Secondary Inorganic Ions Characteristics in PM$_{2.5}$ Along Offshore and Coastal Areas of the Megacity Shanghai

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Abstract  Secondary inorganic ions are important constituents of PM$_{2.5}$ that play an important role in global climate change through direct and indirect radiative forcing. To investigate the influence of ship emissions on coastal cities, we launched a cruise ship campaign offshore of the East China Sea (ECS) and two field observation sites in the megacity of Shanghai using 1-hr time-resolved water-soluble ion chromatography from June 3 to June 27, 2017. Three main secondary inorganic soluble ions in the atmosphere of the ECS, that is, non-sea-salt sulfate (nss-SO$_4^{2-}$), NO$_3^-$ and NH$_4^+$, were 8.87, 4.94, and 4.65 µg m$^{-3}$, respectively. While their values at the Pudong (PD) station in urban Shanghai were 6.33, 9.47, and 4.74 µg m$^{-3}$ and at the Dianshanhu (DSH) station in suburban Shanghai were 7.33, 10.01, and 6.78 µg m$^{-3}$, respectively. Nss-SO$_4^{2-}$ was dominant in the PM$_{2.5}$ in the atmosphere of the ECS (nss-SO$_4^{2-}$/NO$_3^-$ = 1.8), and mainly distributed near the Zhoushan Islands of the ECS. This indicated significant contributions from ship emissions. Based on the Community Multiscale Air Quality model, two main sources of nss-SO$_4^{2-}$ were identified: emissions and horizontal transport. These comprised over 90% of the nss-SO$_4^{2-}$. The influence of ship emissions reached up to 31.6% of the total nss-SO$_4^{2-}$ alongside the cruise ship and near coastal parking ports in the Yangtze River Delta area, suggesting that more attention should be paid to ship emissions.

1. Introduction

With rapid economic development as well as dramatic population growth, the affiliations between coastal urban megacities have become increasingly thoroughly interconnected, especially through marine transportation (F. Xiao et al., 2013). Over the past several decades, lying over the broad shelf of the Northwest Pacific Ocean, the East China Sea (ECS) has played an important role in ocean transport capacity around the world (Kang et al., 2017; G. Zhang et al., 2007). The coastal urban megacity Shanghai handles more than 20% of the world's cargo throughput and is also the largest petrochemical production and fishery resource area (Harshit et al., 2009). The transportation and industrial activities in the ECS have caused both a meteoric increases in the industrialization and urbanization of Shanghai, along with significant increases in regional air pollution (Moldanová et al., 2009; F. Wang et al., 2016). In addition, influenced substantially by the East Asian monsoon, especially during the summer season, marine fine particle matters are subject to long-range transport to inland areas, and these mix with local emissions. This can change precipitation patterns and regional atmospheric stability (Fan et al., 2016; Mao et al., 2020). Therefore, more scientific attention should be paid to investigate the loadings, particle compositions, and sources of marine aerosols, especially in coastal urban megacities and offshore regions where the urban-ocean interaction is intense.

Oceans cover more than 70% of the Earth’s surface, and marine aerosols contribute significantly to the global aerosol load (O’Dowd et al., 2004), playing an important role in cloud albedo, atmospheric chemical reactions, global climate change, and the biogeochemical cycling of nutrients (Davidson et al., 2005; S. Liu et al., 2015; O’Dowd & Leeuw, 2007; Qi et al., 2011). The physical and chemical properties of marine aerosol particles have been investigated in different locations, such as the western North Pacific Oceans (Kawamura et al., 2003), the Atlantic and Indian Oceans (Massling et al., 1999), Yosemite National Park, USA (Carriero et al., 2005), Ulaanbaatar (Jung et al., 2011), Chichijima Island in the western North Pacific (Boreddy
et al., 2014), and a rural site in Tanzania (Boreddy et al., 2015). The atmosphere consists of 30%–80% of marine fine particle matters (Q. Fu et al., 2008; H. W. Xiao et al., 2017), and secondary inorganic ions have a great effect on hydroscopic properties and particle acidity. This may influence Earth’s radiation balance, fog formation and cloud physics, and visibility degradation, as well as human health (Z. Liu et al., 2020; Zou et al., 2017).

Many field campaigns have been conducted, and research has focused on the chemical characteristics of secondary inorganic ions in fine particle matter in offshore areas as well as coastal cities. The mass concentration (Boreddy et al., 2014, 2015), spatial and seasonal variability (Lee et al., 2016), hygroscopic properties (Ye et al., 2013), source apportionment (Wei et al., 2013), acid-base equilibrium (Fang & Xu, 2007), and relationship between secondary inorganic ions have been studied in the Yangtze River Delta region (YRD; Arimoto et al., 1996). H. W. Xiao et al. (2017) discovered that fossil fuel combustion (especially coal in the Chinese coastal regions) was the major source of secondary inorganic ions such as NO$_3^-$ (69.5%) and SO$_4^{2-}$ (57.5%; H. W. Xiao et al., 2017). Hsu et al. (2007) discovered that the nss-SO$_4^{2-}$ to NO$_3^-$ mass ratios reached 3.8 ± 1.9 in East Asia and around the Western Pacific Ocean (Hsu et al., 2007). Boreddy and Kawamura (2016) observed that large amounts of secondary inorganic ions are increasingly transported from the Asian continent to the western North Pacific especially in spring and winter times (Boreddy & Kawamura, 2016). Fan et al. (2016) demonstrated that ship emissions have an important impact on the YRD region and the ECS (Fan et al., 2016). Targeting the physicochemical properties of marine aerosols, many ship-borne cruises have been launched all over the world. Ganguly and Dilip (2005) observed a mass concentration and size distribution of aerosols over the Bay of Bengal (Ganguly & Dilip, 2005). Romagnoli et al. (2019) analyzed organic molecular markers in marine aerosols from atmospheric samples over the Western Mediterranean (Romagnoli et al., 2019). Kong et al. (2014) conducted an intensive sampling campaign at an offshore site of the YRD region to study ion chemistry in the atmosphere (Kong et al., 2014). However, previous studies that have determined the properties of secondary inorganic ions in fine particle matters have typically depended on filter sampling and subsequent offline chemical analyses, but these studies have failed to capture rapid spatial and temporal changes in the atmosphere over long periods of time.

In this study, ship-based time-resolved water-soluble ion (WSI) chromatography is used to measure the concentration of secondary inorganic ions surrounding the ECS in June 2017, and the spatial distribution near the cruise route is described. These results are then compared with data from the coastal megacity of Shanghai. The relationship between the cation/anion ratio ($R_{\text{C/A}}$) and the mass concentration of PM$_{2.5}$ is also investigated. Moreover, by applying Community Multiscale Air Quality (CMAQ) modeling, the urban-ocean interaction of secondary inorganic ions are discussed. By utilizing these observed data sets and the modeling analysis, we can obtain an enhanced understanding of the properties of secondary inorganic ions between the offshore area and a coastal urban megacity and provide essential information for regulating air pollution in marine areas.

2. Methodology

2.1. Cruise Route and Sampling Sites

The ship cruise campaign was conducted over the offshore marine area of the ECS from the Yangtze River Estuary and primarily surrounding the Zhoushan Archipelago during the summer of June 2 to 30, 2017 during which the summer monsoon prevailed. All the observational instruments were placed inside a mobile platform named Hongde77 that was settled in the middle of a sampan. The chimney of the device was on the stern to avert creating smoke pollution of its own. In addition, by using a wind vane in front of the ship, we collected the analyzed air masses when the wind direction was between 120° and 240° (compared to the sailing direction) to avoid the smoke of the ship. At the same time, urban observations were implemented at two sites: the Dianshanhu (DSH) station (120°54′11.86″E, 31°04′26.06″N) and the Pudong (PD) station (121°35′9.67″E, 31°12′25.26″N). The exact date and cruise route during the observation period are depicted in Figure 1.
2.2. Ship-Based and Land-Based Time-Resolved Water-Soluble Ion Chromatography

An ambient ion monitor (AIM, URG-9000D, Thermo Corporation) provided time-resolved direct measurements of cations and anions found both in the particulate and gaseous phases. The instrument consisted of a particle collection unit, two ion chromatograph analyzers (IC) for cation and anion analyses and two eluent generators. Atmospheric aerosols were sampled at a flow rate of 16.7 L min⁻¹ through a PM₂.₅ sharp cut cyclone (13.7 L min⁻¹ using an external air pump). The air sample was drawn through a liquid diffusion parallel-plate denuder that consisted of two cellulose membranes constantly supplied with a 5 mM H₂O₂(aq) solution that separated the gas from the aerosol phase. After filtration, the water-soluble components were injected automatically into the two ICs using a collector. Each analyzer (ICS-1100, Dionex Corporation, Sunnyvale, CA) was equipped with a guard column (IonPac CG12A, 5 μm, 2 × 50 mm for cations and IonPac AG14A, 4 × 50 mm for anions) and an analytical column (IonPac CS12A, 5 μm, 2 × 250 mm for cations and IonPac AS14A, 4 × 250 mm for anions) that could detect six primary cations (Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) and six primary anions (F⁻, Cl⁻, Br⁻, PO₄³⁻, SO₄²⁻, and NO₃⁻) and a self-regenerating suppressor (CSRS 300, 2 mm for cations and ASRS 300, 4 mm for anions). Then the chromatographic columns were scoured by leachate produced by the eluent generators (Dionex EGC 500 KOH for cations and Dionex EGC 500 MSA for anions). Multi-point calibrations were performed bi-weekly for both ICs using calibrated standard solutions (Dionex Corporation, Six Cation-II standard for cation and seven anion standard for anion; Gilio et al., 2015). Another two identical AIMs were settled on the DSH and the PD stations. Multi-point calibrations were performed on all these three AIMs prior and during the actual experiment by using the same calibration standard solutions. To distinguish the effects of anthropogenic and marine sources on the ion concentration, non-sea-salt K⁺, Ca²⁺, and SO₄²⁻ were calculated following Equations 1–3 and assuming that Na⁺ was a conservative tracer of sea salt (M. Zhang et al., 2010):

Figure 1. The itinerary map of the ship campaign from June 1, 2017 to June 30, 2017 at the ECS compared with the PD Station and the DSH Station.
\[
\begin{align*}
\text{nss-K}^{+} & = \text{K}^{+} - 0.037 \times \text{Na}^{+}, \\
\text{nss-Ca}^{2+} & = \text{Ca}^{2+} - 0.038 \times \text{Na}^{+}, \\
\text{nss-SO}_{4}^{2-} & = \text{SO}_{4}^{2-} - 0.253 \times \text{Na}^{+}.
\end{align*}
\]

### 2.3. Ion Balance Calculation

Ion balance calculations are frequently applied to investigate the acid-base balance of WSIs in aerosols (Shen et al., 2009). Equations 4–6 were used to calculate the charge balance between six different types of cations and six different types of anions as follows:

Cation equivalents = \[
\begin{align*}
\text{Na}^{+} & \left(\frac{23}{23}\right) + \text{NH}_{4}^{+} \left(\frac{18}{39}\right) + \text{K}^{+} \left(\frac{39}{39}\right) + \text{Mg}^{2+} \left(\frac{12}{20}\right) + \text{Ca}^{2+} \left(\frac{20}{20}\right),
\end{align*}
\]

Anion equivalents = \[
\begin{align*}
\text{nss-SO}_{4}^{2-} \left(\frac{48}{48}\right) + \text{NO}_{3}^{-} \left(\frac{62}{35.5}\right) + \text{Cl}^{-} \left(\frac{18}{80}\right) + \text{Br}^{-} \left(\frac{18}{19}\right).
\end{align*}
\]

\[R_{(C/A)} = \frac{\text{Cation equivalents}}{\text{Anion equivalents}}.\]

### 2.4. Modeling Calculation

#### 2.4.1. Back Trajectory and Clustering Analysis

The 48 h back trajectories were calculated at 2 hr intervals using the Hybrid-Single Particle Integrated Trajectories (HYSPLIT 4.9) developed by the National Oceanic and Atmospheric Administration Air Resources Laboratory (http://www.arl.noaa.gov/HYSPLIT.php) with a 1° latitude × 1° longitude grid cells, when arriving at the observation site at an elevation of 100 m above ground. The meteorological database was acquired from the Global Data Assimilation System of the National Center for Environmental Prediction (Y. Q. Wang et al., 2009).

#### 2.4.2. Process Analysis

The Weather Research and Forecasting Model (WRF) version 3.8.1 and the CMAQ model version 5.2 were employed to investigate the key parameters affecting pollutants in the sampled air masses. Based on the CMAQ model, the process analysis that calculated the contribution and importance of air pollutant formation in physical and chemical reactions. In detail, the integrated process rate (IPR) that obtained the contribution referred to the horizontal/vertical transport, the cloud/aerosol process, dry compositions, and emissions. In this study, the formation of PM$_{2.5}$, nss-SO$_{4}^{2-}$, and NO$_{3}^{-}$ were calculated using Equations 7 and 8 as follows:

\[
\begin{align*}
\text{Source}_{p,t} & = \frac{\sum_{p,t} IPR_{p,t} \times 100\%}{\sum_{p,t} IPR_{p,t}} \times \left\{ IPR_{p,t} > 0 \right\}, \\
\text{Sink}_{p,t} & = \frac{\sum_{p,t} IPR_{p,t} \times 100\%}{\sum_{p,t} IPR_{p,t}} \times \left\{ IPR_{p,t} < 0 \right\}.
\end{align*}
\]

where \(i\) is the type of research object; \(t\) is the time the observation was collected; \(p\) is the type of atmospheric process; and IPR is the integrated process rate (μg·m⁻³).

#### 2.4.3. Contributions of the Urban and Shipping Emissions Analysis

To investigate the impact of urban-based and shipping emissions on regional PM$_{2.5}$ and its components over the YRD, the WRF-Chem (version 3.8.1) was run for the entire month of June 2017, using three nested domain simulations at horizontal resolutions of 81, 27, and 9 km for each run. Detailed information regarding the model configurations is shown in (Mao et al., 2018). In addition, Fan et al. (2016) and Feng
et al. (2019) provided the descriptions of urban-based and shipping emissions in detail (Fan et al., 2016; Feng et al., 2019).

3. Results and Discussion

3.1. Fine Particle Mass and Ionic Concentrations

A statistical summary of the mass concentration of fine particle and WSIs during the ship cruise and urban campaign from the Shanghai PD station and the DSH station during June 2017 is shown in Table 1. The average mass concentration of PM$_{2.5}$ on the ship cruise was measured to be 36.17 ± 15.86 μg m$^{-3}$, among which the highest concentration reached 118.73 μg m$^{-3}$. In comparison, the average PM$_{2.5}$ mass concentrations at the PD station and the DSH station were 37.55 ± 27.66 and 41.10 ± 25.47 μg m$^{-3}$, respectively. In addition, the highest concentration of PM$_{2.5}$ reached 135.08 μg m$^{-3}$ at the PD station and 121.47 μg m$^{-3}$ at the DSH station. In previous studies, H. Wang et al. (2015) observed that the concentration of PM$_{2.5}$ in the YRD region was 31.0 ± 13.0 μg m$^{-3}$ during summer, and Qiao et al. (2016) measured the PM$_{2.5}$ concentration to be 34.0 ± 18.0 μg m$^{-3}$ during July, using off-line filter sampling (Qiao et al., 2016; H. Wang et al., 2015). In contrast, comprised 57.53% of the PM$_{2.5}$ concentration, the total ionic concentration was 20.88 ± 12.35 μg·m$^{-3}$, among which the mean concentration of nss-SO$_4^{2-}$ (8.87 ± 4.83 μg m$^{-3}$) was the highest followed by NO$_3^-$ (4.94 ± 2.93 μg m$^{-3}$), NH$_4^+$ (4.65 ± 3.47 μg m$^{-3}$), Na$^+$ (1.25 ± 0.50 μg m$^{-3}$), Cl$^-$ (0.62 ± 0.27 μg m$^{-3}$), nss-K$^+$ (0.32 ± 0.17 μg m$^{-3}$), nss-Ca$^{2+}$ (0.23 ± 0.12 μg m$^{-3}$) and Mg$^{2+}$ (0.05 ± 0.03 μg m$^{-3}$) at the ESC offshore area. Occupied 56.30% of the PM$_{2.5}$ mass concentration, the concentration of WSIs in the PD station was 21.14 ± 20.08 μg·m$^{-3}$ (similar to the DSH station, and the WSIs concentration was 24.93 ± 19.18 μg m$^{-3}$ at the DSH station). In previous studies, H. Wang et al. (2015) observed that the concentration of PM$_{2.5}$ in the YRD region was 31.0 ± 13.0 μg m$^{-3}$ during summer, and Qiao et al. (2016) measured the PM$_{2.5}$ concentration to be 34.0 ± 18.0 μg m$^{-3}$ during July, using off-line filter sampling (Qiao et al., 2016; H. Wang et al., 2015). In contrast, comprised 57.53% of the PM$_{2.5}$ concentration, the total ionic concentration was 20.88 ± 12.35 μg·m$^{-3}$, among which the mean concentration of nss-SO$_4^{2-}$ (8.87 ± 4.83 μg m$^{-3}$) was the highest followed by NO$_3^-$ (4.94 ± 2.93 μg m$^{-3}$), NH$_4^+$ (4.65 ± 3.47 μg m$^{-3}$), Na$^+$ (1.25 ± 0.50 μg m$^{-3}$), Cl$^-$ (0.62 ± 0.27 μg m$^{-3}$), nss-K$^+$ (0.32 ± 0.17 μg m$^{-3}$), nss-Ca$^{2+}$ (0.23 ± 0.12 μg m$^{-3}$) and Mg$^{2+}$ (0.05 ± 0.03 μg m$^{-3}$) at the ESC offshore area. Occupied 56.30% of the PM$_{2.5}$ mass concentration, the concentration of WSIs in the PD station was 21.14 ± 20.08 μg·m$^{-3}$ (similar to the DSH station, and the WSIs concentration was 24.93 ± 19.18 μg m$^{-3}$, comprised 60.66% of the PM$_{2.5}$ mass concentration), among which the mean concentration of NO$_3^-$ (9.47 ± 10.36 μg m$^{-3}$) ranked the highest followed by nss-SO$_4^{2-}$ (6.33 ± 4.36 μg m$^{-3}$), NH$_4^+$ (4.74 ± 4.00 μg m$^{-3}$), Cl$^-$ (0.32 ± 0.44 μg m$^{-3}$), nss-K$^+$ (0.11 ± 0.22 μg m$^{-3}$), nss-Ca$^{2+}$ (0.09 ± 0.12 μg m$^{-3}$), Na$^+$ (0.07 ± 0.26 μg m$^{-3}$) and Mg$^{2+}$ (0.01 ± 0.02 μg m$^{-3}$). Such levels of the WSIs concentration were comparable with the data reported by Boreddy et al. (2015) who launched a 12 yr observation of WSIs in the western North Pacific (Boreddy et al., 2015). In addition, Kong et al. (2014) measured 46 μg m$^{-3}$ of WSIs in the PM$_{2.5}$ at an offshore station of the YRD region (Kong et al., 2014). When considering the transformation

Table 1

| Component | ECS | PD station | DSH station |
|-----------|-----|------------|-------------|
| F$^-$     | 0.02 | n.a        | n.a         |
| Cl$^-$    | 0.62 | 0.32       | 0.55        |
| NO$_3^-$  | 4.94 | 9.47       | 10.01       |
| nss-SO$_4^{2-}$ | 8.87 | 6.33       | 7.33        |
| nss-SO$_4^{2-}$/NO$_3^-$ | 1.80 | 0.67       | 0.73        |
| Na$^+$    | 1.20 | 0.07       | 0.05        |
| nss-K$^+$ | 0.32 | 0.11       | 0.16        |
| NH$_4^+$  | 4.65 | 4.74       | 6.78        |
| nss-Ca$^{2+}$ | 0.23 | 0.09       | 0.04        |
| Mg$^{2+}$ | 0.05 | 0.01       | 0.01        |
| Sum (Ions) | 20.88 | 21.14    | 24.93       |
| OC        | 3.12 | 10.59      | 5.00        |
| EC        | 1.67 | 2.65       | 2.10        |
| EC/OC     | 0.54 | 0.25       | 0.39        |
| PM$_{2.5}$ | 36.17 | 37.55    | 41.10       |
| WSI/PM$_{2.5}$ | 57.73% | 56.30%  | 60.66%      |
frequency of PM$_{2.5}$ mass concentration at the ESC offshore area, as shown in Figure 2. PM$_{2.5}$ mass concentration approximately 25–35 μg m$^{-3}$ comprised more than 65%, and this was under a condition of a relative humidity of approximately 90% and a wind speed of approximately 4 m/s. When the PM$_{2.5}$ mass concentration was greater than 35 μg m$^{-3}$, the relative humidity was approximately 75%–80%, and the wind speed was greater than 5 m/s. This type of larger PM$_{2.5}$ mass concentration may have been caused by mixing with sea-salt aerosols during long-range transport. In addition, with the increase of the PM$_{2.5}$ mass concentration from 15 to 95 μg m$^{-3}$, the percentage of WSIs decreased from 80% down to 40%, while organic matter increased from 5% up to 45%. The secondary inorganic ions displayed a similar declining tendency as the WSIs. NH$_4^+$ decreased from 12% down to 7%, nss-SO$_4^{2-}$ decreased from 16% down to 9%, and NO$_3^-$ had the greatest reduction from 37% down to 20%. It can be concluded that organic matter was the primary contributor to the PM$_{2.5}$ mass concentration increase. These results were consistent with those of Z. Han et al. (2008) who found that organic matter accounted for a large (20%–50%) fraction of the fine aerosol mass, especially in large particles (Z. Han et al., 2008).

Figure 2. (a) Transformation of the frequency of PM$_{2.5}$; (b) The relationship between PM$_{2.5}$ and the relative humidity; (c) The relationship between PM$_{2.5}$ and the wind speed; (d) The relationship between PM$_{2.5}$ and the fraction of organic matter; (e) The relationship between PM$_{2.5}$ and the fraction of TWSIs; (f) The relationship between PM$_{2.5}$ and the fraction of NH$_4^+$; (g) The relationship between PM$_{2.5}$ and the fraction of nss-SO$_4^{2-}$; (h) The relationship between PM$_{2.5}$ and the fraction of NO$_3^-$; and (i) The relationship between PM$_{2.5}$ and the fraction of Cl$^-$ by the PM$_{2.5}$ mass concentration.
Secondary inorganic ions, such as nss-SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$, were the main ions that contributed more than 89% to the WSIs (Cheng et al., 2011). In addition, the mass ratio of nss-SO$_4^{2-}$/NO$_3^-$ can be reasonably used to evaluate the contribution of stationary and automobile sources to sulfur and nitrogen in the atmosphere. This ratio was found to be lower in megacities with heavy traffic densities like Beijing, Shanghai, and Guangzhou (Huang et al., 2013; Lv et al., 2010; X. Wang et al., 2018). During this study, the ratio of secondary inorganic ions/WSIs was 88.4% at the ECS, 97.1% at the PD station, and 96.7% at the DSH station. Moreover, the mean ratio of nss-SO$_4^{2-}$/NO$_3^-$ was 1.80 (nss-SO$_4^{2-}$ 8.87 and NO$_3^-$ 4.94 μg m$^{-3}$) at the ECS, while it was 0.67 at the PD station (nss-SO$_4^{2-}$ 6.33 μg m$^{-3}$ and NO$_3^-$ 9.47 μg m$^{-3}$) and 0.73 at the DSH station (nss-SO$_4^{2-}$ 7.33 μg m$^{-3}$ and NO$_3^-$ 10.01 μg m$^{-3}$). This result indicated that nss-SO$_4^{2-}$ was the most dominant secondary inorganic ion near the marine area, whereas NO$_3^-$ predominated in the megacities. The data showed that emissions from anthropogenic activities contributed approximately 50% to the total sulfur emissions (Lefohn et al., 1999). In urban areas, especially in some modern megacities like Shanghai, 60%–70% of the local nss-SO$_4^{2-}$ was formed via the oxidation of SO$_2$ generated primarily from the petrochemical industry and fossil fuel combustion. More than 50% of the local particulate NO$_3^-$ was formed primarily by the oxidation of NO derived primarily from motor vehicles and industrial emissions (Huang et al., 2013; S. Wang et al., 2013). In the offshore area, without numerous automobile emissions, SO$_4^{2-}$ and NO$_3^-$ were primarily generated from ship emissions, whose fuel was rich in sulfur, or the uptake of nitric acid with mineral dust, as well as from marine activities sea-salt production.

In addition, the concentrations of Na$^+$, Mg$^{2+}$, and nss-Ca$^{2+}$ at the ECS were 2 to 15 times higher than that at the PD and DSH stations. The high concentration of Na$^+$ measured was primarily contributed to by sea salt, including NaSO$_4$, NaNO$_3$, and NaCl (Guimbaud et al., 2002). Na$^+$, Mg$^{2+}$, and Ca$^{2+}$ measured at the urban location were originating from coal combustion, dust, construction activities, and long-distance transportation due to the impacts of the East Asia monsoon (Pósfai et al., 1995).

### 3.2. Temporal and Spatial Distribution Based on the Cruise Route

The spatial distributions of fine particle and secondary inorganic ions along the cruise route are displayed in Figure 3. It can clearly be seen that the higher nss-SO$_4^{2-}$ concentration was mainly distributed around the Zhoushan Islands at the ECS, where it reached 43.51 μg m$^{-3}$. The reason why the nss-SO$_4^{2-}$ concentration was higher in these regions can be explained as follows: (a) these levels were affected by the atmospheric transportation from heavy cruise turnover in cargo terminals like Yangshan Harbor and emissions from industries located inland; (b) the emissions were emitted by thousands of fishing boats gathering near the Zhoushan Islands because of the fertile natural fishing area; (c) oceangoing freighters going through the pelagic shipping lane changed to heavy oil that was rich in sulfur. According to Figure 3c, the higher NO$_3^-$ concentration was primarily concentrated alongside the coastline and the pelagic shipping lane, where the highest concentration reached 14.29 μg m$^{-3}$. Automobile vehicles may have contributed to a large proportion of the particulate-related nitrate due to the oxidation of NO to nitric acid and uptake by particles. Moreover, Figure 3d shows the information regarding the mass concentration ratio of nss-SO$_4^{2-}$/NO$_3^-$.

### 3.3. Particulate Ions Balance

$R_{C/A}$ is a good indicator that can reflect the acidity of aerosol particles. The correlation between the equivalent concentrations of cations and anions is displayed in Figure S1 in Supporting Information S1. Good correlation ($R^2 = 0.975$ at the ECS, $R^2 = 0.979$ at the PD station, $R^2 = 0.949$ at the DSH station) between the cations and anions were indeed calculated, indicating that the measured ions had an evident relationship both offshore and at the coastal megacity. $R_{C/A}$ was shown to be 1.23 at the ECS, 1.02 at the PD station and 1.16 at the DSH station, indicating that aerosol particles were alkalescent, and this agreed with the results at coastal megacities like Shanghai and Guangzhou (Xiu et al., 2004). The presence of water-soluble organic
anions (like humic acid) and carbonate may also be of importance for the charge balance. However, we did not have data regarding water-soluble organic anions and carbonate during this campaign.

To obtain a better understanding of the balance between cations and anions, we used the relationship between the mass concentration of PM$_{2.5}$ and the $R_{(C/A)}$ equivalents shown in Figure 4. At the ECS station, it

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**Figure 3.** The concentration of the primary secondary inorganic ions on the itinerary map during ship campaign from June 1, 2017 to June 30, 2017 at the ECS: (a) PM$_{2.5}$ (b) nss-SO$_4^{2-}$ (c) NO$_3^-$ (d) nss-SO$_4^{2-}$/NO$_3^-$; ○Yangshan Harbor ○Zhoushan Islands ○pelagic shipping lane.

**Figure 4.** Transformation of the relationship with the cation and anion equivalents ($R_{(C/A)}$) by the PM$_{2.5}$ mass concentration; (a) The ECS; (b) The PD Station; and (c) The DSH Station.
was observed that $R_{(C/A)} < 1$ when the PM$_{2.5}$ was less than 20 μg m$^{-3}$, indicating that these types of particles were in a acidulous state and then the ratio rose slowly with the mass concentration of PM$_{2.5}$, increasing until $R_{(C/A)} > 1$. This is indicative of particles turning to alkalescent state, and then maintained a balance when PM$_{2.5}$ was greater than 75 μg m$^{-3}$. Additionally, differences among the three sites also appeared that at the ECS, and $R_{(C/A)}$ was greater than one when the PM$_{2.5}$ was less than 20 μg m$^{-3}$ and remained stable when $R_{(C/A)}$ was near 1.2, which was similar to that of the DSH station. However, in contrast to the DSH site, at the PD station, $R_{(C/A)}$ was greater than one when the PM$_{2.5}$ reached 50 μg m$^{-3}$ and remained stable when $R_{(C/A)}$ was near 1.05. With increasing PM$_{2.5}$ concentration, the fraction of nss-SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ decreased, and this made the balance of anions become lower. Such results were consistent with H. Wang et al. (2015) who observed smaller fine particles of $R_{(C/A)} < 1$ and larger ones of $R_{(C/A)} > 1$ (H. Wang et al., 2015).

3.4. Secondary Inorganic Ions Balance

In the atmosphere, ammonia primarily reacts with acidic gases, such as sulfuric, nitric, and hydrochloride acids, to form secondary inorganic ions. Due to its stability and low volatility compared with ammonium chloride, ammonium sulfate was the primary form of ammonia found in the secondary inorganic aerosol particles. The balance of secondary inorganic ions at the ECS, the PD station, and the DSH station are shown in Figure 5. A good correlation was found between NH$_4^+$ and nss-SO$_4^{2-}$, and the derived slopes are 2.14, 1.83, and 1.98, respectively ($R^2 = 0.85, 0.81$, and 0.75, respectively). An even stronger correlation was

![Figure 5. The correlations between the equivalent concentrations of the secondary inorganic ions: (a) NH$_4^+$ with nss-SO$_4^{2-}$; (b) NH$_4^+$ with nss-SO$_4^{2-}$ + NO$_3^-$; (c) NH$_4^+$ with nss-SO$_4^{2-}$ + NO$_3^-$ + Cl$^-$; and (d) NO$_3^-$/nss-SO$_4^{2-}$ with NH$_4^+$/nss-SO$_4^{2-}$.](image)
concentration of PM$_{2.5}$ was 16.12 $\mu$g m$^{-3}$ in which the WSIs were 13.98 $\mu$g m$^{-3}$, representing 86.7%. In the campaign in June 2017 are shown in Figure 6. In Case 1 influenced by marine sources, the mean mass area also contributed nearly to 30%.

The trajectory clusters were rooted in the south inland and accounted for 63.5%–73.5%, whereas the marine area between June 3rd and 5th. However, in Cases 2 and 3, which were primarily influenced by inland sources, the PM$_{2.5}$ concentrations were relatively higher, reaching 49.3, 63.88, and 70.96 $\mu$g m$^{-3}$ (with the WSIs representing 71.3%, 64.3%, and 55.3%, respectively) and 32.10, 44.1, and 49.91 $\mu$g m$^{-3}$ (the WSIs corresponding to 70.2%, 53.4%, and 68.2%, respectively). Compared with the PM$_{2.5}$ concentration, when the air mass originated from the ECS, more pollutants were carried in compared to the other directions. This might have been due to the abundant anthropogenic influence, such as industrial emissions, biomass burning, and vehicle exhaust, primarily concentrated in the inland than at the ECS. Comparing the ratio of WSIs found in PM$_{2.5}$, revealed that the ECS levels were higher than those inland. This is probably due to more organic compounds emitted from coal combustion and the petrochemical industry, which influenced PM$_{2.5}$ as they aged, inducing a decrease in the ratio of WSIs.

3.5. Case Study

The HYSPLIT4 model with a 2-hr period was applied, and the 48 hr back trajectories beginning at a height of 100 m at the three sites were calculated (Seabrook et al., 2011). The back trajectories were classified into three clusters using TrajStat (K. Zhang, Zhou, et al., 2019; Q. Zhang, Xue et al., 2019). According to the different modes of the long-distance transportation by air mass, three typical types of pollutant cases were classified, as shown in Figure S2 in Supporting Information S1 (Moody et al., 1998). Case 1 showed that an air mass was transported from the marine to the urban area between June 3rd and 5th. However, in Case 2 and Case 3 was the opposite. Case 2 showed that the air mass was transported primarily from the northeastern inland between June 7th and 9th, and Case 3 showed that the air mass was transported from both the southern inland and the marine area between June 23rd and 24th. By using the cluster analysis, detailed information regarding the ratio of the air mass from each position was given. In Case 1, all three of the trajectory clusters originated from or through the ECS and the Yellow Sea at the three sites. In Case 2, the trajectory clusters were dominated by the northern direction, accounting for 67.4%–91.8%. Moreover, the trajectory clusters were rooted in the south inland and accounted for 63.5%–73.5%, whereas the marine area also contributed nearly to 30%.

The time series of the concentrations of WSIs in the fine particles during the ship cruise and the urban campaign in June 2017 are shown in Figure 6. In Case 1 influenced by marine sources, the mean mass concentration of PM$_{2.5}$ was 16.12 $\mu$g m$^{-3}$ in which the WSIs were 13.98 $\mu$g m$^{-3}$, representing 86.7%. In comparison, PM$_{2.5}$ at the PD station was 14.90 $\mu$g m$^{-3}$ in which the WSIs were 8.03 $\mu$g m$^{-3}$ i.e., 53.9%. In addition, PM$_{2.5}$ at the DSH station was 12.15 $\mu$g m$^{-3}$, in which the WSIs were 6.76 $\mu$g m$^{-3}$, hence 55.6%. However, in Cases 2 and 3, which were primarily influenced by inland sources, the PM$_{2.5}$ concentrations were relatively higher, reaching 49.3, 63.88, and 70.96 $\mu$g m$^{-3}$ (with the WSIs representing 71.3%, 64.3%, and 55.3%, respectively) and 32.10, 44.1, and 49.91 $\mu$g m$^{-3}$ (the WSIs corresponding to 70.2%, 53.4%, and 68.2%, respectively). Compared with the PM$_{2.5}$ concentration, when the air mass originated from the ECS to the inland, less pollutants were carried in compared to the other directions. This might have been due to the abundant anthropogenic influence, such as industrial emissions, biomass burning, and vehicle exhaust, primarily concentrated in the inland than at the ECS. Comparing the ratio of WSIs found in PM$_{2.5}$ revealed that the ECS levels were higher than those inland. This is probably due to more organic compounds emitted from coal combustion and the petrochemical industry, which influenced PM$_{2.5}$ as they aged, inducing a decrease in the ratio of WSIs.
To obtain a better understanding of the sink and source process of WSIs in PM$_{2.5}$, especially for the primary secondary inorganic ions nss-SO$_4^{2-}$ and NO$_3^-$ at the ECS, an IPR analysis based on the CMAQ model was used. Figure 7b presents the sink and sources of nss-SO$_4^{2-}$ at ECS for Case 1. Emissions and horizontal
transport led to a total of 93% of WSIs, while aerosol processing only contributed to approximately 5%. The main sink was dominated by vertical transport. In comparison, Table S2 in Supporting Information S1 shows that emissions and horizontal transport also contributed approximately 88% to the sources in Case 2 and approximately 91% for Case 3. In addition, the contribution of aerosol processing grew to 10% in Case 2 and 8% in Case 3. In Cases 2 and 3, the air mass transported from inland to the marine area carried obviously more atmospheric pollutants. This may have led to an easier route for nss-SO$_4^{2-}$ formation in the aerosol process. Such results are consistent with those of K. Zhang, Zhou, et al. (2019) and Q. Zhang, Xue, et al. (2019) who pointed out that the contribution from the aerosol processing increased during heavy pollution events (K. Zhang et al., 2019; Q. Zhang et al., 2019). The sources of NO$_3^-$ at the ECS station were however distinct as the two main sources were the aerosol processing (contributing to 49%) and emissions (up to 44%), whereas its sink was dominated by horizontal and vertical transport. As shown in Figure 7a, the sources of PM$_{2.5}$ at the ECS station were primarily direct emissions (more than 80%) and horizontal transport. However, the PM$_{2.5}$ was reduced by vertical transport. Such results indicated that primary emissions, especially from ships whose fuel was diesel or heavy oil, were still primary source of WSIs in the PM$_{2.5}$ at the ECS station, followed by secondary aerosol production and long-term transportation.

3.6. Urban-Ocean Transportation

Coastal urban megacities like Shanghai in the YRD region has a close relationship with the offshore of the ECS station in terms of atmospheric pollutant transportation, influenced by the summer monsoon. Urban-based emissions were primarily from anthropogenic activities, such as thermal power plants, industrial, transportation, residential, and agricultural sources. However, in terms of the ocean-based emissions, shipping emissions from the ships whose fuel was diesel or heavy oil was the key point. Many studies have focused on ship emission inventories in China at the ports of coastal urban megacities such as Shanghai, Shenzhen, and Hong Kong. Ng et al. (2013) established a marine emission inventory of Hong Kong and the Pearl River Delta based on an automatic identification system (AIS; Ng et al., 2013). Fu & Liao (2012) elaborated a ship pollutant emission inventory from the port of Shanghai (Fu & Liao, 2012). Fan et al. (2016) estimated shipping emissions for the first time using AIS in the YRD region (Fan et al., 2016). While Eyring et al. (2005) studied the statistics of emissions from international shipping during the last 50 yr and studied the impact of transport by ships on the atmosphere and climate (Eyring et al., 2005).

Here, we described the relative contribution from shipping emissions to PM$_{2.5}$, NO$_3^-$ and nss-SO$_4^{2-}$ using WRF-Chem, as shown as in Figure 8. Table S1 in Supporting Information S1 shows that the average concentration of NO$_3^-$ was 12.17 ± 2.06 μg m$^{-3}$, the average concentration of nss-SO$_4^{2-}$ was 6.67 ± 1.44 μg m$^{-3}$ and the average concentration of PM$_{2.5}$ was 39.73 ± 7.91 μg m$^{-3}$ according to the modeling results of CMAQ. Compared with the ship cruise and the land campaign data, the modeling results had reasonable confidence intervals. We found that shipping emissions contributed approximately 31.6% of the total nss-SO$_4^{2-}$ to the maximum, and approximately 28.9% of the total NO$_3^-$ to the maximum surrounding the ports and the Zhoushan Islands. This influence of ship emissions dropped to 3% 300 km inland for both nss-SO$_4^{2-}$ and NO$_3^-$. Additionally, nss-SO$_4^{2-}$ due to ship emissions generally occurred along the shipping route. In contrast, ship influence on NO$_3^-$ was not restricted to the shipping route, but also extended to the urban area and was especially concentrated near the parking port. We, therefore, compared urban sources and ocean sources, as well as the interaction between each other. Although the ocean sources comprised an urban less proportion of pollutants comparing to urban sources, ocean source still requires more attention.

In recent years, governmental policies have been unveiled raising pollution control standard of high sulfur emitting industries that use coal combustion, such as power plants and steel industries. Therefore, fewer nss-SO$_4^{2-}$ has been exhausted directly into the open air, which would cause the nss-SO$_4^{2-}$ originating from shipping emissions to be more prominent. Since 2016, governmental regulations concerning ship emission have been successively promulgated. This includes: (a) international and domestic sailing ships should use fuel oil with a sulfur content less than 0.5% when parking at ports and operating in offshore regions; (b) industries should freely improve the performance of diesel engines and install tail gas post-processing devices in both passenger and cargo ships; and (c) at least 29 shore power ports should be built in each container berth, and 21 shore power ports should be built in each cargo berth at the Shanghai port (Fan et al., 2016). The data utilized in this article with a high temporal resolution, such as the as hourly land-cruise WSIs
comparison, are necessary to understand the realistic impacts of shipping traffic and to implement more precise control policies to improve coastal air quality.

4. Conclusion

To compare the characteristics of secondary inorganic ions in PM$_{2.5}$ between the offshore and a coastal urban megacity and obtain a better understanding of the urban-ocean interaction, a ship cruise at the ECS and urban campaign in the PD station as well as the DSH station took place from June 2 to 30 in 2017. The WSIs concentration was $20.88 \pm 12.35 \mu g \text{ m}^{-3}$ and this comprised 57.5% of the PM$_{2.5}$ concentration at the ECS, among which the mean concentration of nss-SO$_4^{2-}$ ($8.87 \pm 4.83 \mu g \text{ m}^{-3}$) was the highest, followed by NO$_3^-$ ($4.94 \pm 2.93 \mu g \text{ m}^{-3}$) and NH$_4^+$ ($4.65 \pm 3.47 \mu g \text{ m}^{-3}$). The concentration of WSIs at the PD station was $21.14 \pm 20.08 \mu g \text{ m}^{-3}$ (similar to the DSH station where the WSIs concentration was $24.93 \pm 19.18 \mu g \text{ m}^{-3}$, corresponding to 60.7% of PM$_{2.5}$ concentration) i.e., 56.3% of the PM$_{2.5}$ concentration, among which the mean concentration of NO$_3^-$ ($9.47 \pm 10.36 \mu g \text{ m}^{-3}$) was the highest, followed by nss-SO$_4^{2-}$ ($6.33 \pm 4.36 \mu g \text{ m}^{-3}$) and NH$_4^+$ ($4.74 \pm 4.40 \mu g \text{ m}^{-3}$). The mean ratio of nss-SO$_4^{2-}$/NO$_3^-$ was 1.80 at the ECS, whereas the PD station was 0.67 and the DSH station was 0.73. This result indicated that nss-SO$_4^{2-}$ was the most dominant secondary inorganic ion near the marine area, whereas NO$_3^-$ predominated in the megacities. Moreover, a higher nss-SO$_4^{2-}$ concentration was primarily distributed near the Zhoushan Islands at the ECS where the highest concentration reached 43.51 $\mu g \text{ m}^{-3}$. The balances of $R_{(C/A)}$ were shown to be 1.23 at the ECS, 1.02 at the PD station, and 1.16 at the DSH station where $R_{(C/A)} < 1$ when mass concentration of PM$_{2.5}$ was small. It then rose slowly with the mass concentration of PM$_{2.5}$ increasing until $R_{(C/A)} > 1$ at all three sites. The relationship between the primary inorganic ions was discussed, and it was shown that the fine particles in the three sites were all in an ammonium-rich condition. Three different cases of long-term transport were

![Figure 8. CMAQ analysis of the emission contributions from the ship in the YRD region: (a) The absolute nss-SO$_4^{2-}$ emission contribution; (b) The relative nss-SO$_4^{2-}$ emission contribution; (c) The absolute NO$_3^-$ emission contribution; and (d) The relative NO$_3^-$ emission contribution.](image-url)
classified (from the sea, from the north inland, and from the south inland) and influenced the ratio of WSIs to PM$_2.5$. ECS had the highest WSI loadings compared to the urban area. Additionally, the sources and sinks of nss-SO$_4^{2−}$ and NO$_3^{−}$ at the ECS were analyzed and it was found that horizontal transport and emission, especially from ships, contributed the most. The influence of ship emissions reached up to 31.6% of the total nss-SO$_4^{2−}$ alongside the cruise ship and near coastal parking ports in the YRD area. This suggested that more attention should be paid to ship emissions.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data sets used in this manuscript were available at https://figshare.com/articles/dataset/_/14073626?file=26562047.

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