Thank you for your careful review and constructive suggestions. These suggestions are quite valuable to us, and help improve our manuscript a lot.

Point-to-point responses

We appreciate the reviewers for their valuable and constructive comments, which are very helpful for the improvement of the manuscript. We have revised the manuscript carefully according to the reviewers' comments. We have addressed the reviewers' comments on a point-to-point basis as below for consideration, where the reviewers' comments are cited in ***black****, and the responses are in* ***blue****.*

Heterogeneous reaction of NO2 on wet surfaces is an important source of HONO. However, there are still many uncertainties in the research on the mechanism of the heterogeneous reaction of NO2 to produce HONO, and a complete consensus has not yet been reached in the scientific research community. Pseudo-steady-state calculations and model simulations also show that HONO levels will be greatly underestimated by considering only homogeneous chemical reactions. At present, the assessment of the contribution of the heterogeneous reaction of NO2 to HONO in the vertical boundary layer has not been fully determined, which hinders the in-depth understanding of the distribution characteristics of tropospheric HONO, the transformation and formation process and its environmental effects. In addition, the research on HONO and its precursors in coastal and offshore scenarios is not sufficient, resulting in a lack of understanding of the ocean-atmospheric nitrogen cycle and the sea-land-atmosphere interaction.
Xing et al. can not only provide data support for the improvement of atmospheric chemistry models, but also provide new insights for exploring the vertical sources of HONO on land and sea and the effect of photolysis on the oxidation capacity of the upper atmosphere, but also for the prevention and control of atmospheric composite pollution and PM2.5. The synergistic control with O3 provides new scientific basis and clues. I suggest publication in ACP after minor revision. The detailed comments are as follows:

1. In this study, the uncertainty evaluation is imperfect. I suggest the authors to add a section or even in the supplement to explain the uncertainties of data or how trustworthy of the presented data in this manuscript.

Re: Thanks for your great comments.
We have supplemented error analysis in the main text as follows.
Main text:

"2.4 Error analysis

For profile retrieval, the error sources can be divided into four different types: smoothing error, measurement noise error, forward model error, and model parameter error (Rodgers, 2004). However, in terms of this classification, some errors are difficult to be calculated or estimated. For example, forward model error, which is caused by an imperfect representation of the physics of the system, is hard to be quantified due to the difficulty of acquiring an improved forward model. Given calculation convenience and contributing ratios of different errors in total error budget, we mainly took into account error sources based on the following classification, which were smoothing and noise errors, algorithm error, cross section error, and uncertainty related to the aerosol retrieval (only for trace gas). Here, we estimated the

contribution of different error sources to the trace gas vertical column densities (VCDs) and AOD, and near-surface (0–200 m) trace gas concentrations and aerosol extinction coefficients (AECs), respectively. The detailed demonstrations and estimation methods are displayed below, and the final results are summarized in Table 3.

a. Smoothing errors arise from the limited vertical resolution of profile retrieval. Measurement noise errors denote the noise in the spectra (i.e., the fitting error of DOAS fits). They can be quantified by averaging the error of retrieved profiles, as the error of the retrieved state vector equals the sum of these two independent errors. We calculated the sum of smoothing and noise errors on near-surface concentrations and column densities, which were 14 and 5 % for aerosols, 16 and 17 % for NO_2, and 20 and 22 % for HONO, respectively in the sea scene. The corresponding values were 13 and 5 % for aerosols, 14 and 16 % for NO_2, and 18 and 20 % for HONO, respectively at SUST and 13 and 5 % for aerosols, 15 and 17 % for NO_2, and 19 and 21 % for HONO at CAMS.
b. Algorithm error is the discrepancy between the measured and modelled DSCDs. This error contains forward model error from an imperfect approximation of forward function (e.g., spatial inhomogeneities of absorbers and aerosols), forward model parameter error from selection of parameters, and error not related to the forward function parameters, such as detector noise (Rodgers, 2004). Algorithm error is a function of the viewing angle, and it is difficult to assign this error to each altitude of profile. Usually, the algorithm errors on the near-surface values and column densities are estimated by calculating the average relative differences between the measured and modeled DSCDs at the minimum and maximum elevation angle (except 90 °), respectively (Wagner et al., 2004). Considering its trivial role in the total error budget, we estimated these errors on the near-surface values and the column densities at 4 and 8 % for aerosols, 3 and 11 % for NO_2, and 20 and 20 % for HONO, according to Wang et al. (2017) and Wang et al. (2020).
c. Cross section error is the error arising from an uncertainty in the cross section. According to Thalman and Volkamer, (2013), Vandaele et al. (1998), and Stutz et al. (2000), we adopted 4, 3, and 5 % for O_4 (aerosols), NO_2, and HONO, respectively.
d. The trace gas profile retrieval error represents the one, which is sourced from aerosol extinction profile retrieval and propagated to retrieved trace gas profile. This error could be roughly estimated based on a linear propagation of the total error budgets of the aerosol retrievals. The errors of trace gases were roughly estimated at 15% for VCDs and 10% for near-surface concentrations for the two trace gases in the sea scene. The corresponding values were 14 and 10 % for near-surface concentrations and VCDs, respectively at SUST, and 14 and 10 % at CAMS.

The total uncertainty was calculated by adding all the error terms in the Gaussian error propagation, and the final results were listed in the bottom row of Table 3. We found that the sum of smoothing and noise errors played a dominant role in the total uncertainty.”

Table 3. Error budget estimation (in %) of the retrieved near-surface (0–200 m) trace gas concentrations and AECs, and trace gas VCDs and AOD.

			Error source				Total
			Smoothing and noise errors	Algorithm error	Cross section error	Related to the aerosol retrieval (only for trace gases)	
Cruise route	Near-surface	aerosol	14	4	4	-	15
		NO_2	16	3	3	15	22
		HONO	20	20	5	15	32
	VCD or AOD	AOD	5	8	4	-	10
		NO_2	17	11	3	10	23
		HONO	22	20	5	10	32
SUST	Near-surface	aerosol	13	4	4	-	14
		NO_2	14	3	3	14	20
		HONO	18	20	5	14	31
	VCD or AOD	AOD	5	8	4	-	10
		NO_2	16	11	3	10	22
		HONO	20	20	5	10	30
CAMS	Near-surface	aerosol	13	4	4	-	14
		NO_2	15	3	3	14	21
		HONO	19	20	5	14	31
	VCD or AOD	AOD	5	8	4	-	10
		NO_2	17	11	3	10	23
		HONO	21	20	5	10	31

2. The authors should explain the meaning of this works clearly. Moreover, I suggest to shorten the abstract, which is quite long and contains too many details.

Re: Thanks for your great comments. We have deleted many unnecessary details and further simplified the abstract as follows. And the meaning of this work has been emphasized by underlining.

"Ship based multi-axis differential optical absorption spectroscopy (MAX-DOAS) measurements were conducted along the marginal seas of China from 19 April to 16 May 2018 to measure the vertical profiles of aerosol, nitrogen dioxide (NO_2), and nitrous acid (HONO). Along the cruise route, we found five hot spots with enhanced tropospheric NO_2 VCDs in Yangtze River Delta, Taiwan straits, Guangzhou-Hong Kong-Macao Greater Bay areas, Zhanjiang Port, and Qingdao port. Enhanced HONO concentrations could usually be observed under high-level aerosol and NO_2 conditions, whereas the reverse was not always the case. To understand the impacts of relative humidity (RH), temperature, and aerosol on the heterogeneous reaction of NO_2 to form HONO in different scenes, the Chinese Academy of Meteorological Sciences (CAMS) and Southern University of Science and Technology (SUST) MAX-DOAS stations were selected as the inland and coastal cases, respectively. The RH turning points in CAMS and SUST cases were both ~65% (60–70%), whereas two turning peaks (~60% and ~85%) of RH were found in the sea cases. As temperature increased, the HONO/NO_2 ratio decreased with peak values appearing at ~12.5℃ in CAMS, whereas the HONO/NO_2 gradually increased and reached peak values at ~31.5℃ in SUST. In the sea case, when the temperature exceeded 18.0℃, the HONO/NO_2 ratio rose with increasing temperature and achieved its peak at ~25.0℃. This indicated that high temperature can contribute to the secondary formation of HONO in the sea

atmosphere. In the inland case, the correlation analysis between HONO and aerosol in the near-surface layer showed that the ground surface is more crucial to the formation of HONO via the heterogeneous reaction of NO_2; however, in the coastal and sea cases, the aerosol surface contributed more. Furthermore, we discovered that the conversion rate of NO_2 to HONO through heterogeneous reaction in the sea case is larger than that in the inland case in higher atmospheric layers (> 600 m). Three typical events were selected to demonstrate three potential contributing factors of HONO production under marine conditions (i.e., transport, NO_2 heterogeneous reaction, and unknown HONO source). This study elucidates the sea-land and vertical differences in the forming mechanism of HONO via the NO_2 heterogeneous reaction and provides deep insights into tropospheric HONO distribution, transforming process, and environmental effects."

3. The methodology section is too simple, especially in the vertical profile inversion module. Authors should provide detailed descriptions even in supplement.

Re: Thanks for your great comments. We have supplemented some contents in Section 2.3 and Supplementary materials as follows.

Re: Thanks for your great comments. We have supplemented some contents in Section 2.3 and Supplementary materials as follows.

Section 2.3: "The detailed retrieval procedure is displayed in Appendix I and Figure S3."

Appendix I: "The maximum a posteriori state vector $\mathbf{x}$ is determined by minimizing the following cost function χ^2.

$$\chi^2 = (\mathbf{y} - F(\mathbf{x},\mathbf{b}))^T \mathbf{S}_\varepsilon^{-1} (\mathbf{y} - F(\mathbf{x},\mathbf{b})) + (\mathbf{x} - \mathbf{x}_a)^T \mathbf{S}_a^{-1} (\mathbf{x} - \mathbf{x}_a) \quad (1)$$

Here, $F(\mathbf{x},\mathbf{b})$ is the forward model, which describes the measured DSCDs $\mathbf{y}$ as a function of the retrieval state vector $\mathbf{x}$ (i.e., aerosol and trace gas vertical profiles) and the meteorological parameters $\mathbf{b}$ (e.g., atmospheric pressure and temperature profiles); $\mathbf{x}_a$ denotes the a priori vector that serves as an additional constraint; $\mathbf{S}_\varepsilon$ and $\mathbf{S}_a$ are the covariance matrices of $\mathbf{y}$ and $\mathbf{x}_a$, respectively. The retrieval of vertical profiles of aerosols and trace gases were classified into two steps (Figure S3). First, we retrieved vertical aerosol profiles based on a series of retrieved O4 DSCDs at different elevation angles. Second, the retrieved aerosol extinction profiles were utilized as the input parameters to the RTM to retrieve NO2 and HONO vertical profiles. Each scanning sequence of DSCD results (~5.5 min) correspond to one retrieved vertical profile information. In this study, we separated the atmosphere into 19 layers from 0 to 3.8 km with a vertical resolution of 0.2 km. Given the low sensitivity of MAX-DOAS measurements to high altitude and low concentration of pollutants above 3.0 km, we only displayed the vertical profiles below 3.0 km in this work."

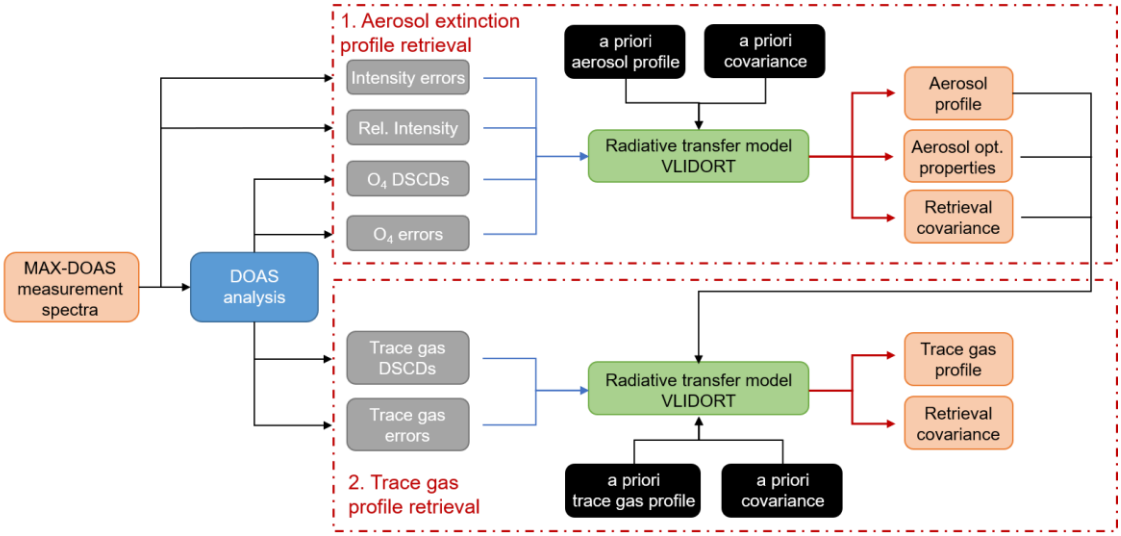

Figure S3. Flowchart of the aerosol and trace gas retrieval algorithm. The dashed-lined red boxes denote the retrieval steps: aerosol and trace gas profile retrieval.

4. Section 3.4: The case study is too subjective. The authors should add detailed reasons for the case selection. Furthermore, section 3.4.2 lacks of sufficient proof.

Re: Thanks for your great comments. We added the reasons for the case selection in front of Section 3.4.1-3.4.3 as follows.

"The important factors and precursors to drive the formation of HONO through heterogeneous reaction had complex evolution and transport characteristics. To further clarify the role of these parameters in the heterogeneous process of NO_2 to form HONO, three typical processes were selected to reveal the favorable conditions for HONO formation at sea scene."

To make demonstrations more reasonable, we have done the following revisions:

1) Supplement a figure about backward trajectories of air masses to support our discussion.

"NO_2 was mainly distributed near the sea surface layer 0–200 m, and a high-concentration NO_2 air mass was found from 1.0–2.0 km during 13:00–14:00 due to the short distance transport of NO_2 emitted from ships in Xiamen port (Figure S13)."

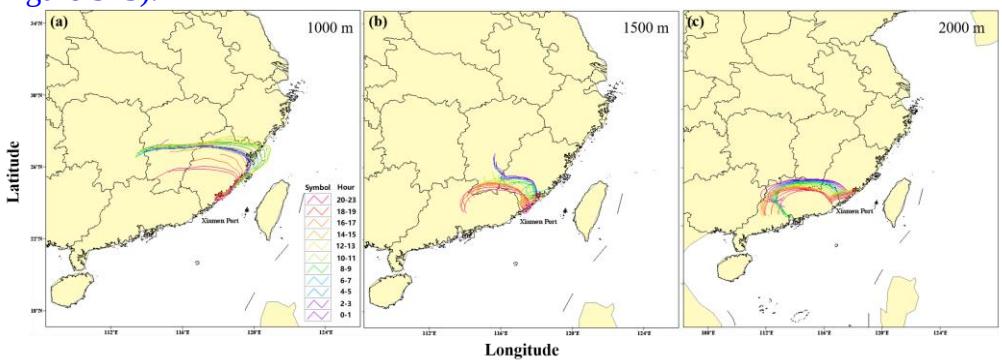

Figure S13. Daily 72-h backward trajectories of air masses in Xiamen port at (a) 1000 m, (b) 1500 m, and (c) 2000 m on 28 April 2018, respectively.

2) Transform some decisive descriptions into inferential ones.

"The higher RH and temperature (Tem) (RH: ~75.0%, Tem: 23.7℃) at 14:00-16:00 than that (RH: ~67.6%, Tem: 23.1℃) at 09:00-11:00 (Figure 14

(d)-(e)) promoted the HONO formation from the heterogeneous reaction of NO_2 on the aerosol surface during 14:00-16:00." -> "The slight increase of RH and temperature (Tem) at 14:00–16:00 (RH: ~75.0%, Tem: 23.7℃) may contribute to HONO formation through heterogeneous reaction of NO_2 on the aerosol surface than that at 09:00–11:00 (Figure 13 (d)-(e), Section 3.2)."

3) Add corresponding citations to support demonstrations.
"The higher SRI accelerated the photolysis of HONO during 09:00-11:00 period" -> "The higher SRI accelerated the photolysis of HONO during 09:00-11:00 period (Kraus et al., 1998)."

5. The conclusion is too long and should be shorten. Moreover, the implication the ship-based observation should be also added.

Re: Thanks for your great comments. We have deleted unnecessary details in the conclusion and supplemented the implication of ship-based observations as follows.

"Currently, many uncertainties in the study of the HONO forming mechanism through the heterogeneous reaction of NO_2 exist. Earlier studies mostly focused on the near-surface layer, and the assessment of the contribution of NO_2 heterogeneous reaction to HONO formation in the vertical direction of the boundary layer is insufficient. Therefore, we aim to learn the sea-land and vertical differences of the HONO forming mechanism from NO_2 heterogeneous reaction and provide deep insights into the distribution characteristics, transforming process, and environmental effects of tropospheric HONO. Ship based MAX-DOAS observations along the marginal seas of China were performed from 19 April to 16 May 2018. Simultaneously, two ground-based MAX-DOAS observations were conducted in the inland station CAMS and the coastal station SUST to measure the aerosol, NO_2, and HONO vertical profiles.

Along the cruise route, we found five hot spots with enhanced tropospheric NO_2 VCDs in Yangtze River Delta, Taiwan straits, Guangzhou-Hong Kong-Macao Greater Bay areas, Zhanjiang Port, and Qingdao port. Under high-level NO_2 conditions in the above five hot spots, we also observed enhanced HONO levels. Contrastingly, the low-concentration HONO accompanied high-level NO_2 in the southeast coastline of Jiangsu province. When peak AOD and NO_2 conditions were observed, enhanced HONO were observed, although the reverse was not always the case.

To understand the impacts of RH, temperature, and aerosol on the heterogeneous reaction of NO_2 to produce HONO, the emission ratios of $\Delta HONO/\Delta NOx$ were calculated to quantify the contribution of the primary HONO source to the total production of HONO. We found that the RH turning points in CAMS and SUST cases were both ~65% (60–70%), whereas two turning peaks (~60% and ~85%) of RH were found in the sea cases. This implied that high RH could contribute to the secondary formation of HONO in sea atmosphere. With increase in temperature, the $HONO/NO_2$ decreased with peak values appearing at ~12.5℃ in CAMS, whereas the $HONO/NO_2$ gradually increased and reached peak values at ~31.5℃ in SUST. In the sea case, when the temperature exceeded 18.0℃, the $HONO/NO_2$ increased with the increasing temperature and achieved peak at ~25.0℃. This indicated that high temperature could promote the secondary formation of HONO in the sea and coastal atmosphere. Additionally, the correlation analysis under different sea-land conditions indicated that the ground surface is more crucial to the formation of HONO from NO_2 heterogeneous reaction in the inland case, whereas the aerosol surface contributed more in the coastal and sea cases.

Furthermore, we found that the $HONO/NO_2$ in the sea case was about 4.5 times larger than that in the inland case above 600 m when AEC was ~0.2 km^{-1}, and the $HONO/NO_2$ ratio in the sea case was about 2 times larger than that in the inland case above 600 m when AEC was ~0.8 km^{-1}, which implied that the generation rate of HONO from NO_2 heterogeneous reaction in the sea case is larger than that in the inland case in higher atmospheric layers (> 600 m). To have a deep understanding of three potential contributing factors of HONO production under marine condition, we selected three typical events, which represented the impacts of transport, NO_2 heterogeneous reaction, and unknown HONO source, respectively.
”