Impact of international shipping emissions on ozone and PM$_{2.5}$ in East Asia during summer: the important role of HONO and ClNO$_2$

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Abstract. Ocean-going ships emit large amounts of air pollutants such as nitrogen oxide (NO$_x$) and particulate matter (PM$_{2.5}$) from ships can be converted to nitrous acid (HONO) and nitryl chloride (ClNO$_2$), which produce hydroxyl (OH) and chlorine (Cl) radicals and recycle NO$_x$, thereby affecting the oxidative capacity and production of secondary pollutants. However, these effects have not been quantified in previous investigations of the impacts of ship emissions. In this study, a regional transport model (WRF-Chem) revised to incorporate the latest HONO and ClNO$_2$ processes was used to investigate their effects on the concentrations of RO$_x$ (RO$_2$ + HO$_2$ + OH) radicals, ozone (O$_3$), and fine particulate matter (PM$_{2.5}$) in Asia during summer. The results show that the ship-derived HONO and ClNO$_2$ increased the concentration of RO$_x$ radicals by approximately 2–3 times in the marine boundary layer. The enhanced radicals then increased the O$_3$ and PM$_{2.5}$ concentrations in marine areas, with the ship contributions increasing from 9 % to 21 % and from 7 % to 10 % respectively. The largest RO$_x$ enhancement was simulated over the remote ocean with the ship contribution increasing from 29 % to 50 %, which led to increases in ship-contributed O$_3$ and PM$_{2.5}$ from 21 % to 38 % and from 13 % to 19 % respectively. In coastal cities, the enhanced levels of radicals also increased the maximum O$_3$ and averaged PM$_{2.5}$ concentrations from 4 %–8 % to 4 %–12 % respectively. These findings indicate that the air quality of coastal cities (Y. Zhang et al., 2017; Liu et al., 2018) and threat public health (Liu et al., 2016; Campling et al., 2013). As international seaborne trade continues to increase, ship emissions are expected to continuously grow at a rate of 3.5 % per year (UNCTAD, 2020), and their impact on the environment is a growing concern.

The effects of ship emissions on the formation of O$_3$ and PM$_{2.5}$ have been extensively evaluated in numerical studies. On the open ocean, ship-generated NO$_x$ reacts with VOCs emitted from ships and from the background atmosphere.
and enhances O₃ formation (Corbett and Fischbeck, 1997; Lawrence and Crutzen, 1999; Aksoyoglu et al., 2016; Huszar et al., 2010; Hoor et al., 2009). In coastal areas, the O₃ levels can also be increased by NOₓ emitted from ships in ports and harbours and through the dispersion of ship-formed O₃ on the open ocean (Wang et al., 2019; Aksoyoglu et al., 2016; Song et al., 2010). On the other hand, ship-generated NOₓ can reduce ozone formation via a titration effect in heavy-traffic ports and within the ship tracks (Wang et al., 2019; Aksoyoglu et al., 2016). Ship emissions have also been shown to increase PM₂.₅ concentrations via direct emissions and via the production of secondary aerosols through the reaction of gaseous precursors (Aksoyoglu et al., 2016; Liu et al., 2018; Lv et al., 2018). Although the formation of O₃ and secondary aerosols is affected by their precursors, it can also be influenced by the levels of radicals, which are key to the oxidation of precursors. Limited attention has been paid to the production of ship-related radicals in evaluating the effects of ship emissions on secondary pollutants.

Recent studies have demonstrated the potentially important roles of two radical precursors and nitrogen reservoirs – nitrous acid (HONO) and nitryl chloride (ClNO₂) – in atmospheric oxidation chemistry (Fu et al., 2019; Li et al., 2016; Sarwar et al., 2014; Simon et al., 2009; L. Zhang et al., 2017). HONO is emitted directly in combustion and soil (Kleffmann et al., 2005) or is produced by heterogeneous reactions of NO₂ on various surfaces (Finlayson-Pitts et al., 2003; Ndour et al., 2008; Monge et al., 2010) and by photolysis of nitrate aerosol (Ye et al., 2017, 2016). ClNO₂ is formed from reactions of N₂O₅, which is produced when NO₂ reacts with O₃, on chloride-containing aerosol at night (Bertram and Thornton, 2009). Photolysis of HONO and ClNO₂ by sunlight produces OH or Cl radicals and recycles NO₂, thereby affecting the oxidation capacity and production of secondary pollutants (Osthoff et al., 2008; Wang et al., 2016). Ships can directly emit HONO (Sun et al., 2020), and the NOₓ that they emit can subsequently produce HONO and ClNO₂ via heterogeneous reactions on sea-salt and ship-emitted particles. Although the production and effects of HONO and ClNO₂ from land-based emissions have been demonstrated over land areas (L. Zhang et al., 2017), few studies have examined the effects of the two reactive nitrogen species from international shipping. Field studies have observed elevated mixing ratios of HONO (0.2 ppb) at a marine site of the Bohai rim in northern China (Wen et al., 2019) and of HONO (126 ppt) and ClNO₂ (1.97 ppb) at a coastal site in southern China (Tham et al., 2014; Zha et al., 2014). These observations suggest the significant contribution of ship emissions to the oxidative capacity of the marine and coastal atmosphere in East Asia.

In this study, we used a revised regional chemical transport model to simulate the spatial distributions of HONO and ClNO₂ produced by ocean-going ships and their effects on the formation of O₃ and PM₂.₅ in East Asia, which is home to 8 of the world’s top 10 container ports and the world’s most trafficked oceans. We selected the summer (July) of 2018 as the study period. During this time, large-scale oceanic winds prevailed in Asia and solar radiation and air temperature reached the highest level for the year. Thus, international shipping is expected to have the most distinctive and perhaps the greatest impact on atmospheric chemistry during this time of year in East Asia.

The remainder of the paper is structured as follows: in Sect. 2, we detail the model setting, emissions, numerical experiments, observational data, and model validation. In Sect. 3, we exhibit the model performance for HONO and ClNO₂ and compare the results with available measurements in marine areas; we then show the formation of ship-related HONO and ClNO₂ and their subsequent effects on radicals, O₃, and PM₂.₅ in oceanic areas and coastal cities. Finally, our conclusions are given in Sect. 4.

2 Methodology

2.1 Model setting

In this study, the WRF-Chem model (version 3.6.1; Grell et al., 2005) with updated gases-phase and heterogeneous-phase mechanisms of new reactive nitrogen species (L. Zhang et al., 2017) was used to simulate the transport, mixing, and chemical transformation of trace gases and aerosols. Briefly, the updated module was based on the default Carbon Bond Mechanism-Z (CBMZ) module (Zaveri and Peters, 1999), in which the O₃ production came from the traditional photochemical mechanisms with only two gas-phase sources of HONO (OH + NO → HONO and HO₂ + NO₂ → HONO) and no chlorine chemistry. In the updated module, CBMZ-Reactive NitrOgen Mechanism (CBMZ-ReNom), the HONO sources included the additional gas-phase reactions between NOₓ and HOₓ (OH + HO₂); the heterogeneous reaction of NO₂ on the particle, urban, leaf (Kurtenbach et al., 2001), and sea surfaces (Zha et al., 2014); and direct emission from vehicles (Kurtenbach et al., 2001; Gutzwiller et al., 2002; Sun et al., 2020). For this study, an additional HONO source from the photolysis of particulate nitrate (PNO₃ → 0.67 HONO + 0.33 NO₂) was included into our model. The photolysis rate constant of PNO₃ (J_PNO₃) was calculated following the approach used in Fu et al. (2019): J_PNO₃ = (8.3 × 10⁻⁵/7/10⁻⁷) × J_HONO_WRF-Chem, where J_HONO_WRF-Chem is the photolysis rate constant of gaseous HNO₃ calculated online in the WRF-Chem model. For ClNO₂ production, the parameterization from Bertram and Thornton (2009) was used to represent the N₂O₅ uptake coefficient and ClNO₂ production yield. This parameterization reproduced the order of magnitude and variation in the observed N₂O₅ and ClNO₂ levels in a background site in Hong Kong (Dai et al., 2020). The other six chlorine species, with relevant photolysis reactions and subsequent reactions between released Cl radical and VOCs, were also added to the default module (L. Zhang et al., 2017).
The details of other chemical and physical schemes for the simulation can be found in L. Zhang et al. (2017).

The model simulations were performed from 28 June to 31 July 2018. The first 72 h of the simulations was considered spin-up time. The initial meteorological conditions were provided by reanalysis data from the Final (FNL) Operational Global Analysis dataset provided by the National Centers for Environmental Prediction (NCEP; http://rda.ucar.edu/datasets/ds083.2/, last access: 1 November 2020). The model had 31 vertical layers with a fixed top of 100 hPa. The domain covered a large part of Asia with a horizontal resolution of 36 km × 36 km (Fig. 1a). The surface layer was 30 m above the ground, and the lowest 11 layers were approximately within the height of the planetary boundary layer at noon.

2.2 Emissions

Five sets of emission inventories (EIs) were used for anthropogenic emissions in our study. For mainland China, the Multi-resolution Emission Inventory for China (MEIC; http://www.meicmodel.org/, last access: 1 November 2020) in 2016 was used. For the rest of Asia, we applied the MIX dataset (http://www.meicmodel.org/dataset-mix, last access: 1 November 2020) for 2010 (Li et al., 2017). For international shipping, the emission database in the Community Emission Data System (CEDS) (McDuffie et al., 2020) for 2017 was used. The HONO emissions from land transportation sources were calculated using their NO\textsubscript{X} emissions and the HONO/NO\textsubscript{X} ratio of 0.8 % for gasoline and 2.3 % for diesel. These commonly used ratios in model studies (Zhang et al., 2016; Fu et al., 2019) are based on the previous measurements of vehicle exhausts (Kurtenbach et al., 2001; Gutzwiller et al., 2002) and are generally consistent with more recent emission result (Liu et al., 2019; Trinh et al., 2017). For ship-emitted HONO, we set the emission ratio of HONO/NO\textsubscript{X} as 0.51 % based on the reported ratio in fresh ship plumes in Chinese waters (Sun et al., 2020). For anthropogenic chlorine emissions, the high-resolution (0.1° × 0.1°) EIs of HCl and fine particulate Cl\textsuperscript{−} for 2014 were applied for mainland China (Fu et al., 2018). These EIs included four sectors and have been shown to offer a reasonable model simulation of particulate chlorine by the WRF-Chem model (Dai et al., 2020). The Reactive Chlorine Emission Inventory (RCEI; Keene et al., 1999) was used for anthropogenic chlorine emissions in the other regions. For natural emissions, the biogenic emissions were calculated by the Model of Emission of Gas and Aerosols from Nature (MEGAN) version 2.1 (Guenther et al., 2006).

The spatial distribution of ship NO\textsubscript{X} emissions is shown in Fig. 1a. The main ship routes with high emission intensity are clearly identified in the ship emission inventory. One major shipping lane is located in the southern Bay of Bengal (BOB) in the Indian Ocean, passes through the Strait of Malacca, and extends to the South China Sea (SCS) and other Asian countries. Distinct shipping lanes are also shown along the coast of the East China Sea (ECS) and the Sea of Japan (SOJ). Over the western Pacific Ocean (WPO), congested ship routes are distributed among Japan and other countries (Southeast Asian countries, Australia, and North America). Based on the distribution of ship NO\textsubscript{X} emissions, six water zones were selected, including three waters around China (SCS; ECS; Bohai Rim, BR), two waters in other regions (SOJ and BOB), and one open ocean (WPO; Fig. 1b). In addition, three densely populated city clusters were chosen (the North China Plain, NCP; the Yangtze River Delta, YRD; and the Pearl River Delta, PRD).

2.3 Experimental setting

Eight simulations were conducted with different emissions and chemistry, as listed in Table 1. In the Def and Def_noship cases, the WRF-Chem model was conducted with default chemistry (i.e. the default CBMZ mechanism with only the two HONO sources and no chlorine chemistry). The differences between Def and Def_noship (i.e. Def – Def_noship) represent the effects of ship emissions with the default nitrogen chemistry. In the Cl and Cl_noship cases, an updated chlorine chemistry in the revised WRF-Chem model was used. The differences between the two cases (i.e. Cl – Cl_noship) represent the effects of ship emissions with the default and additional chlorine chemistry. Similarly, in the HONO and HONO_noship cases, the additional HONO chemistry was used, and the difference between the two cases (i.e. HONO – HONO_noship) represents the default impact of ship emissions with additional HONO chemistry. In the BASE and BASE_noship cases, the integrated HONO and chlorine chemistry are considered. The differences between BASE and BASE_noship represent the shipping impact with the integrated effects of HONO and chlorine species. The results from the BASE experiment will be used to validate the model performance.

Table 1. Experimental setting.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Anth. emis.\textsuperscript{a}</th>
<th>Ship emis.\textsuperscript{b}</th>
<th>HONO chem.\textsuperscript{c}</th>
<th>Chlorine chem.\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Def</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Def_noship</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Cl</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Cl_noship</td>
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<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>HONO</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>HONO_noship</td>
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<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>BASE</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>BASE_noship</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Anthropogenic emissions except for ship emissions. \textsuperscript{b} Ship emissions except for directly emitted HONO. \textsuperscript{c} HONO chemistry. \textsuperscript{d} Chlorine chemistry.
2.4 Observational data and model validation

Meteorological data from surface stations from the NOAA National Climatic Data Center (NCDC; Fig. S1a in the Supplement) comprising wind direction, wind speed, surface temperature, and specific humidity were used to validate model performance for the meteorological parameters. Conventional air pollutant data (NO\textsubscript{2}, PM\textsubscript{2.5}, and O\textsubscript{3}) from surface stations (obtained from China’s Ministry of Ecology and Environment; Fig. S1b) were used to evaluate the simulated air pollutants over mainland China. Table S2 summarizes the statistical performance of our model results. For meteorological parameters, high R values (> 0.85) and low mean bias (MB) values indicate good performance for the meteorological field. For regular air pollutants, the model overpredicted PM\textsubscript{2.5} (MB = 10.6 µg m\textsuperscript{-3}) and slightly underpredicted NO\textsubscript{2} (MB = 3.3 ppbv) and O\textsubscript{3} (MB = 5.5 ppbv). These biases in simulation can be partially explained by uncertainties in the model input, such as the land-use data (Dai et al., 2019) and emission inventory (Li et al., 2017).

The O\textsubscript{3} data from two remote sites, Ryori and Yonagunijima (Yona) in Japan (https://www.data.jma.go.jp/ghg/kanshi/ghgp/o3_e.html, last access: 1 November 2020) and one coastal background site in Hong Kong, Hok Tsui (HT), were used to compare the model performance over the maritime areas. These three sites are located along the coasts of the SCS, ECS, and WPO regions (Fig. 1b). As shown in Fig. S2, with the default chemistry, the model underpredicted the O\textsubscript{3} mixing ratio at the coastal and marine sites, with an underestimation of 2.8, 4.8, and 2.3 ppbv at the HT, Ryori, and Yona sites respectively (Table S3). With the addition of the HONO and ClNO\textsubscript{2} chemistry, the simulated O\textsubscript{3} levels at the marine sites were improved, with an MB of −2.8 to −1.5 ppbv at the HT site, −3.0 to −2.3 ppbv at the Ryori site, and −2.3 to −0.7 ppbv at the Yona site.

3 Results

3.1 Simulated HONO and ClNO\textsubscript{2} and contributions from ship emissions

Figure 2a shows the horizontal distribution of the average HONO at the surface layer in the BASE case. The predicted HONO was widespread over the oceans, with mixing ratios ranging from 0.005 to 0.300 ppbv and distinct higher concentrations along the main shipping lanes. The distribution of HONO was consistent with that of NO\textsubscript{2} (Fig. S3) due to the heterogeneous conversion of NO\textsubscript{2} to form HONO and direct HONO emission from ships. In the vertical direction, the simulated HONO was concentrated at the surface and reached up to 400–600 m in the coastal and marine areas (see Fig. S4). Figure 3 shows the vertical profile of HONO from ship emissions in the nine selected regions. Consistent with the overall HONO vertical distribution, ship-contributed HONO also peaked at the surface in the oceanic areas, with average HONO levels of 3–120 pptv in the marine boundary layer (MBL). The greatest contribution of ship emissions was simulated in the WPO (96 %), followed by the SOJ (80 %), the BOB (49 %), the three Chinese waters (14 %–16 %), and the coastal cities (3 %–12 %). The varying ship contributions in these regions can be explained by the relative strength of the emissions from ships and from the adjacent land areas.

High values of ClNO\textsubscript{2} were simulated along the coasts and peaked in the lower MBL (Fig. 2b), with mixing ratios ranging from 2 to 400 pptv in oceanic areas and the highest value in the BR region. This distribution was in line with
Figure 2. Spatial distributions of the simulation of averaged (a) HONO (in ppbv, whole day) and (b) night-time ClNO$_2$ (in pptv, 18:00–06:00 LST, local standard time) at the surface layer (∼30 m) in July 2018 from the BASE case. The arrows present simulated wind vectors from the BASE case.

Figure 3. Vertical profiles of simulated HONO and night-time ClNO$_2$ (in ppt) from ship emissions and other sources in the nine regions. Also shown are the contributions of ship emissions and other sources to averaged HONO and night-time ClNO$_2$ levels in the marine boundary layer (within 600 m).
that of its precursors, \( \text{N}_2\text{O}_5 \) (Fig. S5) and particulate chloride (Fig. S6). Vertically, the peak value of \( \text{ClNO}_2 \) was simulated in the residual layer (100–300 m; Fig. 3), with mixing ratios of 8–350 pptv in oceanic areas. Similar to HONO, the greatest ship contribution to \( \text{ClNO}_2 \) was also simulated in the WPO (61 %), followed by other oceanic areas (9 %–24 %) and coastal cities (5 %–11 %).

We compared the modelled HONO and \( \text{ClNO}_2 \) with field observations made at some coastal and marine sites (see Table S4). The simulated HONO mixing ratios were 0.1–0.3 ppbv and 0.01–0.1 ppbv over the respective coastal BR and SCS sites and were comparable to the measurements at the marine sites of the BR (0.2 ppbv) (Wen et al., 2019) and SCS (89 pptv) (Table S4). For the coastal areas of other Asian countries, the simulated HONO compared well with the measurements in South Korea (0.60 ppbv) (Kim et al., 2015) and Japan (0.63 ppbv) (Takeuchi et al., 2013). HONO was simulated at approximately 5 pptv in the open ocean and 10–25 pptv along the main shipping lanes (Fig. 2a), which are values comparable to the measured HONO (3–35 pptv) in the open ocean in Europe and North America (Meusel et al., 2016; Kasibhatla et al., 2018; Ye et al., 2016). For \( \text{ClNO}_2 \), the order of magnitude and variation in the measured \( \text{N}_2\text{O}_5 \) and \( \text{ClNO}_2 \) levels at the HT site were reasonably reproduced by our model for early autumn of 2018 (Dai et al., 2020). The model performance of HONO and \( \text{ClNO}_2 \) in the land areas of mainland China for the summer of 2014 was also evaluated by L. Zhang et al. (2017). Overall, our model ability with respect to simulating HONO and \( \text{ClNO}_2 \) is acceptable, and the model results are sufficiently reliable for further analysis.

### 3.2 Impact of ship-derived HONO and chlorine on \( \text{RO}_x, \text{O}_3, \) and PM\(_{2.5}\)

In this section, we evaluate the ship effects on the main atmospheric radicals (\( \text{RO}_x = \text{OH} + \text{HO}_2 + \text{RO}_2 \)), \( \text{O}_3 \), and PM\(_{2.5}\) with the default chemistry (described in Sect. 2.3) and with the additional HONO and chlorine chemistry.

#### 3.2.1 \( \text{RO}_x \)

Figure 4 shows the simulated differences in the average daytime \( \text{RO}_x \) mixing ratios at the surface from the cases with and without ship emissions using different chemistry. The \( \text{RO}_x \) mixing ratio was noticeably increased by ship emissions over oceanic areas, and this enhancement was magnified by the additional nitrogen chemistry. With the default chemistry (Fig. 4a), the average ship contribution to \( \text{RO}_x \) was about 18 % over the whole oceanic area. The addition of the HONO and chlorine chemistry increased the ship contributions to 28 % (Fig. 4b) and 22 % (Fig. 4c) respectively. Photolysis of ship-generated HONO and \( \text{ClNO}_2 \) released radicals (OH and Cl; Fig. S7) and recycled \( \text{NO}_x \), which then oxidized VOCs and gave rise to high levels of \( \text{RO}_x \). With the combined HONO and chlorine chemistry, the ship contribution was further increased to 38 % (Fig. 4d). This combined ship contribution was smaller than the sum of that from the separate HONO and chlorine chemistry (22 % + 28 % = 50 %), which can be explained by the nonlinear interactions of the chemical system. Figure 5 shows the vertical profile of the \( \text{RO}_x \) mixing ratio from ship emissions in the nine regions. The enhanced \( \text{RO}_x \) reached an altitude of greater than 2 km over the oceanic regions, indicating the significant impact of ship-derived HONO and \( \text{ClNO}_2 \) on the oxidative capacity in the marine troposphere.

The largest increase in the ship contribution to \( \text{RO}_x \) was predicted in the WPO region (from 29 % to 50 %; Fig. 9a), followed by other oceanic areas (from 3 %–12 % to 6 %–17 %) and coastal cities (from −2 %–3 % to 4 %–6 %). The maximum ship contribution in the WPO region was consistent with the greatest ship contribution to HONO and \( \text{ClNO}_2 \) in this region (Fig. 4d). In the SCS and BOB regions, the enhanced \( \text{RO}_x \) was more dispersed with the combined nitrogen chemistry than that with the default and separate nitrogen chemistry. In the coastal cities, the \( \text{RO}_x \) mixing ratio was also affected by ship emissions via the transport of ship-generated HONO and \( \text{ClNO}_2 \) by summertime winds.

#### 3.2.2 \( \text{O}_3 \)

Figure 6 shows the simulated differences in the average \( \text{O}_3 \) at the surface from the cases with and without ship emissions. Consistent with the impact of ship emissions on oceanic \( \text{RO}_x \), the oceanic \( \text{O}_3 \) was also noticeably increased (by 9 %) by ship emissions, which was further enhanced by the addition of HONO (12 %) and \( \text{ClNO}_2 \) (14 %) and combined nitrogen chemistry (21 %). The simulated distribution of ship-enhanced \( \text{O}_3 \) with the default chemistry was along the main shipping routes with high \( \text{NO}_x \) emissions (Fig. 6a). \( \text{O}_3 \) formation was highly sensitive to \( \text{NO}_x \) from ship emissions due to the relatively low concentrations of \( \text{NO}_x \) in the marine areas. The larger ship contribution with \( \text{ClNO}_2 \) chemistry than with HONO chemistry may be partially explained by a higher production ozone efficiency by \( \text{NO}_x \) than by NO (from photolysis of HONO) and by the faster reaction rate of Cl radicals than OH radicals with long-lived alkanes.

With the combined impact from HONO and \( \text{ClNO}_2 \), widespread ozone increases were simulated over the SCS, BOB, and WPO regions (Fig. 6d). The combined nitrogen chemistry also increased the ozone concentrations in the coastal areas; in contrast, these concentrations were decreased by HONO or \( \text{ClNO}_2 \) separately. As shown in Fig. 6b and c, distinct ozone enhancement was simulated over the marine area of South Korea and Japan by HONO or \( \text{ClNO}_2 \). However, this enhancement was weakened and even cancelled by their combined effects. We calculated an indicator of the ozone formation regimes based on the ratio of the production rate of \( \text{H}_2\text{O}_2 \) to that of \( \text{HNO}_3 \) (\( \text{P}(\text{H}_2\text{O}_2)/\text{P}(\text{HNO}_3) \)) (Fu et al., 2020). Figure 7, with the combined HONO and \( \text{ClNO}_2 \) chemistry, shows that the \( \text{NO}_x \)-sensitive regime in East Asia

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Figure 4. Averaged daytime RO\textsubscript{X} changes due to ship emissions (06:00–18:00 LST; in pptv) with (a) default chemistry (Def – Def\textsubscript{noship}), (b) default and additional HONO chemistry (HONO – HONO\textsubscript{noship}), (c) default and additional chlorine chemistry (Cl – Cl\textsubscript{noship}), and (d) default and combined HONO and chlorine chemistry (BASE – BASE\textsubscript{noship}). The arrows present simulated wind vectors from the BASE case.

Figure 5. Vertical profiles of daytime RO\textsubscript{X} changes due to ship emissions (in pptv) from different chemistry in the nine regions.

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Figure 6. The 24 h averaged ozone changes (06:00–18:00 LST; in ppbv) due to ship emissions with (a) default chemistry (Def – Def_noship), (b) default and additional HONO chemistry (HONO – HONO_noship), (c) default and additional chlorine chemistry (Cl – Cl_noship), and (d) default and combined HONO and chlorine chemistry (BASE – BASE_noship). The arrows present simulated wind vectors from the BASE case.

Figure 7. The O₃ sensitivity regimes using the (a) Def, (b) HONO, (c) Cl, and (d) the BASE cases. The classification of the ozone sensitivity regime is based on production rates of H₂O₂ to HNO₃, and $P_{H_2O_2}/P_{HNO_3}$ values of < 0.06, 0.06–0.2, and > 0.2 correspond to VOC-limited, transition, and NOₓ-limited conditions respectively (Zhang et al., 2009).
Figure 8. Averaged PM$_{2.5}$ enhancements due to ship emissions (in µg m$^{-3}$) with (a) default chemistry (Def − Def_noship), (b) default and additional HONO chemistry (HONO − HONO_noship), (c) default and additional chlorine chemistry (Cl − Cl_noship), and (d) default and combined HONO and chlorine chemistry (BASE − BASE_noship). The arrows present simulated wind vectors from the BASE case.

was changed to a VOC-sensitive regime, which was probably due to the increase level of NO or NO$_2$ from photolysis of HONO.

Figure S8 shows the vertical profile of ship-generated O$_3$ enhancement in the nine regions. Similar to ship-enhanced RO$_x$, ship-related O$_3$ enhancement stretched from the surface to the lower troposphere (> 2 km) over the marine regions. Because the emissions from ships occur at the sea surface, the vertically enhanced O$_3$ formation was caused by strong convection (Dalsøren et al., 2009).

The ship contribution to O$_3$ formation was also simulated in the WPO region (from 21 % to 38 %; Fig. 9b). Moreover, in other oceanic areas, the contributions of ship emissions were increased from 3 %–18 % to 12 %–24 %, with two distinct O$_3$ enhancements over the BR (~10 ppbv; Fig. 6d) and ECS (15 ppbv) regions. In the three coastal city clusters, the reduced O$_3$ formation was simulated by ship emissions with the default chemistry (from −5 to −1 ppb). Because these coastal cities are in the VOC-limited regime (Fig. 7a), the NO$_x$ from ships would lead to a decrease in chemical O$_3$ production. With the combined HONO and ClNO$_2$ effects, the ship-induced O$_3$ increased to −1 to −5 ppb due to the enhanced radicals and the transport of O$_3$ in the marine areas by ship-generated HONO and ClNO$_2$. The maximum O$_3$ increase in coastal cities also doubled from 3 ppb (5 %) to 7 ppb (11 %), aggravating the negative effects of ship emissions on human health in these regions.

In addition to the above coastal and oceanic areas, ship emissions also exert considerable impact on surface O$_3$ in distant inland areas such as the Sichuan Basin, and, interestingly, there are some “hot spots” of ozone (as well as RO$_x$, Fig. 4a–d, and PM$_{2.5}$, Fig. 8a–d) increase or decrease in the inland areas due to ship emissions (Fig. 6a–d). These hot spots may be a result of the inhomogeneous impact of ship emissions due to complicated dynamic and chemical processes that affect the fate and distribution of ship-emitted pollutants in the inland areas. In particular, the mountainous terrain in southern China may have large influence on the transport of ship emissions to inland areas.

3.2.3 PM$_{2.5}$

Ship-derived HONO and ClNO$_2$ also influence the production of aerosols via changes in radicals and NO$_x$. Figure 8 shows the simulated differences in the average PM$_{2.5}$ at the surface for cases with and without ship emissions. The PM$_{2.5}$ concentration was considerably enhanced by ship emissions, and the additional nitrogen chemistry further increased the simulated PM$_{2.5}$ concentration. With the default chemistry, the average ship contribution to the PM$_{2.5}$ concentration was about 7 % in oceanic areas (Fig. 8a), and it was increased to 10 % with the addition of HONO and ClNO$_2$ chemistry (Fig. 8d). The greatest contribution from shipping to the PM$_{2.5}$ concentration was also simulated over the WPO re-
Figure 9. Contributions of ship emissions with different chemistry (Default, ReNOM_HONO, ReNOM_Cl, and ReNOM) to average mixing ratios of (a) daytime RO\textsubscript{x}, (b) ozone, and (c) PM\textsubscript{2.5}.

Compared with previous studies, our study simulated a higher contribution to average ozone formation and a smaller contribution to average PM\textsubscript{2.5}. We note that the underprediction of NO\textsubscript{2} in our simulation may lead to an underestimation of HONO, and the overpredicted PM\textsubscript{2.5} can result in an overestimation of NO\textsubscript{2} to HONO, and production of CINO\textsubscript{2}. The exact effects of these uncertainties on the ozone and PM\textsubscript{2.5} is difficult to quantify. It is also difficult to discern the differences in our and previous modelling studies due to the differences in the methodologies adopted, including ship emission inventory, model resolution, chemical mechanisms (in addition to different treatment of HONO and CINO\textsubscript{2} chemistry), and period of study. However, all of these studies demonstrate an important impact of ship emissions on atmospheric chemistry and air quality. The key finding of our study is the role of HONO and CINO\textsubscript{2} in driving the oxidation processes, which has not been fully considered in most previous model studies of the impact of shipping on pollutant levels.

4 Conclusions

This study evaluated the production of HONO and CINO\textsubscript{2} from international shipping and their impact on the oxidative capacity, ozone level, and level of fine PM in the maritime and coastal areas of eastern Asia. The results show that photolysis of the two compounds releases OH and Cl radicals, recycles NO\textsubscript{x}, and changes conventional hydroxyl and organic peroxy radicals (RO\textsubscript{x} = OH + HO\textsubscript{2} + RO\textsubscript{2}) by 0.8\%–21.4\% (0.8\%–7.7\% over coasts and 2.6\%–21.4\% over oceans), O\textsubscript{3} by 5.9\%–16.6\% (6.9\%–14.6\% over coasts and 5.9\%–16.6\% over oceans), and PM\textsubscript{2.5} by −1.2\%–8.6\% (−1.2\% to 6\% over coasts and 3.2\%–8.6\% over oceans) at the surface of the western Pacific regions. Their impact extends to the marine boundary layer. The largest contributions of HONO and CINO\textsubscript{2} occur in the relatively remote oceans. Because ocean-going ships are a major source of NO\textsubscript{x}, which is the key chemical precursor to HONO and CINO\textsubscript{2}, it is important to consider the sources and chemistry of these nitrogen compounds in evaluations of the impact of ship emissions.
Competing interests. The authors declare that they have no conflict of interest.

Author contributions. TW initiated the research, and JD and TW designed the paper framework. JD ran the model, processed the data, and made the plots. JD and TW analysed the results and wrote the paper.

Competing interests. The authors declare that they have no conflict of interest.

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References


