3 | 9.4±0.5 | 0.9±0.3 | 9.3±0.2 | 3.6±0.1 | 9.5±0.3 |
| Secondary nitrate          | 3.5±1.0  | 9.6±2.3 | 0.9±0.3 | 9.8±2.6 | 1.0±0.4 | 10.0±2.9 | 3.7±1.0 | 9.9±2.6 |
| Organic carbon             | 1.9±0.5  | 5.2±1.3 | 0.4±0.1 | 4.3±0.8 | 0.4±0.2 | 4.4±1.1 | 1.9±0.5 | 5.0±1.3 |
| Elemental carbon           | 1.6±0.4  | 4.5±1.1 | 0.5±0.3 | 4.3±1.0 | 0.4±0.1 | 4.2±1.0 | 1.7±0.3 | 4.6±0.9 |
| Others                     | 0.5±0.2  | 1.4±0.7 | 0.5±0.1 | 1.3±1.1 | 0.4±0.1 | 2.5±1.1 | 0.1±0.1 | 2.6±0.2 |
Table S3. Source apportionment of PM$_{2.5}$ in the Kaohsiung Harbor resolved by CMB receptor model at nighttime during the PM$_{2.5}$ sampling periods.

| Types of Sources (Nighttime) | February | May | July | November |
|-----------------------------|----------|-----|------|----------|
|                             | Concentration (μg m$^{-3}$) | Percentage (%) | Concentration (μg m$^{-3}$) | Percentage (%) | Concentration (μg m$^{-3}$) | Percentage (%) | Concentration (μg m$^{-3}$) | Percentage (%) |
| Incinerators                | 2.6±0.3  | 5.6±1.2 | 0.6±0.1 | 4.6±1.1 | 0.5±0.1 | 5.6±1.2 | 2.1±0.5 | 5.5±1.2 |
| Petrochemical Plants        | 2.2±0.2  | 4.7±0.2 | 0.4±0.1 | 3.0±0.5 | 0.4±0.1 | 4.3±0.5 | 1.6±0.1 | 4.2±0.4 |
| Steel Plants                | 5.0±0.9  | 10.6±1.4 | 1.0±0.4 | 9.3±1.1 | 0.8±0.2 | 9.3±1.9 | 4.0±0.4 | 10.5±1.4 |
| Oil-fired Boilers           | 4.5±0.1  | 9.6±0.6 | 1.1±0.1 | 9.1±0.7 | 0.9±0.3 | 9.7±0.2 | 3.8±0.3 | 10.0±0.6 |
| Coal-fired Boilers          | 2.8±0.3  | 6.0±0.8 | 0.6±0.1 | 4.8±0.8 | 0.4±0.1 | 4.6±0.7 | 2.1±0.3 | 5.7±0.8 |
| Fugitive Dust               | 3.0±0.1  | 6.4±0.3 | 0.8±0.2 | 7.0±0.1 | 0.7±0.2 | 7.9±0.7 | 2.5±0.2 | 6.7±0.3 |
| Mobile Sources              | 6.0±0.4  | 12.8±1.1 | 1.5±0.4 | 12.9±0.8 | 1.2±0.6 | 13.7±0.3 | 5.0±0.5 | 13.1±1.1 |
| Biomass Burning             | 1.3±0.2  | 2.8±0.6 | 0.3±0.1 | 2.8±0.6 | 0.2±0.1 | 2.3±0.7 | 1.0±0.3 | 2.5±0.6 |
| Sea Salts Spray             | 3.0±0.1  | 6.5±0.5 | 1.2±0.6 | 10.7±1.5 | 0.9±0.1 | 10.1±1.0 | 2.7±0.1 | 7.1±0.3 |
| Cement Plants               | 4.6±0.2  | 3.4±0.2 | 0.4±0.1 | 3.1±0.3 | 0.3±0.1 | 3.2±0.2 | 1.3±0.1 | 3.5±0.2 |
| Secondary Sulfate           | 3.9±0.6  | 8.2±0.7 | 0.9±0.3 | 8.4±0.9 | 0.7±0.3 | 7.6±0.6 | 3.0±0.2 | 8.0±0.7 |
| Secondary Nitrate           | 4.3±1.5  | 8.8±2.6 | 0.9±0.3 | 8.6±2.5 | 0.8±0.4 | 8.5±2.7 | 3.3±1.0 | 8.6±2.6 |
| Organic Carbon              | 2.4±0.8  | 4.9±1.3 | 0.4±0.1 | 3.9±0.8 | 0.3±0.1 | 3.4±0.9 | 1.8±0.5 | 4.7±1.3 |
| Elemental Carbon            | 1.7±0.3  | 3.7±1.1 | 0.5±0.2 | 4.0±0.9 | 0.3±0.1 | 3.7±0.9 | 1.3±0.4 | 3.5±1.1 |
| Others                      | 2.8±0.6  | 6.0±1.1 | 2.4±0.7 | 7.8±0.9 | 1.9±0.6 | 6.2±0.8 | 1.0±0.3 | 6.3±0.9 |
**Table S4** The quality assurance and quality control (QA/QC) of water-soluble ions and metallic elements in PM$_{2.5}$ at the two remote islands in the SCS.

(a) Water-soluble ions (mg/L)

| Ions | F$^-$ | Cl$^-$ | NO$_3$- | SO$_4^{2-}$ | Na$^+$ | NH$_4^+$ | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ |
|------|-------|--------|---------|------------|-------|---------|-------|-----------|-----------|
| MDL  | 0.014 | 0.044  | 0.072   | 0.086      | 0.026 | 0.012   | 0.037 | 0.015     | 0.081     |
| $R^2$| 0.9997| 0.9995 | 0.9978  | 0.9970     | 0.9984| 0.9996  | 0.9988| 0.9999    | 0.9998    |
| RR (%)| 108.44 | 101.54 | 102.1   | 98.41      | 104.50| 97.0    | 111.4 | 106.3     | 109.7     |

(b) Metallic Elements (mg/L)

| Elements | Cr | Ni | As | Cd | Pb | Ti | Al | Fe | Mn | Zn | Ca | K | Mg | V | Cu |
|----------|----|----|----|----|----|----|----|----|----|----|----|---|----|---|----|
| MDL      | 0.017 | 0.005 | 0.017 | 0.002 | 0.037 | 0.011 | 0.062 | 0.011 | 0.020 | 0.005 | 0.035 | 0.062 | 0.036 | 0.009 | 0.006 |
| $R^2$    | 0.9998 | 0.9985 | 0.9999 | 0.9992 | 1 | 0.9976 | 0.9998 | 0.9985 | 0.9985 | 0.9999 | 0.9982 | 0.9973 | 0.9999 | 0.9991 | 0.9993 |
| RR (%)   | 101.3 | 102.1 | 107.3 | 115.1 | 107.1 | 93.2 | 117.1 | 96.6 | 114.2 | 111.1 | 97.1 | 103.7 | 114.2 | 97.5 | 103.8 |

MDL: method detection limit (mg/L); $R^2$: determination coefficient; RR: recovery rate
Figure Captions

Figure S1. Wind roses in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.

Figure S2. Pollution roses in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.

Figure S3. Diurnal variation of enrichment factors in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.

Figure S4. Diurnal variation of chemical content in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.

Figure S5. Source apportionment of PM$_{2.5}$ in the Kaohsiung Harbor in the daytime resolved by CMB receptor model.

Figure S6. Source apportionment of PM$_{2.5}$ in the Kaohsiung Harbor at nighttime resolved by CMB receptor model.

Figure S7. Comparison of PM$_{2.5}$ source apportionment in the Kaohsiung Harbor in the daytime and at nighttime resolved by CMB receptor model.
Figure S1. Wind roses in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.
(a) February  (b) May

(c) July  (d) November

**Figure S2.** Pollution roses in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.
Figure S3. Diurnal variation of enrichment factors in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.
Figure S4. Diurnal variation of chemical content in the Kaohsiung Harbor during the PM$_{2.5}$ sampling periods.
Figure S5. Source apportionment of PM$_{2.5}$ in the Kaohsiung Harbor in the daytime resolved by CMB receptor model.
Figure S6. Comparison of PM$_{2.5}$ source apportionment in the Kaohsiung Harbor in the daytime and at nighttime resolved by CMB receptor model.