

Chemical Characteristics of Marine Fine Aerosols over Sea and at Offshore Islands during Three Cruise Sampling Campaigns in the Taiwan Strait- Sea salt and Anthropogenic Particles

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Abstract. Marine fine aerosols were simultaneously collected over sea and at offshore islands during three cruise sampling campaigns to investigate the spatial distribution of atmospheric fine particles (PM_{2.5}) and the influences of sea salt and anthropogenic particles on the chemical characteristics of PM_{2.5} in the Taiwan Strait. Field sampling results indicated that 15 PM_{2.5} concentrations over sea were generally higher than those at the offshore islands, while the PM_{2.5} concentrations in the daytime were commonly higher than those at nighttime. Moreover, the concentrations of PM_{2.5} were generally higher than those of coarse particles (PM_{2.5-10}) with an exception of the winter cruise in 2014. Moreover, sea salt accounted for 6.5-11.1% and 11.0-13.5% of PM_{2.5} at the offshore islands and over sea, respectively. The contributions of non-sea salt-water 20 soluble ions (nss-WSI) to PM_{2.5} at the offshore islands were obviously higher than those over sea, while the contributions of ss-WSI for PM_{2.5} at the offshore islands were much lower than those over sea during the cruise sampling campaigns. Anthropogenic metallic elements including Zn, Mn, Pb, Cr, and Ni had higher concentrations over sea than those at the offshore islands, suggesting that PM_{2.5} was not only influenced by marine aerosols but also by anthropogenic particles 25 originated from human activities such as industrial processing, fuel burning, and vehicular and shipping exhausts. Higher mass ratios of Ni/Al and Ni/Fe over sea than those at the offshore islands suggested that shipping emissions had higher influences on marine fine particles than crustal dusts in open sea while compared to those at the offshore islands. The carbonaceous contents of PM_{2.5} indicated that the concentrations of organic carbons (OC) were generally higher than those of elemental carbons (EC). The higher mass ratios of organic and elemental carbons (OC/EC) were observed at the central and north Taiwan Strait, and follow by the offshore islands and the south Taiwan Strait. Overall, sea salt and anthropogenic 30 particles had significant influences on the chemical composition of PM_{2.5} over sea and at the offshore islands.

1 Introduction

Sea salt are the most prominent natural emitted particles that might significantly influences regional air quality and global climate change, particularly on the islands and along the coasts. Marine aerosols play an important role in the atmospheric chemistry and physics globally since the ocean occupies about 70% of the earth's surface. Sea salt particles emitted from oceans/seas could influence the radiative balance of the atmosphere (Murphy *et al.*, 1998) and cloud formation (Pierce and Adams, 2006). Oceanic sprays are emitted from the surface of oceans/seas by the bursting of white-cap bubbles, while their concentrations are relatively high on the islands and seashores, and descends rapidly with the distance from the coastline (Chow *et al.*, 1996; Kim *et al.*, 2000; Tsai *et al.*, 2011; Posfai and Buseck, 2010; Seinfeld and Pandis, 2006; Mahowald *et al.*, 2006; Adachi and Buseck, 2015). Moreover, the concentrations of sea salt particles in the ambient air are also affected by wind speed, wind direction, elevation, and topography (Adachi and Buseck, 2015; Hsu *et al.*, 2007).

Previous studies focused mainly on the sea salt concentrations of segregated aerosol particles (i.e. PM₁₀, PM_{2.5-10}, and PM_{2.5}) and the chemical reactions of gaseous acids with atmospheric particles (e.g. sea salt, crustal dusts, and anthropogenic particles) to form secondary inorganic salts, mainly replacing Cl⁻ with SO₄²⁻ and NO₃⁻ and form salts with Na⁺, K⁺, Mg²⁺, and Ca²⁺. The spray droplets of marine aerosols regarded as the largest size distribution have a considerable mass content and are readily deposited on the ground (Lewandowska *et al.*, 2013). Anthropogenic sources including industrial processing, fuel and biomass burning, and vehicular and shipping exhausts emitted elsewhere might also influence the chemical composition of marine fine particles (Tsai *et al.*, 2011; Pandolfi *et al.* 2011; Pey *et al.*, 2013; Johnson *et al.*, 2014). Moreover, the intensity of changes in the chemical composition of marine aerosols is also governed by meteorological factors such as convection, thermal inversion, air humidity, wind speed, and direction, as well as the occurrence of sea and land breezes (Seinfeld and Pandis 1998; Rastogi and Sarin 2005).

An offshore island, the Penghu Islands, located at the southeastern Taiwan Strait is approximately 90 km away from the coastline of the Taiwan Island. The Penghu Islands consists of 97 small islands with a population of 108,000 and a total area of 128.0 km², which has the subtropical weather being mostly influenced by eastern Asian Monsoons. The major air pollution sources in the islands include an oil-fired power plant, a few construction sites, and limited automobiles and fishing boats. The prevailing winds are blown by the northeastern Monsoons in winter and spring and by the southwestern Monsoons in summer and early fall. Thus, long-range transportation is superior to local sources at the Penghu Islands. Previous studies reported that polluted air masses are mainly transported from the coastal regions of East China, Korean Peninsula, and/or South Japan Islands toward the Penghu Islands (Yuan *et al.*, 2004).

Taiwan Strait located between Taiwan and China is one of the busiest marine transportation routes over the worldwide shipping. Large quantity of anthropogenic air pollutants from stationary and mobile sources could be emitted to the atmosphere (such as particulate pollutants) and transported to and across the Taiwan Strait. Additionally, both sides of the Taiwan Strait are the densely populated and thriving industrial areas, where particulate pollutants could be intensively emitted and deposited over the seas and lands via dry/wet deposition and atmospheric dispersion. Moreover, the impacts of

Asian duststorms, biomass burning, and northeastern Monsoons on ambient air quality are commonly observed in spring and winter in this areas, which leads to a large quantity of Asian dusts and anthropogenic particles transported long-range toward the Taiwan Strait.

5 The study aims to inquire the chemical composition and spatial variation of chemical characteristic of atmospheric fine particles and to ascertain how sea salt and anthropogenic particles influence atmospheric PM_{2.5} over sea and at the offshore islands in the Taiwan Strait. The contributions of non-sea salt water-soluble ionic species (nss-WSI) and sea salt water-soluble ionic species (ss-WSI) in the atmospheric PM_{2.5} over sea and at the offshore islands were further investigated in three cruise sampling of marine fine particles during the polluted seasons of winter and spring in 2013-2014.

2 Methods

10 2.1 Sampling Protocol of PM_{2.5}

Atmospheric PM_{2.5} samples were collected during the cruise sampling campaigns as well as at an offshore island (i.e. the Penghu Islands) located in the southeastern Taiwan Strait. High-volume samplers with cascade impactors were applied to simultaneously collect marine PM_{2.5} in an air quality sampling boat as well as atmospheric PM_{2.5} at the Penghu Islands. Figure 1 illustrates the navigation routes/courses during three cruise sampling campaigns in the Taiwan Strait. In this study, we weighted the mass concentrations of both PM_{2.5} and PM_{2.5-10} after appropriate conditioning for each sample. However, only PM_{2.5} samples were used for further chemical analysis. Although sea salt are important component for PM_{2.5-10} samples, this study aimed to investigate the chemical characteristics and spatial variation of marine fine particles (PM_{2.5}) in the atmosphere during the highly polluted seasons and how importance of sea salt and anthropogenic particles influenced PM_{2.5} in the Taiwan Strait. Quartz filters were selected in this study since we are interested in the chemical composition of water-soluble ionic species, metallic elements, and carbonaceous content. Before weighing, the quartz-fiber filters were equilibrated in a desiccator at temperatures between 20°C and 25°C and relative humidities (RH) between 35% and 45% for forty-eight hours. After conditioning, the filters were then weighed by a microbalance with the precision of 1 µg to determine the PM_{2.5} mass. The moisture could be mostly removed in the process of conditioning. (Cheng and Tsai, 2000; Yuan et al., 2006) (Lines 169-176) Previous studies reported that the 24-h mass concentration differences between quartz-fiber fiber and Teflon filters has no significant difference (Appel et al., 1984; Tsai et al., 2012).

During the cruise sampling campaigns, marine PM_{2.5} aerosols were sampled on the board of the air quality sampling boat (R/V OCEAN RESEARCHER III) for three consecutive courses on December 2nd-3rd, 2013 (the winter of 2013, W13), four consecutive courses on April 10th-12th, 2014 (the spring of 2014, S14), and three consecutive courses on December 12th-13th, 2013 (the winter of 2014, W14), respectively. Atmospheric fine particles mixed with marine aerosols were sampled at the fore of the uppermost deck on the shipboard with a high-volume sampler during the voyage to prevent the interferences from the exhaust gases of the air quality sampling boat itself as well as the seawater sprays emitted from the oceanic surface. The

air quality sampling boat sailed to windward during the entire sampling voyage. Consequently, the winds were blown from the prow of the boat in order to avoid the intrusion of oil-burning particles emitted from the air quality sampling boat itself.

In this study, the air quality sampling boat sailed continuously windward in a speed of 10 knots per hour during the sampling cruise periods. Atmospheric fine particles were sampled at the fore of the uppermost deck on the shipboard with a high-

5 volume sampler during the voyage to prevent the interferences from the exhaust gases of the air quality sampling boat itself as the chimney of the sampling boat is located at the poop deck. After carefully checking with the records of wind speeds and wind direction in the sampling boat, it showed that the prevailing wind came mainly from the northeast, which did not blow the plume emitted from the chimney of the sampling boat to the PM_{2.5} sampler during the cruise sampling periods.

10 Additionally, the backward trajectories showed that air masses blown from the north generally had higher PM_{2.5} concentrations than those from the south during the cruise sampling campaign. Each sampling course was arranged to collect PM_{2.5} for continuous 8-12 hours based on the distance of each voyage in the two- or three-day periods, while only one fine particle sample was collected during each sampling course. The courses of PM_{2.5} sampling cruises were named W13C1-

15 W13C3 in the winter cruise of 2013, S14C1-S14C4 in the spring cruise of 2014, W14C1-W14C3 in the winter cruise of 2014. The air quality sampling boat navigated in the Taiwan Strait to collect marine fine aerosols. The objective of cruise sampling over sea in the Taiwan Strait was to investigate the chemical characteristics and spatial variation of atmospheric marine fine particles during the highly polluted seasons (i.e. spring and winter) in the Taiwan Strait (Li et al., 2013a, 2013b,

20 2015, 2016, Hsu et al., 2010). However, the differences of three sampling cruises in this study were to inquire the atmospheric marine fine particles at different regions in the Taiwan Strait rather than in different seasons. The navigation routes of the PM_{2.5} sampling cruises were targeted on southern Taiwan Strait in the winter cruise of 2013, central Taiwan Strait in the spring cruise of 2014, and northern Taiwan Strait in the winter cruise of 2014, respectively.

At the Penghu Islands, also known as the Pescadores Islands, atmospheric PM_{2.5} was sampled on the flat roof of a three-store building at the Xiaomen site (23°33'41"N; 119°35'10"E) which is located at the northwestern coastline of the Penghu Islands and is approximately 10 meters above the ground, 60 meters from the seashore, and 1.1 km from the major roads, respectively. Xiaomen is a fishery village that is about 35 km far from the downtown of Makung City, the main city of the

25 islands, where is situated at the southeastern coastal area of the Penghu islands, in order to avoid the potential influences from anthropogenic sources such as vehicular exhausts and stationary emissions. The sampling of PM_{2.5} was conducted for continuous 24 hours (from 9:00 am to 9:00 am of the sequential day) in the seven-day periods on December 1st-8th, 2013, April 8th-15th, 2014, and December 9th-16th, 2014, respectively. Same high-volume sampler with a cascade impactor was also applied to collect PM_{2.5} samples at the Xiaomen site.

30 **2.2 Chemical Analysis of PM_{2.5}**

After sampling PM_{2.5}, the quartz fiber filters were temporarily stored at 4°C to conserve their chemical stability, and then transported back to the Air Pollution Laboratory of the Institute of Environmental Engineering at National Sun Yat-sen

University within two days for conditioning, weighing, and further chemical analysis. All quartz fiber filters were divided into four identical parts prior to the chemical analysis. In this study, we divided each filter into four identical parts for analyzing the chemical composition of PM_{2.5}. After dividing, each of the identical parts was weighed separately to make sure the accurate fraction of the filter that was used for further chemical analyses. After analyzing the chemical composition, the concentrations of the chemical species were then quantified accordingly. One quarter of each quartz fiber filter was analyzed for water-soluble ionic species of PM_{2.5} by means of ion chromatography (IC) (Dionex, DX-120). The concentrations of the major anions (F⁻, Cl⁻, SO₄²⁻, and NO₃⁻) and cations (NH₄⁺, K⁺, Na⁺, Ca²⁺, and Mg²⁺) were measured. The quartz fiber filters analyzed for ionic species were put into a 15-ml PE bottle, and distilled de-ionized water (D.I. H₂O) was added into each PE bottle for ultrasonic vibration of 60 min or longer.

Another quarter of each quartz fiber filter was digested by microwave digestion method in a 30 mL mixed acidic solution (HNO₃:HCl=1:3) by heating it up to 150-200°C for 2 hours, and then diluted to 50 ml with distilled de-ionized water (D.I. H₂O) for further analysis of metallic elements. Twelve metallic elements of PM_{2.5} including Na, Ca, Al, Fe, Mg, K, Zn, Cr, Ti, Mn, Ni, and Pb were analyzed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer, Optima 2000DV).

The water-soluble ionic species of PM_{2.5} were analyzed by IC, while the metallic contents were analyzed by ICP in this study. This study aims to characterize the chemical composition (especially water-soluble ionic species) of marine fine particles (PM_{2.5}) in the atmosphere during the highly polluted seasons and to investigate how importance of sea salt and anthropogenic particles influenced PM_{2.5} in the Taiwan Strait. Therefore, the discussion of chemical species in PM_{2.5} focused on water-soluble ionic species in the manuscript. Furthermore, the comparison of metallic content in PM_{2.5} focused on anthropogenic sources from their original region in the Taiwan Strait. A scatter diagram has been plotted in Figure 2 shown below per request. It showed that the concentrations of metallic contents (Mg, K, and Ca) analyzed by ICP-AES were always higher than those of water-soluble ionic species analyzed by IC.

The carbonaceous contents (i.e. elemental, organic, and total carbons) of PM_{2.5} were measured with an elemental analyzer (EA) (Carlo Erba, Model 1108). Prior to sampling, the quartz fiber filters had to be pre-heated at 900 °C for 1.5 h to expel the potential organic impurities. This preheating procedure minimized the background carbonaceous species in the quartz fiber filters and matrix, which would interfere with the analytical results, possibly leading to an overestimation of the carbonaceous species of PM_{2.5}. The elemental analyzer was operated using the procedure of oxidation at 1020°C and that of reduction at 500°C, for continuous 15-min heating. Additionally, one eighth of the quartz fiber filter was heated in advance by hot nitrogen gas (340-345°C) for 30 min to expel the organic carbon (OC) fraction, after which the amount of elemental carbon (EC) was determined. Another eighth of the quartz fiber filter was analyzed without heating, and the carbonaceous species thus characterized as total carbon (TC). The amount of organic carbon (OC) could be determined by subtracting the elemental carbon from total carbon. Although the aforementioned thermal analysis was the most widely used method for determining the carbonaceous species in marine PM_{2.5} aerosols, a charring formation error from filter preheating was not

taken into account for correction, and this artifact might cause the overestimation of EC and the underestimation of OC (Li et al., 2013a; 2013b ;2015; 2016).

2.3 Quality Assurance and Quality Control

Quality assurance and quality control (QA/QC) for both sampling and chemical analysis of PM_{2.5} were also employed in this study. Prior to sampling, the flow rate of each PM_{2.5} sampler was carefully calibrated with an orifice calibrator (SENSIDYNE, MCH-01). The high-volume air sampler (TE-6001) was used to collect PM_{2.5} with a sampling flow rate of 1.47 m³/min passing through a PM_{2.5} selective inlet. As the particulates travel through the PM₁₀ size selective inlet the larger particulates are trapped inside of the inlet as the smaller PM_{2.5} particulates continue to travel through the inlet and are collected on the 8" x 10" quartz fiber filter manufactured by Pall Corporation. This method was complied with the sampling method of NIEA A102.12A similar to USEPA Method IO-2.1. Quartz fiber filter was selected for this study because we conducted the chemical analysis of water-soluble ions, metallic elements, and carbonaceous content. Before weighing, the quartz fiber filters were conditioned in a desiccator at temperatures of 20-25°C and relative humidity (RH) of 35-45% for 48 hours. After conditioning, the filters were then weighed by a microbalance (Sartorius MC 5) with the precision of 1 µg to determine the mass of PM_{2.5}. The filters were stored in a weighing chamber at temperatures of 20-25°C and relative humidity of 35-45%. The quartz fiber filters were handled with care, so as to prevent potential contamination and cracking during the sampling procedure, as they were placed on the PM_{2.5} samplers. After sampling, aluminium foil was used to fold the quartz fiber filters, which were then temporarily stored at 4°C and transported back to the laboratory for chemical analysis within two days. The sampling and analytical procedures were similar to those described in previous studies (Cheng and Tsai, 2000; Lin, 2002; Yuan et al., 2006; Tsai et al., 2008; Tsai et al., 2010; Witz et al., 1990). In the sampler, an adapter is placed into the model TE-6001 sampler in lieu of an existing PM₁₀ fractionator. The adapter has a plate that contains multiple impactors for collecting particles larger than PM_{2.5} on a slotted quartz fiber filter. PM_{2.5} is then passed through the impactor and collected on a quartz fiber filter. After sampling, the concentrations of PM_{2.5} and PM_{2.5-10} were determined by weighting the quartz fiber filter and the slotted quartz fiber filter, respectively. Due to the difficulty of identically dividing the slotted quartz fiber filter, we thus solely analyzed the chemical compositions of PM_{2.5}.

Both field and transportation blanks were further undertaken for PM_{2.5} sampling, while reagent and filter blanks were applied for chemical analysis. Summary of QA/QC results for the analysis of chemical species in this study are summarized in Table 1. The determination coefficient (R²) of the calibration curve for each chemical species was required to be higher than 0.995. Background contamination was routinely monitored by using operational blanks (unexposed filters); these were processed simultaneously with the field samples. The present experimental works found that the background interference was insignificant and could thus be ignored in this study. At least 10% of the samples were analyzed by spiking with a known amount of metallic elements and water-soluble ionic species to determine their recovery efficiencies. The results of the

recovery efficiency tests indicated that the recovery efficiencies among every 10 filter samples varied from 96 to 103%. In addition, the results of the reproducibility varied from 97 to 104% for all the chemical species.

2.4 Transport Routes of Air Masses

5 In order to identify the predominant sources of air pollutants, backward trajectory has been widely used to trace the transport routes of air masses (Li et al., 2016). The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) is a widely used model that plots the trajectory of a single air parcel from a specific location and height above ground over a period of time. The 72-hr backward trajectories started at the island site (23°33'41"N; 119°35'10"E) at the altitudes of 100, 350, and 500 m above sea level, respectively.

3 Results and discussion

10 In this Section, we discussed and interpreted the results obtained from this study in the following seven subsections. Subsection 3.1 presents the spatiotemporal variation of $PM_{2.5}$ concentrations over sea and at the Offshore Islands. Subsection 3.2 introduces the transport routes during three cruise sampling campaign. Subsection 3.3 aggregates the chemical characteristic of marine fine particles during three cruise sampling campaign. Subsection 3.4 describes the distribution and source indicators of $PM_{2.5}$ during three cruise sampling campaign over sea and at the offshore islands. Subsection 3.5
15 reconstructs the material balance equation for the gravimetric mass of $PM_{2.5}$ during three cruise sampling campaign. Subsection 3.6 identifies whether the presence of certain metallic elements in $PM_{2.5}$ were primarily due to natural or anthropogenic processes during the sampling cruise. Subsection 3.7 compares the chloride deficit of $PM_{2.5}$ with previous studies, respectively.

20 3.1 Spatiotemporal Variation of $PM_{2.5}$ Concentrations over Sea and at the Offshore Islands

The mass concentrations of $PM_{2.5}$ and $PM_{2.5-10}$, and the mass ratios of $PM_{2.5}/PM_{10}$ over sea and at the offshore islands during the $PM_{2.5}$ sampling campaigns are summarized in Table 2. Limited to the voyage of air quality monitoring boat, each sampling course was arranged to collect $PM_{2.5}$ for only continuous 8-12 hours (i.e. daytime and nighttime) based on the distance of navigation during the sampling cruise over sea. On the islands, $PM_{2.5}$ was sampled for continuous 24 hours. Field
25 sampling results indicated that the concentrations of $PM_{2.5}$ were generally higher than those of $PM_{2.5-10}$ with the exception of the winter cruise in 2014 (W14).

The mass ratios of $PM_{2.5}/PM_{10}$ over sea and at the offshore islands ranged from 42.4% to 44.0% for the winter cruise of 2014 (W14), which were lower than those for other two sampling cruises ranging from 49.2% to 55.7%. The concentrations of $PM_{2.5-10}$ over sea were always higher than those at the offshore islands, indicating that sea salt highly influenced the marine
30 aerosols with a dominant size range of 2.5-10 μm . Higher $PM_{2.5}$ concentrations were commonly observed over sea. The fine

particles might be emitted from vessels including commercial ships and fishery boats were significant contributions to marine fine aerosols and cannot be ignored over the seas and oceans where the marine transportation traffics are busy. Unexpectedly, a similar trend was also observed for $PM_{2.5}$, with an exception of winter cruise of 2013 (W13). There are two possible suggestions or explanations for this phenomenon. One possibility suggested that fine particles emitted from vessels including commercial ships and fishery boats were significant contributions to marine fine aerosols and cannot be ignored over the seas and oceans where the marine transportation traffics are busy. The other possibility indicated that long-range cross-boundary transportation of fine particles emitted from the upwind regions such as China, Korea, and/or Japan could be constantly transported to the target areas and even across the Taiwan Strait.

Moreover, higher $PM_{2.5}$ concentrations were commonly observed in the daytime than those at nighttime for all three cruise sampling campaigns. It was mainly attributed to the facts that higher frequency of human activities such as commercial burning, vehicle and vessel traffics in the daytime than at nighttime. Additionally, the sea-land breezes play an important role in transporting air pollutants to and from urban areas on the coastal regions (*Ding et al., 2004; Tsai et al., 2008*). Previous study stated that the surface wind fields at the Penghu Islands varied in the daytime and at nighttime (Li et al., 2015). In the daytime, air masses were divided into two separate zones. On the west side of the Penghu Islands, a strong northward prevailing wind was coupled with the sea-land breeze, causing by the sea breezes in the southwestern coastal region of the Taiwan Island. Conversely, the surface wind directions moved to the east on the east-side of the Penghu Islands. *Viana et al. (2005)* also stated that atmospheric coastal dynamics exert a significant influence on the levels and composition of atmospheric particles. Sea breezes may penetrate deep inland and cause high pollutant episodes in early afternoon, resulting in higher concentration of marine aerosols in the daytime than that at nighttime (*Ding et al., 2004*).

20 **3.2 Transport Routes of $PM_{2.5}$ Concentrations over Sea and at the Offshore Islands**

Previous study reported that the level of atmospheric $PM_{2.5}$ is affected by meteorological condition, thus $PM_{2.5}$ concentrations in spring and winter was much higher than those in fall and summer in the Taiwan Strait (Li et al., 2016b). However, the results of backward trajectory analysis were not shown in this manuscript. Our previous study indicated that the corresponding trajectories were clustered into three major transport routes according to their airflow directions and regions through which air masses traveled toward the Taiwan Strait (Li et al., 2016b). During the consecutive courses in the winter of 2013 (W3), air masses originated from Mongolia were transported across the northern, central, and southeastern China. During the consecutive courses in the spring of 2014 (S14), air masses originated from northern and northeastern China were transported through the coastal regions of central China, East China Sea, and southeastern China toward the Taiwan Strait. During the consecutive courses in the winter of 2014 (W14), air masses originated from northern and northeastern China are transported through the coastal regions of central and southeastern China toward the Taiwan Strait. Results from backward trajectories showed that the concentrations of $PM_{2.5}$ blown from the north were generally higher than

those from the south. PM_{2.5} samples were collected over sea and at the offshore site during the high pollution seasons in this study.

In this study, 72-hour backward trajectories ending at the Penghu Islands at the altitudes of 100, 350, and 500 m above sea level, respectively, were simulated to represent air masses toward the Taiwan Strait. Air masses originated from Mongolia were transported through northern and central China, and finally across the East China Sea to the offshore site during the three sampling cruises. The results indicated that anthropogenic chemical species were evenly dispersed over sea for the same trajectory during the air pollution episodes, causing the carbonaceous species stably distributed over sea and at the offshore site.

3.3 Chemical Characteristics of PM_{2.5} over Sea and at the Offshore Islands.

3.3.1 Water-soluble Ions of PM_{2.5}

The chemical compositions of PM_{2.5} sampled over sea and at the offshore islands in the Taiwan Strait during the cruise sampling campaigns are summarized in Table 3. NO₃⁻, SO₄²⁻ and NH₄⁺ that were associated together in the same particulate system in the likely form of NH₄NO₃, and [NH₄]₂SO₄ or NH₄HSO₄. Particulate phase NH₄⁺ concentrations can be calculated using the stoichiometric ratios of different compounds and compared with the measurements. Nitrate is in the form of NH₄NO₃, while sulfate is in the forms of either (NH₄)₂SO₄ or NH₄HSO₄ which can be estimated by equations (1) and (2).

$$(NH_4)_2SO_4 = 0.38 \times SO_4^{2-} + 0.29 \times NO_3^- \quad (1)$$

$$NH_4HSO_4 = 0.192 \times SO_4^{2-} + 0.29 \times NO_3^- \quad (2)$$

Previous study indicated that ammonia is known to neutralize sulfuric acid irreversibly, and then nitric acid. Additionally, hydrochloric acid may react with gaseous ammonia to form ammonium chloride aerosols. However, in thermodynamic equilibrium conditions ammonium chloride is reported to be 2-3 times more volatile than ammonium nitrate (*Stelson and Seinfeld, 1982*) and its formation occurs later. Thus, ammonia is believed to be neutralized firstly by sulfuric acid and forms ammonium sulfate and/or ammonium bisulfate (*McMurry et al., 1983; Wang et al., 2005; Du et al., 2010*). In this study, we assumed that both sulfate (SO₄²⁻) and bisulfate (HSO₄⁻) could be neutralized by ammonia with various portions. The most abundant water-soluble ionic species of PM_{2.5} were NO₃⁻, SO₄²⁻, NH₄⁺, Cl⁻, and Na⁺ indicating that secondary inorganic aerosols (SIAs) and sea salt was the major portion of PM_{2.5}. Results obtained from the calculation of nitrate showed that the predominant inorganic compounds of PM_{2.5} were ammonium nitrate (NH₄NO₃) and ammonium bisulfate (NH₄HSO₄), which was formed by the neutralization of sulfuric and nitric acids with ammonia. The ionic balance (i.e. A/C) of ionic species ranged from 0.7 to 1.0, including that PM_{2.5} were acidic particles. The results indicated that both sea salt and anthropogenic secondary particles were the major contributors to marine fine aerosols in the Taiwan Strait (*Li et al., 2016*). Particularly, the mass concentrations of SO₄²⁻ (3.6-6.5 μg m⁻³) were approximately 1.4-1.9 times higher than those of NO₃⁻ (2.5-4.0 μg m⁻³),

indicating that anthropogenic particles came mainly from the sulfur-containing sources rather than the nitrogen-containing sources.

Moreover, the contributions of sea salt (Cl^- and Na^+) to $\text{PM}_{2.5}$ over sea were commonly higher than those at the offshore islands. It was mainly attributed to the facts that sea salt particles could be massively generated from the surface of the ocean/sea by the bursting of white-cap bubbles (Chow *et al.*, 1996). The concentrations of sea salt in marine aerosols are the highest over sea and then descend rapidly with the distance away from the coastline (Kim *et al.*, 2000; Tsai *et al.*, 2011). The replacement of chloride from sea-salt particles with acids is caused by the formation of sulfate and nitrate in the marine aerosols. Particularly, nitric acid prefers to react with sodium chloride (NaCl) to form stable sodium nitrate (NaNO_3) over sea and at the offshore islands (Wall *et al.*, 1988; Fang *et al.*, 2000).

The percentages of SIAs (i.e. the summation of SO_4^{2-} , NO_3^- , and NH_4^+) ranged from 13.4% to 16.9%, from 8.8% to 11.5%, and from 3.9% to 6.7% in $\text{PM}_{2.5}$ collected in the courses of W13C1, S14C1, and W14C3, respectively, that was navigated in the southern Taiwan Strait. In these courses, the collected fine particles were mainly considered as a mixture of marine aerosols and anthropogenic particles emitted from southern Taiwan, particularly the Kaohsiung City. The contributions of SO_4^{2-} , NO_3^- , Cl^- , and Na^+ to $\text{PM}_{2.5}$ collected in the southern Taiwan Strait were obviously higher than other regions. The accumulation of particulate matter in the near-ocean region due to sea-land breeze had a regular influence on the physicochemical properties of atmospheric particles in the coastal region of southern Taiwan (Tsai *et al.*, 2010). The air masses for $\text{PM}_{2.5}$ samples W13C2, S14C2, and W14C2 were mainly from marine environments adjacent to the Penghu Islands. The concentrations of water-soluble ionic species in $\text{PM}_{2.5}$ for these courses were relatively lower than those for other courses. Moreover, higher contributions of SIAs to $\text{PM}_{2.5}$ were generally observed in the daytime than those at nighttime in the southern Taiwan Strait. The second highest contributions of water-soluble ionic species to $\text{PM}_{2.5}$ were observed in the courses of W13C3, S14C4, and W14C3, which navigated along the coast of the Taiwan Island on its way back to the Kaohsiung Harbor. In these three courses, $\text{PM}_{2.5}$ was considered as a mixture of marine aerosols and anthropogenic particles mainly emitted from pollution sources in central Taiwan Island where the largest coal-fired power plant in Taiwan is located at the western coast of Taiwan Island.

The concentrations of sea salt can be estimated by the equations (3), where 1.47 is the mass ratio of $(\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{HCO}_3^-) / \text{Na}^+$.

$$\text{Sea salt} = \text{Cl}^- + 1.47 \times \text{Na}^+ \quad (3)$$

Table 3 summarizes the estimated mass concentrations of sea salt and their contributions to $\text{PM}_{2.5}$ over sea and at the offshore islands during three cruise sampling campaigns. As shown in Table 3, the estimated sea salt results indicated that the concentrations of sea salt over sea ($3.5\text{-}5.7 \mu\text{g m}^{-3}$) were always higher than those at the offshore islands ($2.9\text{-}3.6 \mu\text{g m}^{-3}$), while the contributions of sea salt to $\text{PM}_{2.5}$ over sea (12.4-16.1%) were constantly higher than those at the offshore islands (7.7-13.2%) during the cruise sampling campaigns. Previous studies reported that the sea salt concentrations in PM_{10} was 53.4% at Point Reyes, Central CA (Chow *et al.*, 1996), 24.7% at San Nicolas Island in South Coast Air Basin of Southern California (Kim *et al.*, 2000), 11.2~15.8% at the coastal region of Southern Taiwan (Tsai *et al.*, 2011), 3.1~13.5% at Gosan,

Jeju, South Korea (Han et al., 2003), and 2.81% and 1.62% in PM₁₀ and PM_{2.5}, respectively, at the coastal region of South Korea (Park et al., 2015), respectively. The contributions of sea salt to PM_{2.5} were consistent well with Tsai et al. (2011) in the South Taiwan and Han et al. (2003) in South Korea.

3.3.2 Comparison of Sea Salt and Non-Sea Salt Content of PM_{2.5}

5 Sea salt are one of the abundant aerosols in the atmosphere of the coastal regions (Posfai and Buseck, 2010; Seinfeld and Pandis, 2006; Mahowald et al., 2006; Adachi and Buseck, 2015). Previous studies reported that sodium (Na⁺) is an excellent tracer of sea salt elsewhere, particularly in the coastal regions (Ooki et al., 2002). Other alternative tracers of sea salt would be Cl⁻ or Mg²⁺ which are abundant in the seawater. In the atmosphere, chloride (Cl⁻) of the aerosol particles along the coastline or even intrusion to far inland could be partially depleted due to the chemical reactions of sea salt with acidic
 10 compounds such as sulfuric or nitric acids. This approach prevents the inclusion of non-sea salt ions such as K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, and NO₃⁻ in the sea salt particles and allows for the loss of Cl⁻ through chloride depletion process, assuming that all measured Na⁺ in aerosol particles is derived from seawater.

We further reviewed the literatures for the mass ratios of various water-soluble ions (K⁺, Mg²⁺, Ca²⁺, SO₄²⁻) to sodium (Na⁺) in the seawater. Previous studies have commonly used these ratios to estimate the non-sea-salts water-soluble ions in the
 15 aerosol particles. The non-sea salt water-soluble K⁺, Mg²⁺, Ca²⁺, and SO₄²⁻ can be estimated by equations (4)-(7).

$$\text{nss-K}^+ = \text{K}^+ - 0.038 \times \text{Na}^+ \quad (4)$$

$$\text{nss-Mg}^{2+} = \text{Mg}^{2+} - 0.12 \times \text{Na}^+ \quad (5)$$

$$\text{nss-Ca}^{2+} = \text{Ca}^{2+} - 0.038 \times \text{Na}^+ \quad (6)$$

$$\text{nss-SO}_4^{2-} = \text{SO}_4^{2-} - 0.251 \times \text{Na}^+ \quad (7)$$

20 Figure 3 and Table 4 show the water-soluble ion concentrations and the contributions of sea salt and non-sea salt water-soluble ion (ss- and nss-WSI) concentrations in PM_{2.5} over sea and at the offshore islands in the winter and spring of 2013-2014. The major nss-WSI in PM_{2.5} were non-sea salt SO₄²⁻ (nss-SO₄²⁻) and non-sea salt NO₃⁻ (nss-NO₃⁻), while the major ss-WSI in PM_{2.5} were ss-Cl⁻ and ss-Na⁺, over sea and at the offshore islands. The percentages of nss-WSI in PM_{2.5} were ordered as: nss-SO₄²⁻ (10.8%-15.0%) > NH₄⁺ (3.7%-6.7%) > nss-K⁺ (0.7%-2.2%) > nss-Mg²⁺ (1.0%-2.2%) > nss-Ca²⁺ (0.9%-1.3%),
 25 respectively. The results indicated that atmospheric PM_{2.5} in the Taiwan Strait was mainly influenced by anthropogenic particles rather than sea salt. This phenomenon was not only observed at the offshore islands, but was also found in the open sea. Furthermore, the contributions of nss-WSI to PM_{2.5} at the offshore islands were obviously higher than those over sea, while the contributions of ss-WSI to PM_{2.5} at the offshore islands were generally lower than those over sea, respectively. It suggested that anthropogenic particles emitted from inland sources or local emissions could be probably accumulated at the
 30 offshore islands rather than over sea.

Figure 4 illustrates the percentages of non-sea salt water-soluble ionic species in the measured water-soluble ionic species of PM_{2.5} sampled over sea and at the offshore islands during the cruise sampling campaigns. The contribution of nss-SO₄²⁻ to

total SO_4^{2-} ranged from 90.8% to 92.9% over sea and from 93.7% to 96.2% at the offshore islands, respectively. Similar trends were observed for the mass percentages of nss- K^+ to total K^+ (96.0-96.9%) as well as nss- Ca^{2+} to total Ca^{2+} (83.1-93.2%) at the offshore islands. Previous study reported that water-soluble ionic species of Na^+ and Mg^{2+} are usually expected to be conservative tracers of sea salt, while Ca^{2+} may have additional sources, such as continentally derived gypsum or oceanic CaCO_3 (Johansen et al., 1999). In this study, the remaining nss- Ca^{2+} was assumed to be present as CaCO_3 .

3.3.3 Metallic Elements of $\text{PM}_{2.5}$ over Sea and at the Offshore Islands

Previous studies reported that the metallic elements of $\text{PM}_{2.5}$ are probably attributed from three major sources, including crustal, anthropogenic, and oceanic sources (Chester et al., 2000; Zhao et al., 2015). The metallic elements lead (Pb) and zinc (Zn) are often considered as the markers associated with traffic sources (Querol et al., 2001; Manoli et al., 2002; Fang et al., 2003; Cao et al., 2009). Potassium (K) is associated with primary particles emitted from coal combustion and biomass burning. Zn, Ni, Pb, and Mn were largely from the industrial emissions such as metallurgical processes (Pacyna, 1998), while Ni and Zn could be also partially from the tail exhausts of motor vehicles and vessels (Lee et al., 1999). Zhao et al. (2015) reported that atmospheric pathway has been recognized as an important source for many oceanic chemicals, including Fe (Duce and Tindale, 1991; Gao et al., 2001), Al (Kang et al., 2009), Cu (Kocak et al., 2005), Zn (Spokes et al., 2001; Kang et al., 2009), and Pb (Lin et al., 2000; Kocak et al., 2005; Kang et al., 2009). Many studies concluded that the concentrations of crustal-originated (Al, Ca, and etc.) atmospheric particles were obviously decreased when air masses were blown from their origins to the downwind regions during the long-range transport (LRT) processes (Gao et al., 1992a; Spokes et al., 2001; Han et al., 2008; Zhao et al., 2015).

Table 5 shows that the most abundant metallic elements of $\text{PM}_{2.5}$ were crustal and sea salt elements (Na, Al, Fe, Mg, K, and Ca) and followed by anthropogenic elements (Zn, Ni, and Pb). The highest metallic element concentrations of $\text{PM}_{2.5}$ were commonly observed at the offshore islands, while compared to those observed over sea. Among the crustal elements, Al, Fe, and Ca were the richest metals, with a much higher concentration of Al than other crustal elements. Metallic element Al is often considered as an indicator of mineral dusts (Hsu et al., 2010), which is one of the major common crustal-originated elements in the dust particles. Kang et al. (2011) reported that high Al concentration is generally observed during the Asian duststorm events in East Japan Sea. The percentages of Al to $\text{PM}_{2.5}$ account for 12.4% in Yellow Sea and East China Sea (Zhao et al., 2015), which are higher than those in Bohai Sea (Ji et al., 2011). In this study, the percentages of Al to $\text{PM}_{2.5}$ ranged from 2.8% to 3.2% at the offshore islands and from 1.5% to 2.2% over sea, respectively. The percentages of Al to $\text{PM}_{2.5}$ in the Taiwan Strait were lower than those in Yellow Sea and East China Sea since the Taiwan Strait were located at the lower latitude regions than those in Yellow Sea and East China Sea regions, where air masses containing dusts could be blown from the dust-originated sources to the downwind regions. The percentages of metallic elements of Mg and Ca to $\text{PM}_{2.5}$ ranged from 1.7% to 2.9% and from 1.5% to 2.8% at the offshore islands, respectively, while those ranged from 2.1% to 3.2% and from 1.5% to 3.0% over sea in the Taiwan Strait, respectively. The metallic elements of Mg and Ca over sea

were higher than those at the offshore site. It was probably attributed to the coupling of seawater and terrestrial substances, and some metallic element of Ca might be originated from anthropogenic sources (Zhang *et al.*, 2007; Zhao *et al.*, 2015). The percentages of K to PM_{2.5} ranged from 1.8% to 2.5% at the offshore islands and from 1.8 % to 3.3% over sea in the Taiwan Strait, respectively. The metallic element of K in PM_{2.5} was generally originated from biomass burning and marine aerosols (Chow *et al.*, 1995). Higher contributions of K in PM_{2.5} were generally observed over sea than those at the offshore islands in the Taiwan Strait, suggesting that the bubbles of sea salt in the marine environments could emit and transport K-rich particles in the atmosphere.

Nickel (Ni) as an anthropogenic metal has been reported as one of two recognized indicators for shipping emissions (Pandolfi *et al.* 2011; Pey *et al.*, 2013; Johnson *et al.*, 2014), while Al and Fe are two major tracers for crustal emitted dusts (Hsu *et al.*, 2010). Consequently, the mass ratios of Ni/Al and Ni/Fe could be treated as important indicators of particles emitted from vessel exhausts. As shown in Table 5, the mass ratios of Ni/Al and Ni/Fe over sea (0.35 and 0.88, respectively) were higher than those at the offshore islands (0.30 and 0.69, respectively). The results indicated that shipping emissions had higher influences on the marine fine particles than crustal dusts in the open sea while compared to those at the offshore islands, which concurred with previous study reported by Li *et al.* (2016).

3.3.4 Carbonaceous Contents of PM_{2.5} over Sea and at the Offshore Islands

Previous studies indicated that the mass ratio of OC and EC (OC/EC) has been widely used in previous studies to determine whether the carbonaceous aerosol particles are mainly primary or secondary (Ho *et al.*, 2015; Li *et al.*, 2016). A high OC/EC ratio coupled with a poor correlation implies an influx of urban air pollutants from elsewhere or the formation of secondary organic carbon (SOC) from photochemical reactions (Castro *et al.*, 1999). On the other hand, a high correlation indicates primary emission and a secondary formation derived from the primary organic carbon (POC) (Turpin *et al.*, 1991; Strader *et al.*, 1999; Li *et al.*, 2016). Moreover, particulate organic matter (POM) can be estimated by multiplying the measured OC by a factor (1.6) to compensate for other atoms such as H, O and N in the organic molecule (Turpin and Lim, 2001).

Figure 5 illustrates the spatiotemporal variation of carbonaceous contents and their mass ratios (OC/EC) of PM_{2.5} sampled over sea and at the offshore islands during three cruise sampling campaigns. Carbonaceous compounds in the atmosphere consist mainly of elemental and organic carbons (EC and OC). EC is a product of incomplete combustion from residential coals, motor vehicle fuels, and biomass burning. OC originates from primary anthropogenic sources like above mentioned combustions and from the formation of secondary OC by chemical reactions in the atmosphere. The concentrations of OC in PM_{2.5} were always higher than those of EC at the offshore site and over sea around the Taiwan Strait, while the OC/EC ratio ranged from 2.2 to 2.7, respectively. The concentrations of OC were mostly higher at the offshore site than those over sea during the sampling periods. The OC/EC ratios ranged from 2.3 to 2.6 at the offshore site, and from 2.2 to 2.6 at the south Taiwan Strait (routes of W13C1, S14C1, and W14C1), 2.2 to 2.7 at the central Taiwan Strait adjacent to Penghu Islands (routes of W13C2, S14C2, and W14C2), 2.2 to 2.5 at the routes which were adjacent to coastline of western Taiwan Islands

of returning to Kaohsiung Port (W13C3, S14C4, and W14C3), and accounted for 2.6 at the northern Taiwan Strait (S14C3), respectively. The higher OC/EC ratios were generally observed at the central and northern Taiwan Strait, and follow by the coastline of western Taiwan Islands and southern Taiwan Strait. Previous studies indicated that the OC/EC ratio has been used in many previous studies to determine whether the carbonaceous aerosols are primary or secondary. A high OC/EC ratio coupled with a poor correlation implies an influx of urban pollutants from elsewhere or the formation of secondary OC (SOC) from photochemical reactions. On the other hand, a high correlation indicates primary emission and a secondary formation derived from the primary carbon (*Turpin et al., 1991; Strader et al., 1999*). Previous reports also appointed that high OC/EC ratio in fall and winter might be resulted from (1) more coal burning for space heating in winter at the North China; (2) more conversion of semi-volatile organic materials into particles in lower temperatures; and (3) more secondary organic carbon production as air masses passed from industrial and highly pollutant areas under specific meteorological conditions in fall and winter (*Duan et al., 2007; Li et al., 2016*).

Table 6 compares the concentrations of TC, OC, and EC in $PM_{2.5}$ with previous studies. The total carbon concentrations were close to those at the Penghu site located at an offshore island where clean marine air can dilute $PM_{2.5}$ from long-range transport, resulting in local emission accumulation and lower OC and EC levels at the Penghu Islands. The OC/EC ratios ranged from 3.0-7.0 on the southeastern coastline of China and from 1.9 to 2.9 on the southwestern coastline of the Taiwan Strait, respectively. The OC/EC ratios obtained from this study ranged from 2.6 to 2.8 at the Taiwan Strait which were generally lower than those reported by *Chou et al., 2010* (2.6 to 2.9) and *Tasi et al., 2010* (1.9 to 2.9). The comparison of OC/EC ratios showed the variation of carbonaceous species analyzed with different analytical methods. The carbonaceous concentrations of particulate matter analyzed using thermal optical reflectance (TOR) and thermal optical transmittance (TOT) were generally higher than those using elemental analysis (EA).

3.4 Distribution and Source Indicators of $PM_{2.5}$ over Sea and at the Offshore Islands

The results of the distribution percentage of chemical characteristics to $PM_{2.5}$ during the three courses over Taiwan Strait indicated that water-soluble ionic species, metallic elements, and carbonaceous content accounted for 46.1-52.0%, 14.7-19.3%, and 14.0-19.9% of $PM_{2.5}$ during the sampling courses in the winter of 2013, respectively; 44.4-54.1%, 13.1-15.7%, and 13.3-17.9% during the sampling courses in the spring of 2014, respectively; 42.7-45.8%, 12.3-13.4%, and 15.2-18.8% during the sampling courses in the winter of 2014, respectively. The results indicated that the distribution of water-soluble ionic species and carbonaceous contents on the offshore islands were generally higher than those over sea. Previous study reported that the emissions of huge amounts of particulates from various sources (e.g., textile plants at the Jinjing River Basin) could result in the higher percentages of ionic and carbonaceous contents at the Taiwan Strait (*Li et al., 2016a*). The results were close to those at the Penghu site located at an offshore island.

There are several ratios of chemical species can be used as valuable indicators to appoint atmospheric particles from specific sources (Cao et al., 2012; Arimoto et al., 1992). Previous researches reported that the mass ratios of EC/TC, K⁺/TC, and TC/SO₄²⁻ can be used to identify the sources from biomass burning (VanCuren, 2013). When the mass ratio of EC/TC ranges from 0.1 to 0.2, K⁺/TC ranges from 0.5 to 1.0, and TC/SO₄²⁻ ranges from 6 to 15, it suggests that the sources were mainly contributed from biomass burning (VanCuren, 2013). The mass ratios of NO₃⁻/nss-SO₄²⁻ have also been used to evaluate the contributions from stationary and mobile sources (Arimoto et al., 1992). The mass ratios of NO₃⁻/nss-SO₄²⁻ higher than unity indicated that the sources of particles were mainly from mobile sources. Conversely, the mass ratios of NO₃⁻/nss-SO₄²⁻ lower than unity suggested that the sources of particles came mainly from stationary sources. Table 7 compares the mass ratios of major chemical species over sea and at the offshore islands. The mass ratios of EC/TC, K⁺/TC, NO₃⁻/nss-SO₄²⁻, and TC/SO₄²⁻ during the three courses over Taiwan Strait ranged from 0.28±0.01 to 0.30±0.02 in the winter of 2013 (W13), 0.10±0.02 to 0.17±0.05, 0.66±0.05 to 0.71±0.03 in the spring of 2014 (S14), and 0.94±0.05 to 1.18±0.08 in the winter of 2014 (W14), respectively, while similar trends reported at the southeastern coastline of the Taiwan Strait (Li et al., 2016a). Previous studies reported that high SO₄²⁻ and NO₃⁻ concentrations observed at the Penghu site and the Kaohsiung site were mainly from stationary sources due to burgeoning industrial development in the southwestern coastal region of Taiwan (Tsai et al., 2011; Li et al., 2016a). According to the reports from VanCuren (2003), atmospheric aerosols with high nss-SO₄²⁻/NO₃⁻ ratios were attributed mainly from stationary sources.

3.5 Reconstruction of PM_{2.5} over Sea and at the Offshore Islands

PM_{2.5} was estimated by material balance equation for gravimetric mass (Chow et al., 1996). In this study, PM_{2.5} was summed by nine major chemical compositions: nitrate (NO₃⁻), sulfate (SO₄²⁻), ammonium (NH₄⁺), chloride (Cl⁻), organic matter (OM), elemental carbon (EC), crustal materials (CM), sea salt, and others. Organic material (OM) was estimated from an organic carbon (OC) multiplier (f) that accounts for unmeasured hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) in organic compounds (Chow et al., 1996). Multipliers of 1.4 to 1.8 have been found to best represent the complex mixture of organic molecules in OM (POM) (Chow et al., 1996). A factor of 1.6 for converting OC to OM was used in this study. Crustal materials can be estimated using a method reported by Wedepohl (1995) (Crustal materials= 12*[Al]), while sea salt was estimated by equation (3). Therefore, PM_{2.5} concentrations were reconstructed by the following equation, (8),

$$[PM_{2.5}] = SO_4^{2-} + NO_3^- + NH_4^+ + (\text{Organic.Materials}) + (\text{Elemental.Carbon}) + (\text{Crustal.Materials}) + (\text{Sea.Salt}) + (\text{Trace.Element}) + (\text{Others}) \quad (8)$$

Table 8 compares the major chemical components of PM_{2.5} at the coastal sites around the Taiwan Strait and East China Sea. Consistent with previous studies, organic materials (OM), SO₄²⁻, NO₃⁻, and crustal materials (CM) were the major components for the reconstruction of PM_{2.5} concentration. The results indicated that SO₄²⁻, NO₃⁻, crustal materials, and organic materials are important components in PM_{2.5} at all coastal sites. The contribution of SO₄²⁻, NO₃⁻, and organic materials were similar to other coastal sites.

3.6 Enrichment Factors of PM_{2.5} over Sea and at the Offshore Islands

To identify whether the presence of certain metallic elements in aerosols were primarily due to natural or anthropogenic processes, the enrichment factor (EF) of each metallic element was further determined in this study. In previous studies, the particle-induced X-ray emission or proton-induced X-ray emission (PIXE) was used to determine the elemental characteristics of atmospheric particles (Artaxo et al. 1992). In this study, we analyzed ionic species and metallic content by IC and ICP-AES. Comparing different methods for analyzing chemical composition is difficult to calculate the enrichment factors of ionic species (e.g. Cl⁻), respectively. In this study, same methods were applied to analyse PM_{2.5} samples collected at the target region, which should be comparable for the enrichment factors of PM_{2.5} over sea and at the offshore islands. Thus, we used the presence of certain metallic elements in aerosols surrounding the Taiwan Strait primarily due to natural or anthropogenic processes in the target regions. Although Al, Fe, and Ca are prominent crustal elements which have been used as the reference elements in previous literatures, aluminum (Al) was used as the reference element for the EF calculations for this particular study. The non-crustal EF can be estimated by equation (9) (Chester et al., 2000).

$$EF = \frac{(C_x / Al)_{aerosol}}{(C_x / Al)_{crust}} \quad (9)$$

where $(C_x / Al)_{aerosol}$ represents the concentration ratio of specific metallic element (C_x) to Al in aerosols; and $(C_x / Al)_{crust}$ represents the corresponding ratio of specific metallic element (C_x) to Al in the crustal matter.

The EF values of metallic elements in PM_{2.5} over sea and at the offshore islands are depicted in Figure 6. The order of the EF values for various metallic elements had quite similar trend no matter where atmospheric PM_{2.5} were sampled. For least ten measured metallic elements, their EF values were in the range of 0.1 to 10000 and highly relevant. Trace elements Ni and Cr were highly enriched ($100 < EF < 10000$) in PM_{2.5}, while Mn and Pb were moderately enriched ($10 < EF < 100$) at all sites around the Taiwan Strait. Previous studies reported that metallic elements with $EF > 10$ have an important proportion of non-crustal sources and that a variety of emission sources could contribute to their loading in the ambient air. The EF values of crustal elements Mg, K, Ca, and Fe in PM_{2.5} ranged from 1 to 10 over sea and at the offshore islands, and their EF values were quite consistent for fine particles sampled at different sites. It suggested that these crustal elements were likely originated from same natural sources and had no enrichment in PM_{2.5}. In comparison, high EF values of Ni, Cr, Mn, and Pb in the range of 10-10000 suggested that these trace elements were mainly originated from anthropogenic sources. Previous study reported that metallic elements Cr and Ni in PM_{2.5} were mainly from anthropogenic combustion sources, while Cr and Ni in PM_{2.5-10} had more soil-related origins (Chow et al., 1995).

3.7 Ratio of Chloride to Sodium Ions and Chloride Deficit of PM_{2.5}

Previous studies reported that sea salt particles contribute significant fraction to particulate matter at the locations close to the sea (Chow et al., 1996; Manders et al., 2009; Tsai et al., 2011; Park et al., 2015). The ratio of Cl⁻/Na⁺ in fresh sea salt is about 1.8 in the mass fraction (Pytkowicz and Kester, 1971) or 1.16 (Riley and Chester, 1971) in the ionic equivalents. The

chloride (Cl⁻) in the sea salt particles could be continuously lost to the gas phase as HCl and chlorine compounds while acidic species existed in the atmosphere. **Chloride replacement** is the process by which acidic species, mainly nitrate, sulfate, and organic acids, react with NaCl in the sea salt particles and replace chloride in the form of HCl. *Virkkula et al. (2006)* reported that in the polluted areas where strong acids (H₂SO₄ and HNO₃) or their precursors are present, simple acid displacement reactions are likely responsible for most of the chloride depletion. These reactions lead to large (even up to 100%) chloride deficits if enough acidic species and/or time are available. The chloride deficit can be calculated by equation (10) as follows (*Quinn et al., 2000*),

$$Cl^- \text{ deficit (\%)} = \frac{[Cl^-]_{\text{original}} - [Cl^-]_{\text{meas}}}{[Cl^-]_{\text{original}}} \times 100\% = \frac{1.8 \times [Na^+]_{\text{meas}} - [Cl^-]_{\text{meas}}}{1.8 \times [Na^+]_{\text{meas}}} \times 100\% \quad (10)$$

where $1.8 \times [Na^+]$ is the expected Cl⁻ concentration in the original sea salt, in the absence of any loss of Cl⁻ and all Na⁺ in the marine aerosols of sea-salt origin, Cl⁻_{meas} is the chloride measured in the aerosol particles.

Previous studies indicated that the mass ratio of Cl⁻/Na⁺ has a tendency to decrease as the distance from the sea or the coast increases due to the depletion of Cl⁻ (*Chow et al., 1996; Kim et al., 2000; Dasgupta et al., 2007; Park et al., 2015*). Figure 7 illustrates the chloride deficit and the molar ratio of Cl⁻/Na⁺ in PM_{2.5} over sea and at the offshore islands in the Taiwan Strait. The molar ratio of Cl⁻/Na⁺ ranged from 0.93 to 1.08 over sea and from 0.94 to 0.98 at the offshore islands, respectively. *Park et al. (2015)* reported that the molar ratio of Cl⁻/Na⁺ varies significantly with locations, generally high at the coastal sites and low at the inland and urban sites. However, this cruise campaign showed no significant trend of chloride deficit over sea and at the offshore islands. Narrow chloride deficits ranging from 16.2% to 19.2% were observed at the offshore islands, while the chloride deficit varied significantly from 7.6% to 23.0% over sea. Lower chloride deficits were mostly observed for the cruise courses navigated along the coastline of Taiwan Island during the cruise sampling campaigns.

The chloride deficit measured in the marine aerosols sampled at the coastal regions and open seas are compared and summarized in Table 9. In East China Sea, the Cl⁻ deficit reported by *Park et al. (2004)* was accounted for 55% for fine-mode particles and 16% for coarse-mode particles during the normal periods. However, *Hsu et al. (2007)* reported that the Cl⁻ deficits were higher 86% and 98% for fine-mode particles; and 29% and 30% for coarse-mode particles sampled at the Dongsha islands in South China Sea. The higher Cl⁻ deficit on South China Sea was obviously higher than those on East China Sea. In this study, the Cl⁻ deficit at the offshore site and over sea in the Taiwan Strait ranged from 16.2% to 19.2% at the offshore islands and from 7.6% to 20.4% over sea, respectively. The East China Sea and the Taiwan Strait received much more Asian outflow of acidic gases from Asian continent (*Streets et al., 2000; Carmichael et al., 2002; Uematsu, et al., 2010*), while air masses transported toward South China Sea were not only blown from South China but also from biomass burning emitted from the Southeast Asia, particularly the Indochina Peninsula (*Arndt et al., 1997*). The aged air masses were transported toward the South China Sea, causing higher SO₂-rich air pollutants over sea. According to *Li et al. (2016)*, their results indicated that the averaged Cl⁻ deficits ranged from 38.2% to 43.4% at the west-side sites, from 37.0% to 42.7% at the east-side sites, and from 16.2% to 19.4% at the offshore site, respectively, in the Taiwan Strait. The results of Cl⁻ deficits

obtained from these cruise sampling campaigns were consistent quite well with *Park et al. (2004)* and *Tsai et al. (2010)*, which showed a tendency to increase with the distance from the coastline.

4 Conclusions

The mass concentrations and chemical characteristics of marine fine aerosols over sea at the offshore islands during cruise sampling campaigns in the Taiwan Strait were investigated. Overall, the concentrations of $PM_{2.5}$ were generally higher than those of $PM_{2.5-10}$ in the Taiwan Strait. The concentrations of $PM_{2.5-10}$ over sea were always higher than those at the offshore islands, indicating that sea salt highly influenced the marine aerosols. A similar trend was also observed for $PM_{2.5}$, suggesting that fine particles emitted from vessel exhausts were significant contributions to marine fine aerosols and cannot be ignored in the Taiwan Strait. Another possibility was that anthropogenic fine particles emitted from upwind regions such as China, Korea, and/or Japan could be transported toward the Taiwan Strait. Moreover, higher $PM_{2.5}$ concentrations were commonly observed in the daytime rather than those at nighttime.

Chemical analysis of $PM_{2.5}$ indicated that both secondary inorganic aerosols (SIAs) and sea salt were the major portion of $PM_{2.5}$ in the Taiwan Strait. The mass concentrations of SO_4^{2-} were higher than those of NO_3^- , implying that anthropogenic fine particles in the Taiwan Strait came mainly from the sulfur-originated sources rather than the nitrogen-originated sources. The contributions of sea salt to $PM_{2.5}$ sampled over sea were higher than those at the offshore islands. Moreover, the mass concentrations of estimated nss-WSI in $PM_{2.5}$ were much higher than those of ss-WSI both at the offshore islands and over sea, indicating that fine particles in the Taiwan Strait was mainly influenced by anthropogenic particles rather than sea salt. This phenomenon was not only observed at the offshore islands, but was also found in the open sea. The contributions of nss-WSI to $PM_{2.5}$ at the offshore islands were obviously higher than those over sea, while the contributions of ss-WSI to $PM_{2.5}$ at the offshore islands were generally lower than those over sea.

The major metallic contents of marine $PM_{2.5}$ were crustal elements and followed by anthropogenic elements. The concentrations of anthropogenic metallic elements (Zn, Mn, Pb, Cr, and Ni) over sea were higher than those at the offshore islands. These anthropogenic metallic elements came probably from industrial process emissions, fuel and coal burning, and vehicular and vessel exhausts. However, higher mass ratios of Ni/Al and Ni/Fe over sea (0.35 and 0.88, respectively) than those at the offshore islands (0.30 and 0.69, respectively) suggested that shipping emissions had higher influences on marine fine particles than crustal dusts in open sea while compared to those at the offshore islands. This study also revealed that primary organic carbons (POC) were major source of $PM_{2.5}$ over sea and at the offshore islands while compared to secondary organic carbons (SOC).

This cruise sampling campaign further showed no significant trend of chloride deficit over sea and at the offshore islands. A narrow chloride deficit ranging from 16.2% to 19.2% was observed at the offshore islands, while the chloride deficits varied significantly from 7.6% to 23.0% over sea. Lower chloride deficits were commonly observed for the cruise courses navigated along the coastline of Taiwan Island during the cruise sampling campaigns.

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Table 1. Summary of QA/QC results for the analysis of chemical species in this study.

Species	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cr	Ni	Al	Fe	Mn	Zn	Ca	K	Mg	Pb
R ²	0.999	0.999	0.997	0.997	0.998	0.999	0.998	0.999	0.999	0.999	0.997	0.999	0.999	0.999	1.000	0.997	0.999	0.999	1.000
MDL	0.011	0.036	0.058	0.070	0.021	0.010	0.030	0.012	0.066	0.014	0.004	0.050	0.009	0.016	0.004	0.028	0.050	0.029	0.030
Blank	ND	0.070	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Duplicate Analysis																			
RPD (%)	1.08	2.03	2.04	9.84	2.09	1.94	1.11	1.06	1.09	0.52	0.51	0.53	0.53	0.47	0.52	0.54	0.54	0.52	0.58
Spike analysis																			
Recovery Rate (%)	111.1	109.7	105.9	96.2	90.85	91.3	105.2	95.05	91.65	94.0	1.04	97.0	91.5	105.5	90.5	102.0	104.5	106.5	106.5

R²: determination coefficient calibration curve ; MDL: method detection limit ; RPD: relative percentage difference; Units of MDL and Blank: µg m⁻³

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Table 2. The mass concentrations of PM_{2.5} and PM_{2.5-10}, and the mass ratios of PM_{2.5}/PM₁₀ over sea and at the offshore islands during three cruise sampling campaigns.

5	Sampling Sites	Sampling Abbr.	Day/Night Samples	Sampling Duration	Sampling Periods	PM _{2.5} (µg m ⁻³)	PM _{2.5-10} (µg m ⁻³)	PM ₁₀ (µg m ⁻³)	PM _{2.5} /PM ₁₀ (%)	Reference
	On the Island	W13	Daily	24 hrs	Winter 2013	28.2	23.3	51.5	54.8	
		S14	Daily	24 hrs	Spring 2014	22.7	19.7	42.4	53.5	
		W14	Daily	24 hrs	Winter 2014	38.1	30.3	68.3	55.7	
10	Over Sea	W13C1	Nighttime	8 hrs	Winter 2013	21.5	22.2	43.7	49.2	
		W13C2	Daytime	12 hrs		27.0	22.2	49.2	55.0	
		W13C3	Nighttime	12 hrs		26.0	23.4	49.3	52.6	
		S14C1	Nighttime	12 hrs	Spring 2014	30.2	29.3	59.5	50.8	This study
		S14C2	Daytime	12 hrs		31.7	31.1	62.7	50.5	
		S14C3	Nighttime	12 hrs		31.3	30.5	61.8	50.7	
15		S14C4	Daytime	16 hrs		33.4	31.2	64.6	51.7	
		W14C1	Nighttime	8 hrs	Winter 2014	38.6	52.5	91.1	42.4	
		W14C2	Daytime	12 hrs		43.5	55.3	98.8	44.0	
		W14C3	Nighttime	12 hrs		38.3	51.0	89.3	42.9	
20	West-side of the Taiwan Strait	XM,FZ	Daily	24 hrs	Winter 2013	67.4	54.7	122.0	55.2	
					Spring 2014	78.6	51.0	129.6	60.6	
					Winter 2014	85.8	75.0	160.8	50.3	Li et al., 2016a
	East-side of the Taiwan Strait	KH, TC, TP	Daily	24 hrs	Winter 2013	48.0	22.98	71.0	67.6	
					Spring 2014	33.8	28.5	62.3	54.3	
					Winter 2014	53.4	54.6	108.0	49.5	

25 Islands represents the Xiaomen site at the Penghu Islands.

Table 3. Chemical composition of PM_{2.5} sampling over sea and at the offshore islands during three cruise sampling campaigns.

Cruise Campaigns	Winter 2013 (W13) (n=4)				Spring 2014 (S14) (n=5)					Winter 2014 (W14) (n=4)			
Sampling Sites	Islands		Over Sea		Islands		Over Sea			Islands		Over Sea	
Species	W13	W13C1	W13C2	W13C3	S14	S14C1	S14C2	S14C3	S14C4	W14	W14C1	W14C2	W14C3
PM _{2.5}	28.2	21.5	27.0	26.0	22.7	30.2	31.7	31.3	33.4	37.6	38.6	43.5	38.3
SO ₄ ²⁻	4.8	3.6	4.1	4.2	4.3	4.9	4.4	4.6	5.0	6.5	5.2	5.6	5.3
NO ₃ ⁻	3.1	2.5	2.6	2.9	2.3	3.0	2.9	2.9	3.2	4.0	3.2	3.4	3.4
NH ₄ ⁺	1.2	0.8	1.0	1.2	1.1	2.0	1.9	1.9	2.1	2.2	2.4	2.6	2.3
Cl ⁻	1.8	1.7	1.9	2.0	1.5	2.2	2.1	2.1	2.2	1.4	2.8	2.8	2.9
Na ⁺	1.2	1.2	1.3	1.3	1.0	1.5	1.3	1.5	1.4	1.0	1.9	2.0	1.9
K ⁺	1.5	0.5	0.7	0.5	1.1	0.4	0.5	0.3	0.5	0.9	0.5	0.7	0.6
Mg ²⁺	0.5	0.6	0.6	0.6	0.5	0.7	0.7	0.6	0.6	0.6	0.8	0.8	0.6
Ca ²⁺	0.3	0.3	0.4	0.3	0.5	0.4	0.4	0.4	0.5	0.6	0.5	0.6	0.6
A/C	0.9	0.9	0.9	1.0	0.8	0.8	0.8	0.8	0.8	0.9	0.7	0.7	0.8
Mg	0.8	0.7	0.7	0.8	0.6	0.7	0.8	0.7	0.8	0.6	0.8	0.9	0.8
K	1.7	0.7	0.8	0.8	1.5	0.6	0.6	0.6	0.7	1.2	0.8	0.9	0.7
Ca	0.4	0.7	0.6	0.6	0.6	0.8	0.8	0.7	0.8	0.7	0.6	0.7	0.7
Cr	0.1	0.0	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.3	0.2	0.3	0.3
Mn	0.2	0.2	0.2	0.3	0.2	0.2	0.3	0.3	0.3	0.2	0.2	0.2	0.2
Fe	0.4	0.1	0.4	0.2	0.4	0.2	0.3	0.2	0.3	0.3	0.2	0.3	0.3
Zn	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2
Al	0.9	0.3	0.5	0.6	0.6	0.7	0.7	0.7	0.7	1.2	0.8	0.8	0.8
Pb	0.1	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.3	0.4	0.3
Ni	0.3	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
OC	4.1	2.3	2.9	2.5	2.8	3.1	3.3	3.0	3.2	5.1	4.2	5.2	4.5
EC	1.5	1.1	1.3	1.1	1.2	1.3	1.2	1.2	1.4	2.0	1.7	2.1	1.8
Sea salt	3.6	3.5	3.8	3.9	3.0	4.5	3.9	4.2	4.3	2.9	5.5	5.7	5.7
Sea salt/PM _{2.5} (%)	12.7	16.1	13.9	15.0	13.2	14.7	12.4	13.4	12.8	7.7	14.3	13.1	14.8
WSI/PM _{2.5} (%)	50.8	52.0	46.1	49.9	54.1	49.9	44.4	45.3	46.4	45.8	44.7	42.7	45.7
Metal/PM _{2.5} (%)	19.3	15.4	14.7	16.7	15.7	13.5	13.7	13.1	14.6	12.5	12.3	12.3	13.4
Carbon/PM _{2.5} (%)	19.9	15.6	15.4	14.0	17.9	14.6	14.3	13.3	13.9	18.8	15.2	16.8	16.6

Unit: $\mu\text{g m}^{-3}$; n: sample numbers; WSI: water-soluble ionic species; Metal: total metallic contents; Carbon: total carbonaceous contents; A/C: the ratio of micro-equivalent concentrations of anions and cations

Table 4. The concentrations of sea-salt and non-sea salt water-soluble ionic species of PM_{2.5} over sea and at the offshore islands during three cruise sampling campaigns.

Cruise Campaigns	Winter 2013 (W13)				Spring 2014 (S14)					Winter 2014 (W14)			
Sampling Sites	Islands	Over Sea			Islands	Over Sea				Islands	Over Sea		
Species	W13	W13C1	W13C2	W13C3	S14	S14C1	S14C2	S14C3	S14C4	W14	W14C1	W14C2	W14C3
PM _{2.5}	28.2	21.5	27.0	26.0	22.7	30.2	31.7	31.3	33.4	37.6	38.6	43.5	38.3
nss-K ⁺	1.4	0.4	0.6	0.5	1.0	0.4	0.5	0.2	0.4	0.9	0.4	0.6	0.5
nss-Mg ²⁺	0.4	0.4	0.4	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.6	0.6	0.4
nss-Ca ²⁺	0.2	0.3	0.4	0.3	0.5	0.3	0.4	0.3	0.5	0.5	0.4	0.6	0.5
nss-SO ₄ ²⁻	4.5	3.3	3.7	3.9	4.0	4.5	4.0	4.2	4.7	6.3	4.7	5.2	4.8
NO₃⁻	3.1	2.5	2.6	2.9	2.3	3.0	2.9	2.9	3.2	4.0	3.2	3.4	3.4
ss-K ⁺	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1
ss-SO ₄ ²⁻	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.4	0.4	0.3	0.5	0.5	0.5
ss-Ca ²⁺	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1
ss-Mg ²⁺	0.1	0.1	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2
meas-Cl ⁻	1.8	1.7	1.9	2.0	1.5	2.2	2.1	2.1	2.2	1.4	2.8	2.8	2.9
meas-Na ⁺	1.2	1.2	1.3	1.3	1.0	1.5	1.3	1.5	1.4	1.0	1.9	2.0	1.9

Unit: $\mu\text{g m}^{-3}$; nss: non-sea salt ions; ss: sea salt ions; meas: measured ions
 Islands represents the Xiaomen site at the Penghu Islands

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Table 5. The percentages of metallic elements, Ni/Fe, and Ni/Al in PM_{2.5} sampled in Asia.

Sampling Locations	Sampling Periods	Ti μg m ⁻³	Fe μg m ⁻³	Mn μg m ⁻³	Ca μg m ⁻³	Mg μg m ⁻³	K μg m ⁻³	Al μg m ⁻³	Pb μg m ⁻³	Ni μg m ⁻³	Cr μg m ⁻³	Zn μg m ⁻³	Ni/Fe	Ni/Al	References
Penghu Islands	Dec 2013- Dec 2014	1.2±0.6	1.3±0.4	0.7±0.3	2.0±0.9	2.3±1.2	2.2±1.6	3.0±1.2	0.7±0.1	0.9±0.3	0.6±0.1	0.6±0.2	0.7±0.3	0.3±0.1	This study
Taiwan Strait	Dec 2013- Dec 2014	1.1±0.3	0.8±0.2	0.8±0.2	2.2±1.2	2.4±1.3	2.3±0.9	2.0±1.0	0.8±0.1	0.7±0.1	0.5±0.1	0.4±0.1	0.9±0.4	0.4±0.1	This study
West-side of Taiwan Strait	June 2013- April-2015	1.1±0.4	0.9±0.3	0.6±0.1	2.0±1.0	1.9±0.9	2.5±1.3	1.2±0.5	0.6±0.3	0.6±0.2	0.4±0.2	0.7±0.4	0.7±0.2	0.5±0.2	Li et al., 2016
East-side of Taiwan Strait	June 2013- April-2015	1.0±0.3	1.0±0.5	0.7±0.2	2.2±1.3	2.4±1.3	3.1±1.1	1.1±0.6	0.7±0.3	0.7±0.2	0.6±0.1	0.7±0.3	0.7±0.3	0.6±0.2	Li et al., 2016
Over Sea of Taiwan Strait	June 2013- April-2015	1.2±0.2	1.0±0.5	0.8±0.2	2.8±1.7	3.1±1.8	4.5±2.0	1.2±0.3	1.0±0.3	0.8±0.2	0.9±0.3	0.8±0.4	0.8±0.3	0.7±0.2	Li et al., 2016
East China Sea	Spring 2011	0.8	5.3	0.0	6.5	2.9	-	12.4	0.0	0.0	-	0.2	-	-	Zhao et al., 2015
Taipei	Spring 2000	0.2	0.0	0.1	2.0	0.6	-	3.0	0.1	-	-	0.3	-	-	Hsu et al., 2004
Bohai Sea	2006-2007	0.0	0.1	0.0	4.7	3.1	-	1.1	0.0	-	-	0.0	-	-	Ji et al., 2011
East China Sea	Spring 2008	0.1	0.8	0.0	1.4	0.8	-	0.8	0.0	-	-	0.9	-	-	Wu et al., 2010

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Table 6. Comparison of OC and EC around the Taiwan Strait and East China Sea.

City	Location	Sampling Periods	PM _{2.5} μg m ⁻³	TC μg m ⁻³	OC μg m ⁻³	EC μg m ⁻³	OC/EC	References
Xiamen	Southeast coastline of China	2011-2013	51.5±20.4	10.0	8.7±4.0	1.3±0.2	6.6	Wu et al., 2015
Quanzhou		2011-2013	53.9±14.8	10.5	10.1±3.0	1.5±0.3	6.8	Wu et al., 2015
Putian		2011-2013	50.3±14.4	9.3	8.1±2.0	1.2±0.2	7.0	Wu et al., 2015
Fuzhou		2011-2013	58.7±14.8	13.8	12.0±2.9	1.8±0.4	4.2	Wu et al., 2015
Xiamen		2009-2010	72.1±34.2	22.6	19.3±9.5	3.3±1.3	5.8	Zhang et al., 2011
Fuzhou		2007-2008	44.3±16.3	10.7	8.50	2.2	3.9	Xu et al., 2012
Xiamen		2013-2015	60.8±23.7	10.5	7.9	2.6	3.0	Li et al., 2016a
Fuzhou		2013-2015	56.0±16.3	10.1	8.0	2.1	3.5	Li et al., 2016a
Kaohsiung-Inland	Southwestern coastline of Taiwan Strait	2006-2009	56.5	7.3	5.4	1.9	2.9	Tsai et al., 2010
Kaohsiung-offshore		2006-2009	46.1	5.2	3.4	1.8	1.9	Tsai et al., 2010
Kaohsiung	Southwestern coastline of Taiwan Strait	2013-2015	43.8±19.6	7.6	5.2	2.4	2.2	Li et al., 2016a
Taichung	Central coastline of Taiwan Strait	2013-2015	37.5±11.3	6.7	4.5	2.2	2.1	Li et al., 2016a
		2003-2007	47.9±2.0	13.2	9.5±0.4	3.7±0.1	2.6	Chou et al., 2010
New Taipei City Cap Fuguei	North coastline of Taiwan Strait	2013-2015	26.1±6.7	5.0	3.6	1.4	2.6	Li et al., 2016a
		2003-2007	28.0±0.9	5.1	3.8±0.2	1.3±0.1	2.9	Chou et al., 2010
Penghu islands	Islands on Taiwan Strait	2003-2007	23.3±0.7	3.0	2.2±0.2	0.8±0.0	2.8	Chou et al., 2010
		2013-2015	26.3±6.2	4.4	3.2	1.2	2.6	Li et al., 2016a
		2013-2015	29.5±6.2	5.6±1.3	4.0±0.9	1.6±0.3	2.6	In this study
Over sea	Taiwan Strait	2013-2015	32.2±6.3	4.8±1.2	3.4±0.9	1.4±0.3	2.4	In this study

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Table 7. Comparison of chemical composition ratios for PM_{2.5} around the Taiwan Strait and East China Sea.

Sampling Sites	Location	EC/TC	K ⁺ /TC	NO ₃ ⁻ /nss-SO ₄ ²⁻	TC/SO ₄ ²⁻	Reference
Xiamen	Southeast coastline of China	0.25±0.01	0.16±0.08	0.57±0.11	0.96±0.15	Li et al., 2016a
Fuzhou	Southeast coastline of China	0.20±0.02	0.14±0.09	0.68±0.03	1.25±0.27	Li et al., 2016a
Penghu	Islands on Taiwan Strait	0.26±0.04	0.22±0.05	0.59±0.06	1.07±0.12	Li et al., 2016a
Kaohsiung	Southwestern coastline of Taiwan Strait	0.31±0.02	0.11±0.07	0.52±0.13	0.98±0.13	Li et al., 2016a
Taichung	Central coastline of Taiwan Strait	0.32±0.02	0.12±0.07	0.64±0.06	1.05±0.09	Li et al., 2016a
Taipei	North coastline of Taiwan Strait	0.27±0.04	0.13±0.10	0.63±0.09	1.06±0.16	Li et al., 2016a
Fuzhou	Southeast coastline of China	0.2	0.02	0.41	0.99	Xu et al., 2012
Xiamen	Southeast coastline of China	0.17	0.05	0.47	1.17	Zhang et al., 2012
Xiamen	Southeast coastline of China	0.18	-	0.45	1.19	Zhao et al., 2015
Qingdao	Southeast coastline of China	0.19	0.09	0.95	1.54	Cao et al., 2012
Hong Kong	Southeast coastline of China	0.34	0.04	1.02	0.94	Cao et al., 2012
Shanghai	Central coastline of China	0.24	0.04	1.03	1.51	Cao et al., 2012
Seoul, Korea	Korea	0.25	0.03	0.87	1.72	Heo et al., 2008
Yokohama	Southeast coastline of Japan	0.34	0.02	1.07	1.5	Khan et al., 2010
W13	Taiwan Strait	0.30±0.02	0.17±0.05	0.71±0.03	0.99±0.12	In this study
S14	Taiwan Strait	0.29±0.01	0.13±0.07	0.66±0.05	0.94±0.05	In this study
W14	Taiwan Strait	0.28±0.01	0.10±0.02	0.67±0.02	1.18±0.08	In this study

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Table 8. The distribution of major chemical components of PM_{2.5} at the coastal sites around the Taiwan Strait and East China Sea.

Sampling Sites	Location	Average Conc.	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Organic Materials	Crustal Materials	Elemental Carbon	Sea Salt	References
Xiamen	Southeast coastline of China	59.2	11.1	6.0	4.8	12.7	12.6	2.5	4.5	Li et al., 2016a
Fuzhou	Southeast coastline of China	53.6	8.0	5.3	4.2	12.8	14.2	2.0	4.9	Li et al., 2016a
Penghu	Islands on Taiwan Strait	23.6	3.9	2.1	0.8	4.6	7.8	1.1	2.1	Li et al., 2016a
Kaohsiung	Southwestern coastline of Taiwan Strait	41.8	7.6	3.7	1.9	8.2	10.4	2.3	3.7	Li et al., 2016a
Taichung	Central coastline of Taiwan Strait	35.6	5.9	3.5	1.5	6.9	8.7	2.0	2.6	Li et al., 2016a
Taipei	North coastline of Taiwan Strait	24.9	4.4	2.6	1.0	5.5	7.0	1.3	2.2	Li et al., 2016a
Xiamen	Southeast coastline of China	74.2	12.6	7.4	6.7	25.2	13.4	5.2	-	Cao et al., 2012
Shanghai	Central coastline of China	139.4	20.9	16.7	13.9	44.6	29.3	8.4	-	Cao et al., 2012
Qingdao	Southeast coastline of China	134.8	21.6	18.9	14.8	41.8	24.3	5.4	-	Cao et al., 2012
Hong Kong	Southeast coastline of China	88.4	21.2	9.7	7.1	22.1	15.9	6.2	-	Cao et al., 2012
Seoul	Korea	37.6	5.8	5.2	3.7	11.4	2.8	2.9	-	Heo et al., 2008
Yokohama	Southeast coastline of Japan	37.6	6.9	1.8	4.1	8.2	-	3.5	-	Khan et al., 2010
W13	Taiwan Strait	25.7	4.2	2.8	1.1	4.7 [†]	5.4 [*]	1.2	3.7 ^{**}	In this study
S14	Taiwan Strait	29.8	4.6	2.9	1.8	5.0 [†]	7.2 [*]	1.3	4.0 ^{**}	In this study
W14	Taiwan Strait	39.5	5.7	3.5	2.4	7.6 [†]	8.7 [*]	1.9	4.9 ^{**}	In this study

5 Unit: $\mu\text{g m}^{-3}$; OM[†]=1.6*OC (in this study); CM^{*}=12*[Al] (in this study); Sea Salt^{**}=[Cl]⁻+1.47*[Na]⁺ (in this study).

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Table 9. Comparison of chloride deficit measured in marine aerosols at the coastal regions and in the remote oceans.

Regions/Seasons	Sample Size Range	Cl ⁻ Deficit Percentages	References
South China Sea/winter	Coarse and fine aerosols	86% and 98% for fine-mode; 29% and 30% for coarse-mode	Hsu, et al., 2007
East China Sea/(Korea) spring during Asian dust periods (ADS) and non-Asia dust periods (NADS)	Coarse and fine aerosols	40% for fine-mode and 13% for coarse-mode during ADS periods, while during NADS periods 55% for fine-mode and 16% for coarse-mode	Park et al., 2004
East coast of US/spring	Size-segregated aerosols	14%	Keene and Savole, 1998
Tropical northern Atlantic ocean/ spring	Coarse and fine aerosols	29.7±9.9% for fine-mode and 11.9±13.3% for coarse-mode.	Johansen et al., 2000
Northern Indian Ocean/ late spring and summer	SW monsoon and inter-monsoon period	3.5±6.3% in SW monsoon and 15.0±9.0 in the inter-monsoon periods	Johansen et al., 1999
Tropical Arabian Sea/spring	Coarse and fine aerosols	89±9% for fine-mode and 25.6±21.3% for coarse-mode.	Johansen and Hoffmann, 2004
NW Mediterranean Sea	Size-segregated aerosols	18.5±14.5%	Sellegri et al., 2001
Southwestern coastal area of Taiwan Strait/ inland and offshore areas	Coarse and fine aerosols	33.8±9.7% on inland and 22.5±6.9% on offshore for fine-mode; 33.8±9.1% on inland and 15.4±3.1% on offshore for coarse-mode.	Tsai et al., 2010
West-side, east-side, offshore areas and sampling boat on sea of Taiwan Strait (2013-2015)	Fine aerosols	40.1% on west-side, 41.2% on east-side, 27.8% on offshore area, and 23.5% on sea	This study
Offshore and sea samples at the Taiwan Strait/ winter and spring	Fine aerosols	16.20% to 19.19% at offshore site, 7.56% to 20.41% over sea	This study
Coastal Antarctica	Size-segregated aerosols	10–20%	Jourdain and Legrand, 2002; Rankin and Wolff, 2003

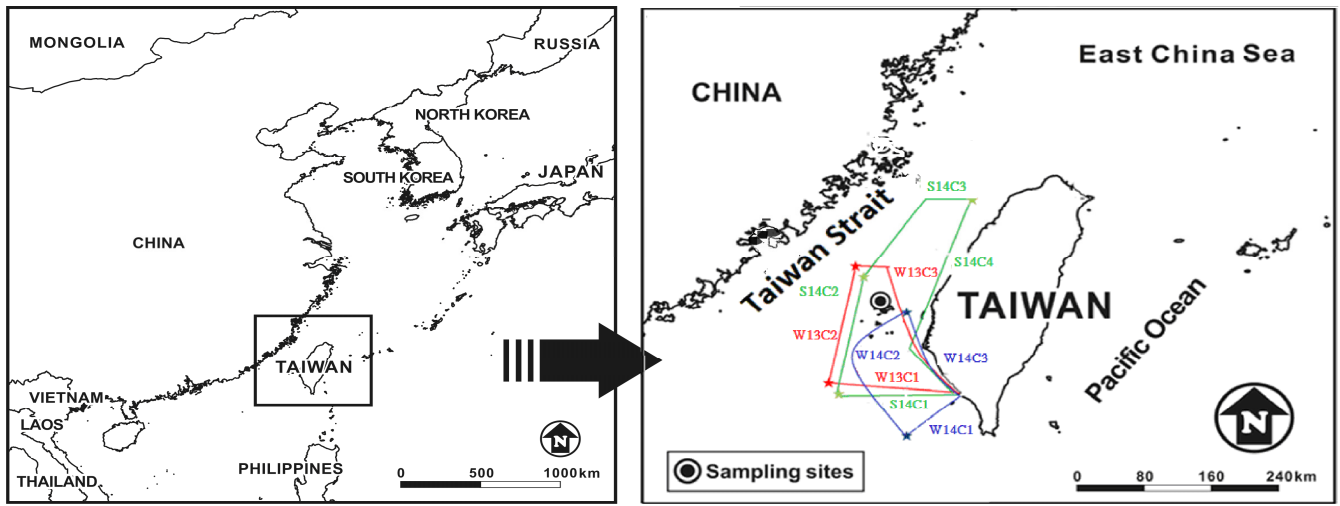


Figure 1. The navigation routes and courses during three cruise sampling campaigns in the Taiwan Strait.

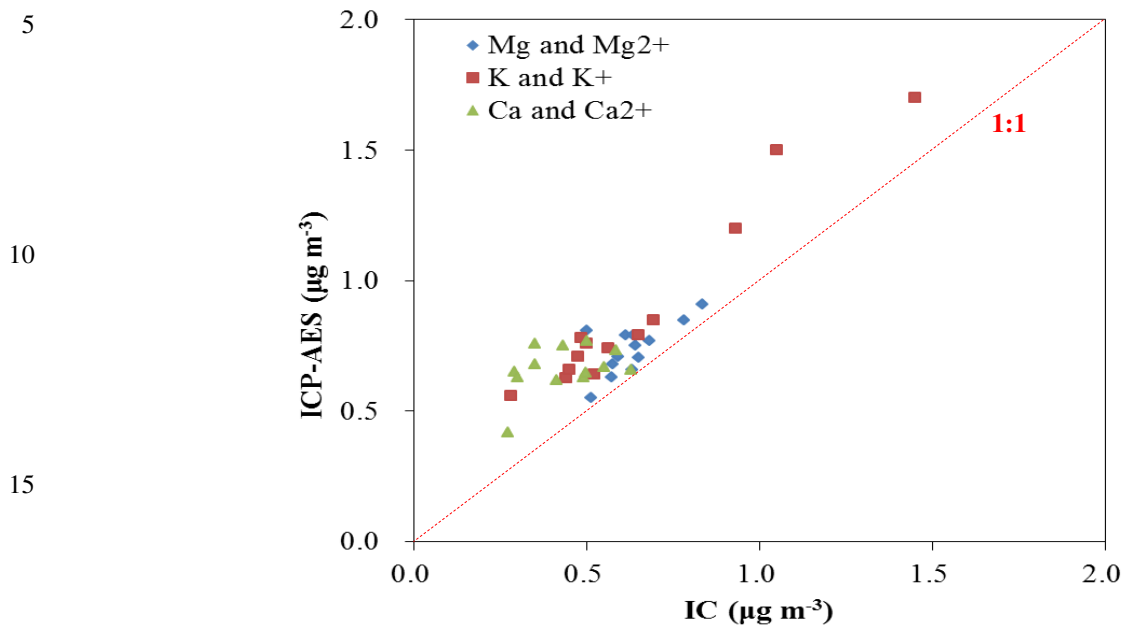


Figure 2. Comparison of the the chemical species of $PM_{2.5}$ analyzed with IC and ICP-AES.

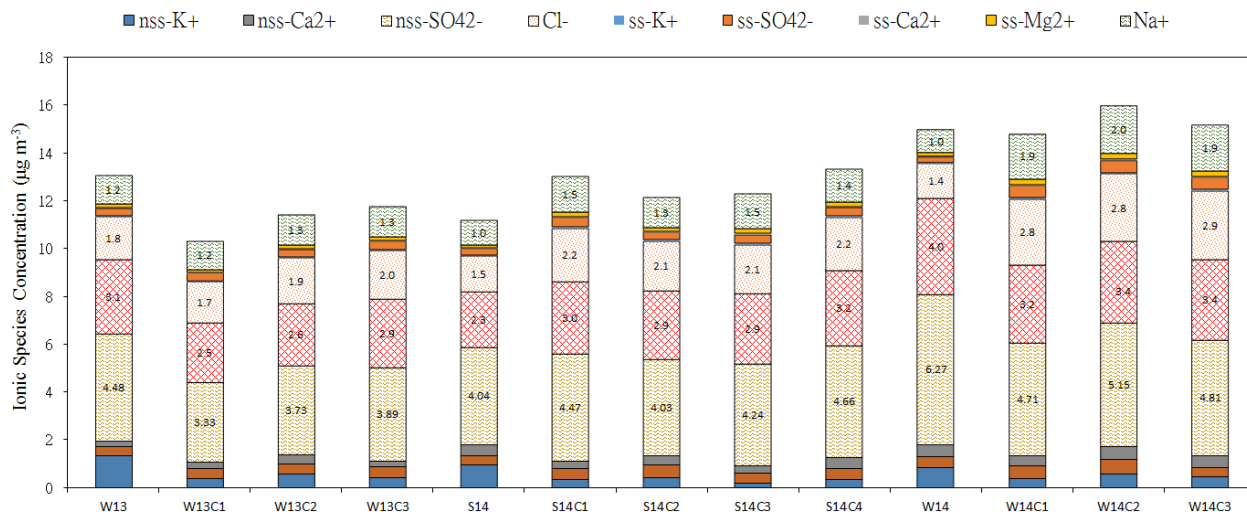
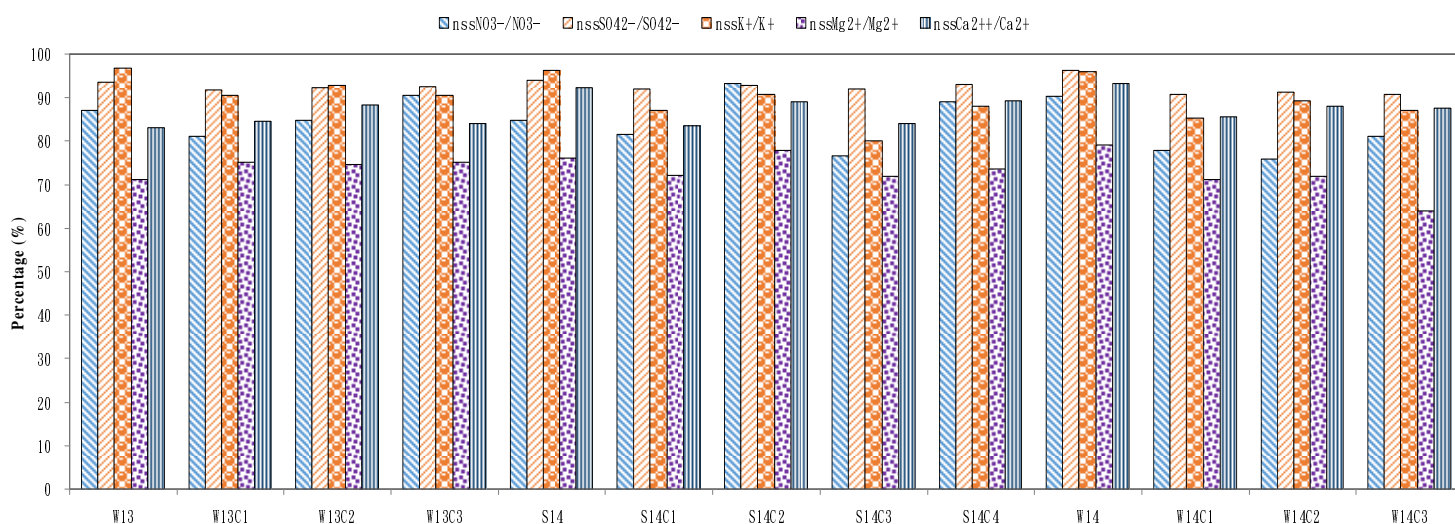


Figure 3. The concentrations of sea salt- and non-sea salt-water-soluble ions and their contribution to $PM_{2.5}$ sampled during the cruise sampling campaigns.

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20 Figure 4. The percentages of non-sea salt water-soluble ionic species in the measured water-soluble ionic species of $PM_{2.5}$ sampled over sea and at the offshore islands during the cruise sampling campaigns.

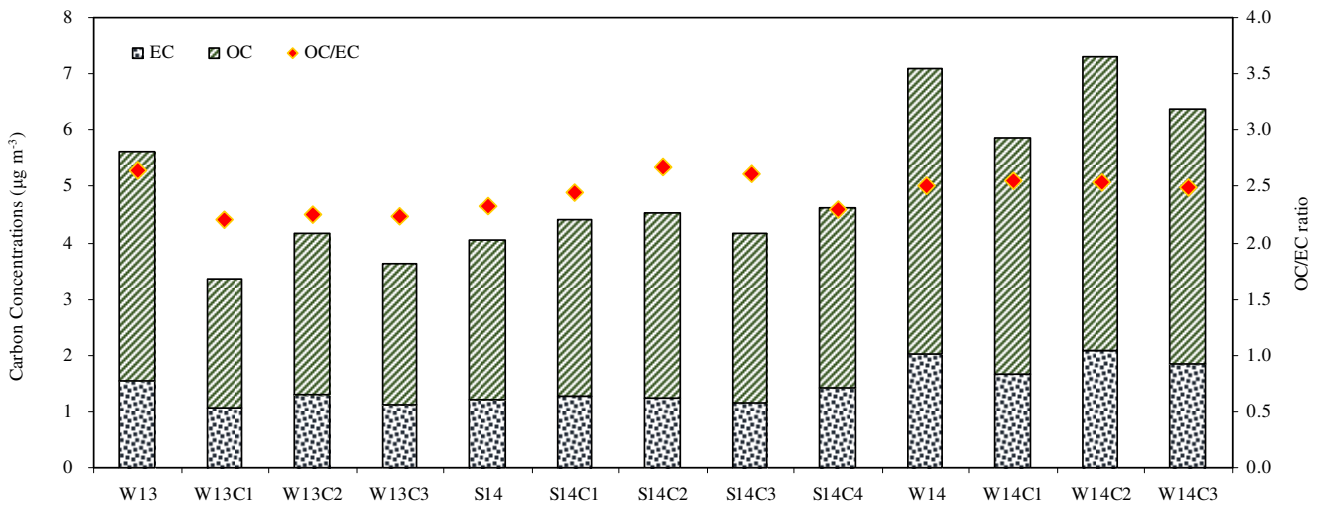
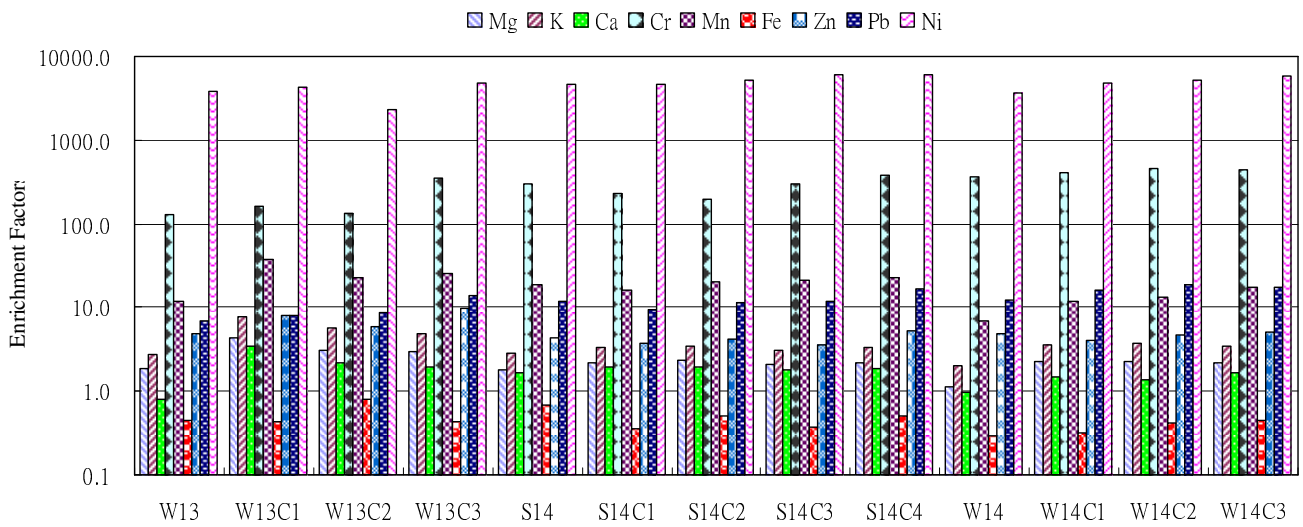


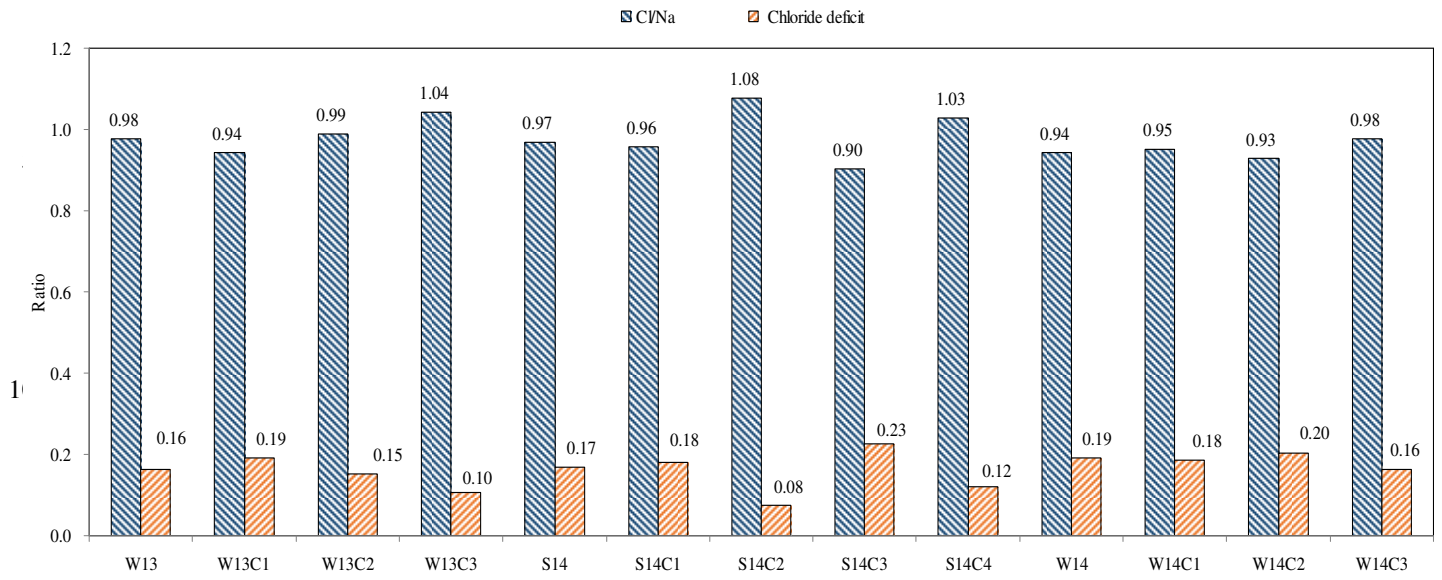
Figure 5. The variation of estimated concentrations of OC, EC and OC/EC ratios in PM_{2.5} over sea and at the offshore islands during the cruise sampling campaigns.



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Figure 6. The enrichment factors of metallic elements in PM_{2.5} over Sea and at the Offshore Islands.

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15 **Figure 7. The chloride deficit and the molar ratio of Cl/Na⁺ in PM_{2.5} over sea and at the offshore islands during the cruise sampling campaigns.**

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