Chemical characteristics, source apportionment, and regional transport of marine fine particles toward offshore islands near the coastline of northwestern Taiwan Strait

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Abstract
This study aims to investigate the spatiotemporal variation, chemical composition, and source apportionment of marine fine particles (PM2.5) as well as their regional transport toward the Matsu Islands located near the coastline of northwestern Taiwan Strait. Four offshore island sites located at the Matsu Islands were selected to conduct both regular and intensive sampling of marine PM2.5. Water-soluble ionic species, metallic elements, and carbonaceous contents were then analyzed to characterize the chemical characteristics of marine PM2.5. In order to identify the potential sources and their contributions to marine PM2.5, chemical mass balance (CMB) receptor model was employed along with the backward trajectory simulation to resolve the source apportionment of marine PM2.5 and to explore their transport routes in different seasons. The results showed that high PM2.5 concentrations were commonly observed during the northeastern monsoon periods. Additionally, marine PM2.5 concentration decreased from the west to the east with the highest PM2.5 at the Nankang Island and the lowest PM2.5 at the Donyin Island in all seasons, indicating an obvious concentration gradient of PM2.5 transported from the continental areas to the offshore islands. In terms of chemical characteristics of PM2.5, the most abundant water-soluble ions of PM2.5 were secondary inorganic aerosols (SO42−, NO3−, and NH4+) which accounted for 55–81% of water-soluble ions and 29–52% of marine PM2.5. The neutralization ratios of PM2.5 were always less than unity, indicating that NH4+ cannot solely neutralize nss-SO42+ and NO3− in marine PM2.5 at the Matsu Islands. Although crustal elements (Al, Ca, Fe, K, and Mg) dominated the metallic content of marine PM2.5, trace anthropogenic metals (Cd, As, Ni, and Cr) increased significantly during the northeastern monsoon periods, particularly in winter. Organic carbons (OCs) were always higher than elemental carbons (ECs), and the mass ratios of OC and EC were generally higher than 2.2 in all seasons, implying that PM2.5 was likely to be aged particles. During the poor air quality periods, major air mass transport routes were the northern transport and the anti-cyclonic circulation routes. Source apportionment results indicated that fugitive soil dusts and secondary aerosols were the major sources of marine PM2.5 at the Matsu Islands, while, in winter, biomass burning contributed up to 15% of marine PM2.5. This study revealed that cross-boundary transport accounted for 66–84% of PM2.5 at the Matsu Islands, suggesting that marine PM2.5 at the Matsu Islands has been highly influenced by anthropogenic emissions from neighboring Fuzhou City as well as long-range transport from Northeast Asia.

Keywords Offshore islands · Marine fine particles (PM2.5) · Spatiotemporal variation · Chemical characteristics · Transportation routes · Regional transport
**Introduction**

The effects of fine particles (PM$_{2.5}$) on human health and ambient air quality have attracted increasing global attentions for the past decades (Li et al. 2016). Primary and secondary PM$_{2.5}$ could be emitted directly from natural and anthropogenic sources as well as chemically formed in the atmosphere, which potentially contains complicated inorganic and organic constituents (Kaneyasu et al. 1995; Kocak et al. 2007; Li et al. 2013a). Exposure to high PM$_{2.5}$ level poses a considerable risk to health problems, such as aggravation of asthma, respiratory symptoms, and even cardiovascular and respiratory diseases (Anderson et al. 1992; Dockery et al. 1993). Long-term exposure to PM$_{2.5}$ is highly associated with an increase in the risk of cardiopulmonary mortality by 6–13% per 10 µg/m$^3$ of PM$_{2.5}$ (Beelen et al. 2008; Pope III et al. 2002; Stanek et al. 2011). In addition to human health, high PM$_{2.5}$ concentration could cause poor ambient air quality, atmospheric visibility attenuation (i.e., regional haze), and global climate change and interfere with the earth’s radiation balance due to its complicated physicochemical characteristics of atmospheric PM$_{2.5}$. Chemical composition (e.g., SO$_4^{2−}$ and NO$_3^{−}$) and size distribution (0.4–0.9 µm) of PM$_{2.5}$ play a crucial role in atmospheric visibility degradation (Yuan et al. 2002; Lee et al. 2005; Yuan et al. 2006).

Recently, more and more counties have regulated PM$_{2.5}$ as a criteria air pollutant in the ambient air quality standards, whereas PM$_{2.5}$ has been monitored in a regular basis for local, regional, and global scales. In particular, intensive sampling of atmospheric PM$_{2.5}$ has been widely undertaken in the highly polluted metropolitan and industrial areas. However, they are mostly undertaken in the lands and seldom conducted in the seas or at the islands. For the past decades, China has experienced rapid economic and industrial development and thus significantly increases its fossil fuel consumption and anthropogenic emissions of particles, resulting in severe environmental problems, particularly poor ambient air quality and human health. The Matsu Islands situated at the Minjiang Estuary faces Fuzhou City in the southeastern coast of China. The Matsu Islands have absolutely no industrial and mobile sources, which conserved it as a background environment in a long-term period. However, its ambient air quality became poor recently and in some occasions even worse than the ambient air quality of major cities in Taiwan.

The Matsu Islands are located in the northern margin of the subtropical monsoon weather with an annual average temperature of about 19.3 °C and uneven seasonal variation of rainfall. The prevailing winds are blown from the northeast from October to May of sequential year, while the southwestern monsoons occur mainly from June to September. The Matsu Islands have only a population of about 11,000 and a total area of 29.5 km$^2$ and has no large-scale anthropogenic sources. Major stationary sources at the Matsu Islands include a 14.2-MW diesel-fired utility power plant, two breweries, and a few gas stations. However, high PM$_{10}$ concentration up to 129 µg/m$^3$ has been recorded by Taiwan EPA’s ambient air quality monitoring station located at the Nankang Island in the spring of 2011 (Liao et al. 2018).

Previous atmospheric PM$_{10}$ concentration measured at the Matsu Islands showed that PM$_{10}$ concentration in summer was always the lowest in the whole year, while high PM$_{10}$ concentrations were generally observed during the periods from late fall to early spring of the sequential year (Liao et al. 2018). The temporal variation of PM$_{10}$ concentration correlated with wind direction in the marine boundary layer which was closely related with poor ambient air quality (Pollutants Standard Index, PSI > 100) during the prevalence of northeastern monsoons commonly occurs in the seasons of winter and spring. However, there are very few PM$_{2.5}$ sampling campaigns that have been conducted at offshore islands such as the Matsu Islands all over the world. The chemical characteristics and source apportionment of marine PM$_{2.5}$ as well as the influences of regional transport on marine PM$_{2.5}$ have not been thoroughly investigated so far.

Accordingly, this study aims to investigate the spatiotemporal variation and chemical characteristics of marine PM$_{2.5}$ at the Matsu Islands. The source identification and apportionment of marine PM$_{2.5}$ were further determined by a CMB receptor model and backward trajectory simulation. The percentages of cross-boundary transport (CBT) contributed to marine PM$_{2.5}$ at the Matsu Islands in different seasons were further estimated.

**Experimental methods**

**Sampling methods and site description**

Marine PM$_{2.5}$ was simultaneously sampled at four offshore island sites at the Matsu Islands including Nankang (NK) (119°55′N, 26°10′E), Beigang (BG) (119°58′N, 26°13′E), Donyin (DY) (120°29′N, 26°21′E), and Chiukung (CK) (119°93′N, 25°97′E) townships (see Table 1 and Fig. 1). In this study, a PM$_{2.5}$ sampler (BGI, PQ-200) was applied to collect marine PM$_{2.5}$ at each sampling site. Both regular and intensive samplings of marine PM$_{2.5}$ were conducted from July 2013 to May 2014. Regular sampling was conducted to simultaneously collect 24-h PM$_{2.5}$ (from 8:00 am to 8:00 am of sequential day) at four sampling sites once every 8 days excluding the rainy days. It means that PM$_{2.5}$ samples would not be collected at all four sampling sites if it rained at any sampling site due to the limitation of ferry transportation to the four island sites as well as the shortage of manpower to rearrange the complementary sampling of PM$_{2.5}$ in the following few days. Intensive sampling was undertaken to simultaneously collect 24-h PM$_{2.5}$ at four island sites for five
consecutive days on November 18–22, 2013. Intensive sampling mainly focused on increasing the temporal frequency of PM$_{2.5}$ sampling during a typical PM$_{2.5}$ episode occurred at the Matsu Islands. As a result, a total of 39 PM$_{2.5}$ samples were collected at each island site in the Matsu Islands, including 34 regular samples and 5 intensive samples (see Table 3).

The concentration contours of PM$_{2.5}$ over the Matsu Islands in four seasons was plotted respectively based on the seasonal average concentrations of PM$_{2.5}$ sampled at four island sites (see Table 3) by a spatial plotting software (SURFER) which has been widely used to describe the spatial distribution of air pollutants for metropolitan district, industrial areas, and rural areas (Otvos et al. 2003; Shaocai et al. 2004; Tsai et al. 2010).

**Analytical methods of chemical composition**

Posterior to field sampling of marine PM$_{2.5}$, quartz fiber filters were temporarily stored at 4 °C and then transported back to the Air Pollution Laboratory in the Institute of Environmental Engineering at National Sun Yat-sen University for further conditioning, weighing, and chemical analysis. Each quartz fiber filter was cut into four identical portions for further analyzing the chemical composition of PM$_{2.5}$. Among them, one quarter of the filter was analyzed for water-soluble ionic species by putting it inside a 15-mL polypropylene (PE) bottle and pouring the distilled de-ionized water (D.I. H$_2$O) into each bottle for dissolving ions in an ultrasonic vibration process for at least 60 min. An ion chromatography (Dionex, Model DX-120) was used to analyze the concentration of major anions (F$^-$, Cl$^-$, SO$_4^{2-}$, and NO$_3^-$) and cations (NH$_4^+$, K$^+$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$) of marine PM$_{2.5}$.

Another quarter of the quartz fiber filter was initially digested in a 20-mL mixed acid solution (HNO$_3$/HClO$_3$ = 3:7) at 150–200 °C for at least 2 h, and then diluted to 25 ml with distilled de-ionized water (D.I. H$_2$O) for metallic element analysis. The metallic elements of PM$_{2.5}$ including Cr, Mn, Fe, Ni, Zn, Cd, Pb, Mg, K, Ca, Ti, Al, and As were then analyzed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer, Model Optima 2000DV).
By cutting one quarter of the filter into two identical parts, two eights of the filters were further used to measure the carbonaceous content of marine PM$_{2.5}$. The carbonaceous content including elemental, organic, and total carbons (OC, EC, and TC) were measured with an elemental analyzer (EA) (Carlo Erba, Model 1108). Before weighing, all quartz fiber filters were baked at 900 °C for 1.5 h to remove carbon impurities from the filters. The preheating procedure would minimize the background carbon in the quartz fiber filter matrix, which might cause interference with the analytical results, leading to a possible overestimation of the carbonaceous content of PM$_{2.5}$. The elemental analyzer was operated in the procedure of oxidation and reduction at 1020 and 500 °C, respectively, with continuous heating for 15 min. Among these two filters, one eighth of the filter was heated in advance using nitrogen gas at 340–345 °C for at least 30 min to expel the organic carbon (OC) fraction from the filters, after which the amount of elemental carbon (EC) was determined. Another eighth of the quartz fiber filter was analyzed without heating to determine the total carbon (TC) of PM$_{2.5}$. As a result, the amount of OC was then estimated by subtracting EC from TC.

Quality assurance and quality control

The quality assurance and quality control (QA/QC) for both PM$_{2.5}$ sampling and chemical analysis were further conducted in this study. Prior to conducting PM$_{2.5}$ sampling, the flow rate of each PM$_{2.5}$ sampler was calibrated with a film flowmeter (Sensidyne, Model MCH-01). Quartz fiber filters were then carefully handled and placed on the PM$_{2.5}$ samplers to prevent potential interferences during the sampling procedure. After sampling, aluminum foil was used to fold the sampled quartz fiber filters, which were then temporarily stored at 4 °C and transported back to the Air Pollution Laboratory in the Institute of Environmental Engineering at National Sun Yat-sen University for further chemical analysis.

The sampling and analytical procedure was similar to that described in various previous studies (Cheng and Tsai 2000; Lin, 2002; Yuan et al. 2006; Tsai et al. 2010). Both field and transportation blanks were undertaken for PM$_{2.5}$ sampling, while reagent and filter blanks were applied for chemical analysis. The field blanks were exposed in the field when the quartz fiber filters were placed and removed from the PQ-200 samplers. Background contamination was routinely monitored by using operational blanks (unexposed filters), which were proceeded simultaneously with field samples. In this study, the field blanks were extremely low, normally below or close to the method detection limit. Therefore, the background contamination/interference was insignificant and can thus be ignored. The determination coefficient ($R^2$) of the calibration curve for each chemical species analyzed is required to be higher than 0.995. At least 10% of the samples were analyzed by spiking with a known amount of metallic and ionic species to determine their recovery percentages.

Chemical transformation of SO$_2$ and NO$_x$

Secondary inorganic compounds including sulfate and nitrate are the major components contained in the fine particles. To determine the degree of atmospheric transformation of SO$_2$ to SO$_4^{2-}$ and NO$_x$ to NO$_3^-$, respectively, the sulfur and nitrogen oxidation ratios (i.e., SOR and NOR) were employed, and these ratios are defined as follows (Colbeck and Harrison 1984; Ohta and Okita 1990):

$$\text{SOR} = \frac{S_{\text{nss-SO}_4^{2-}}}{S_{\text{nss-SO}_4^{2-}} + S_{\text{SO}_2}}$$  \hspace{1cm} (1)

$$\text{NOR} = \frac{N_{\text{NO}_3^-}}{N_{\text{NO}_3^-} + N_{\text{NO}_2}}$$  \hspace{1cm} (2)

where nss-SO$_4^{2-}$ is the excess non-sea salt sulfate that was calculated by subtracting the amount of SO$_4^{2-}$ of marine particles from that of SO$_4^{2-}$ in the particles (Kaneyasu et al. 1995; Cheng et al. 2000). The units of $S_{\text{nss-SO}_4^{2-}}$, $S_{\text{SO}_2}$, $N_{\text{NO}_3^-}$, and $N_{\text{NO}_2}$ are neq/m$^3$. The average concentrations of SO$_2$ and NO$_x$ during each sampling periods were obtained from the ambient air quality monitoring station nearby the sampling site at the Matsu Islands.

CMB receptor model

The source apportionment of PM$_{2.5}$ could be assessed by using a receptor model based on the principle of chemical mass balance (CMB) (Ke et al. 2007; Kothai et al. 2008; Yatkin and Bayram 2008; Wang et al. 2008). Since the detailed descriptions of CMB receptor model (i.e., CMB8) are available elsewhere, only a brief summary is presented herein.

The CMB receptor model uses the emission profiles of prominent sources to estimate their contributions to a specific receptor. It is assumed that the total concentration of a particular chemical species at the receptor site is the linear summation of each individual contribution from various sources. The CMB receptor model uses the results of the least-square regression analysis of the chemical composition of PM$_{2.5}$ to estimate the most appropriate contributions of emission sources. Therefore, the CMB receptor model resolves a least-square solution to a set of linear equations. The solution expresses each receptor’s concentration of a chemical species as a linear summation of the products of source profiles and source contributions. In this study, the input parameters for CMB receptor modeling included 24 chemical species of PM$_{2.5}$ (see Figs. 5, 9, and 10) and source profiles covering 32 potential sources (see Table 2). Source profiles (the fractional amount of each species in the emissions from each
source type) and receptor concentrations, each with realistic uncertainty estimates, serve as input data to the CMB receptor model. The model output consists of the contribution from each source type to the total ambient aerosol mass, as well as to the concentrations of individual chemical species. The CMB receptor modeling results are further evaluated by several fit indices, such as $R^2 \geq 0.8$, $\chi^2 \leq 4.0$, $T$ statistics $\geq 2.0$, and mass percentages accounting for 80–120%. The source profiles used in this study have been reported by USEPA and Southern California Air Quality Study and research data obtained from the investigation on the chemical composition of PM$_{2.5}$ and the source profiles of primary sources in Taiwan (see Table 2).

### Results and discussion

#### Spatiotemporal variation of PM$_{2.5}$ at the Matsu Islands

The spatial distribution and temporal variation of PM$_{2.5}$ concentration over the target region were determined and plotted

| Source no. | Codes   | Sources             | Researchers                  |
|------------|---------|---------------------|------------------------------|
| SCT004     | PBPR11  | Petroleum cracking plant | U.S. EPA (1991)             |
| SCT007     | PP004   | Industrial boilers (Oil) | Cheng et al. (2001)          |
| SCT008     | PP005   | Industrial boilers (Coal) | Cheng et al. (2001)          |
| SCT009     | PETRO1  | Petroleum industry | U.S. EPA (1991)             |
| SCT010     | STEEL1  | Steel industry      | Chiang et al. (1993)         |
| SCT011     | STEEL2  | Coke plants         | Chiang et al. (1993)         |
| SCT012     | STEEL3  | Sinter plants       | Chiang et al. (1993)         |
| SCT013     | STEEL4  | Electric arc furnaces | Yuan et al. (2003)          |
| SCT020     | CEMENT  | Cement industry     | Chiang et al. (1993)         |
| SCT023     | VEHICLE2| Vehicular exhausts | Chow, J.C. (1991)           |
| SCT024     | VEHICLE3| Diesel exhausts     | Chow, J.C. (1991)           |
| SCT025     | DUST1   | Paved road dust in South Taiwan | Cheng et al. (1998) |
| SCT026     | DUST2   | Paved road dust in Central Taiwan | Cheng et al. (1998) |
| SCT027     | DUST3   | Paved road dust in South Taiwan | Yuan et al. (1991) |
| SCT028     | DUST4   | Paved road dust in Central Taiwan | Chiang et al. (1993) |
| SCT029     | DUST5   | Unpaved road dust in Central Taiwan | Chiang et al. (1993) |
| SCT031     | SOIL1   | Soil dust            | U.S. EPA (1991)             |
| SCT033     | MARIN1  | Marin in Central Taiwan | Cheng et al. (1998)         |
| SCT034     | MARIN2  | Marin in South Taiwan | Chen et al. (1998)          |
| SCT035     | VB001   | Biomass burning      | Cheng et al. (1999)         |
| SCT037     | SO4     | Secondary sulfate    | Wang et al. (2006)           |
| SCT038     | NO2     | Secondary nitrate    | Wang et al. (2006)           |
| SCT039     | STONE   | Stone processing industry | Li et al. (2013b)         |
| SCT040     | CEMENT2 | Cement industries    | Li et al. (2013b)           |
| SCT041     | CERM1   | Ceramic plants       | Li et al. (2013b)           |
| SCT042     | CERM2   | Tile industries      | Li et al. (2013b)           |
| SCT043     | COAL    | Coal burning         | Li et al. (2013b)           |
| SCT044     | COAA    | Coal ash             | Li et al. (2013b)           |
| SCT045     | SOIL2   | Fugitive dust        | Li et al. (2013b)           |
| SCT046     | VB002   | Biomass burning      | Li et al. (2013b)           |
| SCT047     | CONST   | Construction dust    | Li et al. (2013b)           |
| SCT048     | DUST6   | Road dust            | Li et al. (2013b)           |

The source profiles used in this study were mainly obtained from the researcher’s finding of the chemical composition of PM$_{10}$ emitted from various emission sources. Only limited source profiles are referred from USEPA and Southern California Air Quality Study and local emission source profiles.
by the concentrations of marine PM$_{2.5}$ sampled at four island sites in the Matsu Islands. Figures 2 and 3 illustrate the seasonal variation of wind speed, wind direction, and PM$_{2.5}$ concentration contours. On the whole, field sampling results indicated that low monthly average PM$_{2.5}$ concentrations were commonly observed in summer, while high monthly average PM$_{2.5}$ concentrations mostly occurred in winter and early spring (see Table 3). It was further found that a maximum PM$_{2.5}$ concentration level of 82.6 $\mu$g/m$^3$ was observed during the northeastern monsoon periods, which was approximately 9.5 times higher than the lowest PM$_{2.5}$ concentration of 8.7 $\mu$g/m$^3$. From the perspective of spatial distribution, PM$_{2.5}$ concentrations had a tendency to decrease from the west coastline to the easternmost island (site DY) in all seasons. Moreover, PM$_{2.5}$ concentrations decreased from the north to the south in fall and winter, while an opposite trend was observed in spring and summer. In particular, PM$_{2.5}$ concentrations observed at DY were always the lowest while compared to other three sampling sites in the Matsu Islands. It is worth noting that the spatial distribution of marine PM$_{2.5}$ was, however, inconsistent with the seasonal prevailing wind direction, suggesting that marine PM$_{2.5}$ at the Matsu Islands might not be solely influenced by long-range transport, but also by other factors, such as local anthropogenic emissions from neighboring Fuzhou City, which has been pointed out in our previous findings at the Kinmen Islands (Li et al. 2013a, b).

In addition, to plot the contours of PM$_{2.5}$ concentration in a domain of interest, an air trajectory scheme was further
applied to track the transport routes of air masses moving toward the Matsu Islands. In general, hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) is a commonly used track model to plot both backward and forward trajectories of an air parcel moved to a specific site at various heights above ground over a period of time. In this study, the backward trajectories were plotted for 120 h in four typical routes as illustrated in Fig. 4. The routes were drawn starting from a site of 119°44′N, 26°10′E with the heights of 100, 200, and 300 m, respectively, to track the transport routes of air parcels arriving at the Matsu Islands. As far as the transport routes were concerned, PM$_{2.5}$ concentrations of the northern routes mainly during the northeastern monsoon periods were mostly higher than those of the southern routes. Accordingly, the concentrations of marine PM$_{2.5}$ were highly influenced by meteorological conditions, particularly the prevalent winds. We also found that the concentrations of marine PM$_{2.5}$ in spring, fall, and winter were much higher than those in summer.

**Chemical composition of PM$_{2.5}$ at the Matsu Islands**

The seasonal variation of water-soluble ionic species (WSIs) of marine PM$_{2.5}$ sampled at the Matsu Islands is illustrated in Fig. 5. It showed that the most abundant water-soluble ionic species of PM$_{2.5}$ were SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$, indicating that the probable chemical component of PM$_{2.5}$ was secondary inorganic aerosols (SIAs) composed of ammonium sulfate ((NH$_4$)$_2$SO$_4$) and ammonium nitrate (NH$_4$NO$_3$), which concurred with previous studies (Yao et al. 2003; Han et al. 2007; Somoltes 2008).

**Table 3** Seasonal variation and spatial distribution of marine PM$_{2.5}$ concentrations in the Matsu Islands

| Sampling sites | Summer ($n = 28$) | Fall ($n = 52^a$) | Winter ($n = 40$) | Spring ($n = 36$) |
|---------------|------------------|------------------|------------------|------------------|
| Nankang (NK)  | 17.07 ± 9.87     | 27.49 ± 12.97    | 47.91 ± 21.18    | 41.65 ± 15.14    |
| Beigang (BG)  | 17.93 ± 8.30     | 26.79 ± 13.00    | 46.31 ± 19.88    | 39.73 ± 14.06    |
| Donyin (DY)   | 16.57 ± 7.29     | 22.83 ± 12.53    | 42.44 ± 20.69    | 35.17 ± 14.78    |
| Chiukung (CK) | 17.01 ± 6.92     | 24.10 ± 10.48    | 44.17 ± 18.71    | 36.40 ± 13.83    |
| Spatial average | 17.14 ± 7.64   | 25.30 ± 12.15    | 45.21 ± 19.25    | 38.24 ± 13.74    |

$^a$ A total of 32 regular samples and 20 intensive samples were collected in Fall
Kocak et al. 2007; Tsai et al. 2012). Overall, SIAs accounted for as high as 55–81% of WSIs and 29–52% of marine PM$_{2.5}$, indicating that marine PM$_{2.5}$ at the Matsu Islands were contributed not solely from oceanic sprays but also from secondary aged particles originated from inland anthropogenic sources.

Figure 6 illustrates the neutralization of nss-$\text{SO}_4^{2-} + \text{NO}_3^-$ by $\text{NH}_4^+$ or $\text{NH}_4^+ + \text{Na}^+$. Neutralization ratios (NRs), defined as the equivalent ratio of $\text{NH}_4^+/(\text{nss-}\text{SO}_4^{2-} + \text{NO}_3^-)$ in PM$_{2.5}$, were generally lower than unity, indicating that PM$_{2.5}$ were mainly acidic particles and $\text{NH}_4^+$ cannot solely neutralize both nss-$\text{SO}_4^{2-}$ and $\text{NO}_3^-$. Furthermore, as shown in Fig. 7, the equivalent ratios of nitrate to non-sea salt sulfate ($\text{NO}_3^- / \text{nss-}\text{SO}_4^{2-}$) in all seasons ranged from 0.21 to 0.84, suggesting that these acidic fine particles were mainly attributed from sulfur-rich fuel burning sources, i.e., heavy oil burning from industrial boilers and coal burning from coal-fired power plants.

As for the NRs of PM$_{10}$ at the Matsu Islands, they were slightly lower than those at the inland sites although their differences were insignificant (Li et al. 2013a). Previous study reported that oceanic sprays seem to be influential to marine PM$_{2.5}$ at the offshore islands while compared to those at the in-land regions (Lee et al. 2005). In this study, Na$^+$ is thought to be taken into consideration at the Matsu islands since Na$^+$ could play an acidic neutralizer.

Sulfur and nitrogen oxidation ratios (i.e., SOR and NOR) were further applied to determine the degrees of atmospheric chemical transformation of $\text{SO}_2$ to $\text{SO}_4^{2-}$ and $\text{NO}_2$ to $\text{NO}_3^-$, respectively. These two ratios can be used to identify the existence and extent of aged secondary inorganic aerosols. Figure 8 illustrates the SOR and NOR of PM$_{2.5}$ sampled at the Matsu Islands. As reported in previous studies, SOR and NOR lower than 0.25 and 0.10, respectively, are thought as
primary particles, while SOR and NOR higher than 0.25 and 0.10, respectively, are secondary particles (Ohta and Okita 1990). This study found that the SOR and NOR of marine PM$_{2.5}$ were mostly higher than 0.25 and 0.1, respectively, indicating that marine PM$_{2.5}$ was mainly aged secondary inorganic aerosols (SIAs). These results showed that PM$_{2.5}$ sampled at the Matsu Islands were highly influenced by cross-boundary transport rather than local emissions. Furthermore, the SOR of PM$_{2.5}$ was higher than the NOR of PM$_{2.5}$, indicating that secondary sulfate containing particles formed by SO$_2$ contributed more than secondary nitrate containing particles formed by NO$_2$ in marine PM$_{2.5}$ sampled at the Matsu Islands.

To further identify whether the metallic elements in marine PM$_{2.5}$ at the Matsu islands were primarily from natural or anthropogenic processes, the enrichment factor (EF) of each metallic element was determined and applied as the first step in evaluating the influences of crustal sources on the components of atmospheric PM$_{2.5}$ (Sailesh and Mukesh 2010; Chester et al. 2000). The seasonal variation of metallic elements in PM$_{2.5}$ sampled at four island sites is illustrated in Fig. 9. It showed that crustal metals (i.e., Al, Fe, Ca, and Mg) contributed the major portion of metallic content in PM$_{2.5}$ in all seasons, while trace anthropogenic metals (i.e., Cd, As, Ni, and Cr) appeared mainly during the northeastern monsoon periods (i.e., fall, winter, and spring), showing that the northeastern monsoons could blow fine particles (PM$_{2.5}$) containing trace metals from the upwind source regions to the Matsu Islands. Al, Fe, and Ca are the main metallic elements in the earth’s crustal particles which are probably emitted from wind-blown dust, paved and unpaved roads, cement plants, and so on. However, anthropogenic metals could be transported toward the Matsu Islands through cross-boundary transport during the periods of northeastern monsoons.

Finally, Fig. 10 illustrates the seasonal variation of carbonaceous contents including organic, elemental, and total carbons (i.e., OC, EC, and TC) of marine PM$_{2.5}$ sampled at the Matsu Islands. It showed that the seasonal average concentrations of total carbons were ordered as winter > spring > fall > summer. Overall, it was observed that the mass concentrations of TC in PM$_{2.5}$ in winter and spring were higher than those in fall and summer. Additionally, the concentrations of OC in PM$_{2.5}$ were always higher than those of EC in four seasons at all sampling sites. These findings were in accordance with previous literature, reporting that elemental carbon (EC) originates primarily from direct emissions from combustion sources, while organic carbon (OC) is mainly emitted from either primary anthropogenic sources or secondary organic aerosols that are chemically formed in the atmosphere (Gray...
et al. 1986; Turpin et al. 1990). Furthermore, the seasonal average mass ratios of OC to EC (OC/EC) ranged from 2.2 to 2.8 which were mostly higher than 2.2 (Gray et al. 1986; Hildemann et al. 1991), showing that PM$_{2.5}$ sampled at the Matsu Islands was also highly influenced by aged secondary organic aerosols (SOAs) during the sampling periods. As far as the seasonal variation, the mass ratios of OC/EC in winter and spring were commonly higher than those in fall and summer.

### Source apportionment of PM$_{2.5}$ at the Matsu Islands

The types of potential sources and their contributions to marine PM$_{2.5}$ at the Matsu Islands was further resolved by using a receptor model based on chemical mass balance (i.e., CMB8.0) (Ke et al. 2007; Kothai et al. 2008; Wang et al. 2008; Yatkin and Bayram 2008). Figure 11 and Table 4 show the source apportionment of PM$_{2.5}$ during the regular and intensive sampling periods at the Matsu Islands. Although the source types and their contribution percentages varied with seasons, the major sources of PM$_{2.5}$ at the Matsu Islands were soil dusts, secondary sulfate and nitrate aerosols, and agricultural debris burning (i.e., biomass burning). Oceanic spray (i.e., sea salts) and vehicular exhausts contributed about 8% of PM$_{2.5}$, respectively. Additionally, the contribution of agricultural debris burning (i.e., biomass burning) could rise up significantly to as high...
as 9–13% of PM$_{2.5}$ in fall, winter, and spring, reflecting that the open burning of agricultural debris was frequently occurred at the Matsu Islands in these three seasons. It is also worth noting that, during the northeastern monsoon periods, air parcels were mainly transported northerly toward the Matsu Islands due to the dominant high-pressure anti-cyclonic circulation system centering in the Mongolian Plateau. Air parcels blown from northern and northeastern China could migrate downwards along the eastern coastline of China, passing through major metropolitan areas and industrial complexes in the Yangtze River Delta (YRD) and several rapidly developing regions such as Shandong, Jiangsu, and Zhejiang Provinces in the coastal regions of southeastern China.

During the regular sampling periods, secondary sulfate and nitrate, fugitive dusts, biomass burning, vehicular exhausts, sea salts, petrochemical plants, iron works, and waste incinerators contributed 20.2%, 29.9%, 8.9%, 8.2%, 5.1%, 3.9%, 3.2%, and 2.2% of marine PM$_{2.5}$, respectively. Moreover, during the intensive sampling periods, secondary sulfate and nitrate, fugitive dusts, sea salts, waste incinerators, petrochemical plants, biomass burning, organic carbon, and vehicular exhausts contributed 26.4%, 31.5%, 8.3%, 7.1%, 5.3%, 5.0%, 4.9%, and 3.56% of PM$_{2.5}$.

Fig. 9 Seasonal variation of metallic elemental concentration for marine PM$_{2.5}$ sampled at the Matsu Islands

Fig. 10 Seasonal variation of carbonaceous concentration for marine PM$_{2.5}$ sampled at the Matsu Islands
respectively. It shows that the contribution percentages of secondary sulfate and nitrate, fugitive dusts, sea salts, waste incinerators, and petrochemical plants during the intensive sampling periods were higher than those during the regular sampling periods.

**CBT of PM$_{2.5}$ at the Matsu Islands**

This study further estimated the contribution percentages of cross-boundary transport (CBT) for marine PM$_{2.5}$ at the Matsu Islands. The cross-boundary transport of PM$_{2.5}$ was defined as the PM$_{2.5}$ emitted from the upwind sources and migrated toward the Matsu Islands. During the sampling periods of this particular study, the lowest PM$_{2.5}$ concentration of 8.70 μg/m$^3$ measured in an annual basis can be treated as the background level of PM$_{2.5}$ at the Matsu Islands by assuming that the variation of mixing layer height and meteorological conditions were somewhat negligible. The deduction of the background PM$_{2.5}$ concentration from the field measured PM$_{2.5}$ concentrations can be assumed as the contributions of CBT to PM$_{2.5}$ transported toward the Matsu Islands.

Figure 12 illustrates the contribution percentages of various sources of PM$_{2.5}$ transported toward the Matsu Islands in different seasons. It showed that secondary sulfate and nitrate aerosols were mainly attributed from the dramatic increase of cross-boundary transport. Similar trends were also observed for industrial processes, soil dusts, and carbonaceous materials. The overall contribution percentages

![Fig. 11 Contribution percentages of potential sources for regular and intensive sampling periods of marine PM$_{2.5}$ sampled at the Matsu Islands](image)

**Table 4** The contribution of potential sources for regular and intensive sampling of marine PM$_{2.5}$ at the Matsu Islands

| Sources                        | Regular sampling | Intensive sampling |
|--------------------------------|------------------|--------------------|
|                                | Summer | Fall | Winter | Spring | Summer | Fall | Winter | Spring |
| Incineration plants            | 1.51%  | 2.79%| 2.15%  | 2.22%  | 7.08%  |
| Petroleum plants               | 3.40%  | 4.22%| 3.15%  | 4.66%  | 5.32%  |
| Steel plants                   | 2.82%  | 2.86%| 5.30%  | 1.69%  | 1.64%  |
| Industrial boilers (Oil)       | 6.31%  | –    | 3.94%  | 1.41%  | 4.15%  |
| Coal-fired boiler              | –      | –    | –      | 2.30%  | –      |
| Vehicular exhausts             | 12.44% | 7.71%| 5.09%  | 7.75%  | 3.56%  |
| Street dust                    | 26.05% | 35.50%| 25.95% | 32.07% | 31.50% |
| Oceanic spray                  | 3.17%  | 6.67%| 5.73%  | 4.66%  | 8.34%  |
| Secondary sulfate              | 16.02% | 10.99%| 13.35% | 17.73% | 19.87% |
| Secondary nitrate              | 6.27%  | 5.66%| 4.84%  | 6.12%  | 6.58%  |
| Secondary organic carbon       | 1.37%  | 3.95%| 4.82%  | 7.59%  | 4.88%  |
| Secondary elemental carbon     | –      | 3.34%| 0.83%  | –      | –      |
| Biomass burning                | 3.76%  | 13.13%| 8.91%  | 9.99%  | 5.01%  |

– no contribution to marine PM$_{2.5}$
of cross-boundary transport to PM$_{2.5}$ at the Matsu Islands in summer, fall, winter, and spring were estimated as 66.3%, 77.0%, 83.9%, and 81.5%, respectively, which were higher than those at the Penghu Islands (36.4–76.8%), the Dongsha Islands (26.5–82.5%), and the Taiwan Island (54.7%) (Hung 2018). The results indicated that cross-boundary transport played a crucial role in the originality and chemical composition of marine PM$_{2.5}$ as compared to local emissions at the Matsu Islands. Even in the summer season, cross-boundary transport from neighboring Fuzhou City and/or upwind sources could contribute approximately two thirds of marine PM$_{2.5}$ at the Matsu Islands. In the seasons of winter and spring, more than four fifths of PM$_{2.5}$ at the Matsu Islands was contributed by cross-boundary transport. The present study strongly suggested that cross-boundary transport from upwind anthropogenic sources contributed major portion of marine PM$_{2.5}$ sampled at the Matsu Islands.

Conclusions

Both regular and intensive samplings of PM$_{2.5}$ at the Matsu Islands showed that high PM$_{2.5}$ concentrations were mostly observed in winter and spring, particularly during the northeastern monsoon periods, while low PM$_{2.5}$ concentrations commonly occurred in summer. Although the spatial distribution of PM$_{2.5}$ concentration seemed to vary with seasons, the highest PM$_{2.5}$ concentrations were always found at the Nankang Island (NK). It showed very likely that high PM$_{2.5}$ concentration was mainly attributed to cross-boundary transport of PM$_{2.5}$ emitted from anthropogenic sources from either neighboring Fuzhou City or upwind northern regions. Additionally, marine PM$_{2.5}$ sampled at the Matsu Islands was characterized as aged sulfur-rich acidic particles. Secondary inorganic aerosols ($\text{SO}_4^{2-}$, $\text{NO}_3^-$, and $\text{NH}_4^+$) were the most abundant water-soluble ionic species of PM$_{2.5}$, indicating that the dominant inorganic components of PM$_{2.5}$ were ammonium sulfate and ammonium nitrate. Crustal elements contributed the major portion of metallic content in PM$_{2.5}$ in all seasons, while trace metals appeared apparently during the northeastern monsoon periods, showing that the northeastern monsoons could migrate atmospheric fine particles containing trace metals from the upwind anthropogenic sources to the Matsu Islands. The mass ratios of OC/EC always higher than 2.2 suggested that secondary organic aerosols (SOAs) could be formed during the transport procedure. A further study employing receptor modeling found four major sources of marine PM$_{2.5}$ at the Matsu Islands, namely soil dusts, secondary sulfate, secondary nitrate, and biomass burning. As a whole, this study revealed that cross-boundary transport (CBT) has tremendous impact on the presence of marine PM$_{2.5}$ at the Matsu Islands. More than four fifths of PM$_{2.5}$ at the Matsu Islands was resulted from the cross-boundary transport in the seasons of winter and spring, particularly during the northeastern monsoon periods.

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