An itemized response (blue words) to the reviewer's comments and suggestions

We sincerely appreciate the reviewer for the comments concerning our manuscript entitled "Roles of oceanic ventilation and terrestrial outflow in the atmospheric non-methane hydrocarbons over the Chinese marginal seas" [EGUSPHERE-2023-2935]. These comments are all valuable and very helpful for improving our paper and have an important guiding significance to our future research. We have made changes to the manuscript and tried our best to improve the manuscript following these comments.

The changed portion in the revised manuscript is highlighted in blue. The primary corrections in the revised manuscript and the detailed responses to the comments of the reviewer are as follows.

This paper presents an analysis of canister measurements of NMHCs at several coastal Chinese cities and over the Chinese marginal seas (along with seawater measurements) to assess the relative impact of oceanic versus terrestrial sources over the seas. Their analysis, which used back trajectories and air-sea fluxes calculated from their measurements, determined that alkanes were primarily impacted by terrestrial sources, whereas alkenes had a larger contribution from oceanic ventilation, with higher NMHC ocean fluxes closer to the coast. PMF analysis confirmed these findings, and provided a more detailed source apportionment of the contributions from industrial, vehicle, terrestrial, and oceanic sources.

I found this paper to be relatively well-written and provides new data in a region that has not been frequently studied. However, as is the conclusions are underwhelming; the fact that this study "highlights the significant influence of terrestrial outflow on the distribution and composition of NMHCs in the nearshore atmosphere of

China…"doesn't seem to me a surprising or new finding. I think the paper needs to do more to demonstrate the implications of this—it begins to do so in lines 467-478 with the discussion of ozone formation potential, but I think it needs more. I suggest editing down some of the correlation and distance analysis earlier in the paper (which all reiterates the same conclusions) and expanding the final section. Perhaps the authors could include a modeling analysis on the impact of air quality (ozone and SOA) over the marginal seas? Or, they could at least expand the source apportionment section and do more to highlight what are the underlying air quality implications? I would support publication after this main concern has been addressed.

Reply: Thanks for your suggestion. In order to assess the impact of air quality (ozone and SOA) over the marginal seas, we calculated the ozone formation potential (OFP) and secondary organic aerosol formation potential (P_{SOAP}) of atmospheric C2-C5 NMHCs. In addition, we examined the impact of terrestrial outflow on oceanic atmosphere environment, in conjunction with the tropospheric aerosol concentrations and ozone level during the investigation period. The modifications are as follows:

Line 175-185:

"**2.5 Calculation of OFP and P_{SOAP} of NMHCs**

To assess the environmental implications of NMHCs, the ozone formation potential (OFP, μg m^{-3}) and secondary organic aerosol (SOA) formation potential (P_{SOAP}, μg m^{-3}) are calculated using Eq. (5) and Eq. (6), respectively (Carter, 1994).

$$OFP_i = MIR_i \times C_i \quad (5)$$

$$P_{SOAPi} = \sum C_i \times SOAP_i \times FAC_{toluene}/100 \quad (6)$$

Where C_i represents the concentration of NMHCs; MIR_i (g O_3/g VOCs) and $SOAP_i$ (relative to toluene = 100) are constants that represent the maximum incremental reactivity and SOA potential of i, respectively (Carter, 2010); $FAC_{toluene}$ is the fractional aerosol coefficient of toluene, which has a value of 5.4% (Grosjean and Seinfeld, 1989). Specific data was listed in supplementary Table S11."

Line 527-555:

Contributions of terrestrial/oceanic NMHCs to SOA and ozone

"The P_{SOAP} of C2-C5 NMHCs in the atmosphere over the Chinese marginal seas was 0.41 ± 0.18 μg m^{-3}, with terrestrial sources contributing the majority (0.32 ± 0.14 μg m^{-3}), accounting for approximately 78% (Fig. 8a). Specifically, the P_{SOAP} from terrestrial alkanes and alkenes were 0.17 ± 0.07 and 0.15 ± 0.06 μg m^{-3}, respectively, while marine sources contributed 0.02 ± 0.01 and 0.07 ± 0.03 μg m^{-3} for alkanes and alkenes, respectively. Additionally, troposphere aerosol concentrations over the Chinese marginal seas during the investigation period were calculated using data from the NASA Goddard Earth Sciences Data and Information Services Center (GES DISC), ranging from 0.77 to 3.98 μg m^{-3}, with an average of 1.80 ± 0.71 μg m^{-3}. The aerosol concentrations decreased from the coastal areas towards the open sea (Fig. 8b), suggesting an obvious influence of terrestrial inputs on the aerosol levels in the coastal atmosphere. Based on the remote sensing data, it is roughly estimated that terrestrial C2-C5 NMHCs contribute ~18% to the total aerosol concentration, indicating their non-negligible role in influencing the atmospheric aerosol levels over the marginal seas. Similarly, the OFP of alkanes and alkenes from terrestrial sources were 2.35 ± 1.01 and 1.18 ± 0.51 μg m^{-3}, respectively, significantly higher than those from marine sources (0.14 ± 0.06 μg m^{-3} for alkanes and 0.50 ± 0.21 μg m^{-3} for alkenes) (Fig. 8c). However, the ozone distribution in the offshore atmosphere of China showed a decreasing trend from north to south (Fig. 8d). The marine atmosphere generally acts as a net ozone sink with ozone being primarily removed by photochemical degradation (Monks et al., 1998; Conley et al., 2011). The increasing solar radiation intensity from north to south enhances ozone degradation rates, likely dominating the ozone distribution in China's offshore atmosphere. Notably, satellite observations (GES DISC) during this investigation period indicated that the tropospheric ozone was approximately 82.6 ± 3.08 μg m^{-3} over the Chinese marginal seas. Among this, terrestrial C2-C5 NMHCs contributed around 4% to total ozone concentration, suggesting a certain impact of

terrestrial outflow on the tropospheric ozone in these regions."

Line 574-578:

"Terrestrial sources (including industrial activities, vehicular exhaust, and vegetation emission) primarily constitute the NMHCs in the nearshore atmospheres, and it partially influences atmospheric SOA and ozone levels. This indicates the potential importance of terrestrial outflow in shaping the air quality and regulating climate dynamics in the marginal seas."

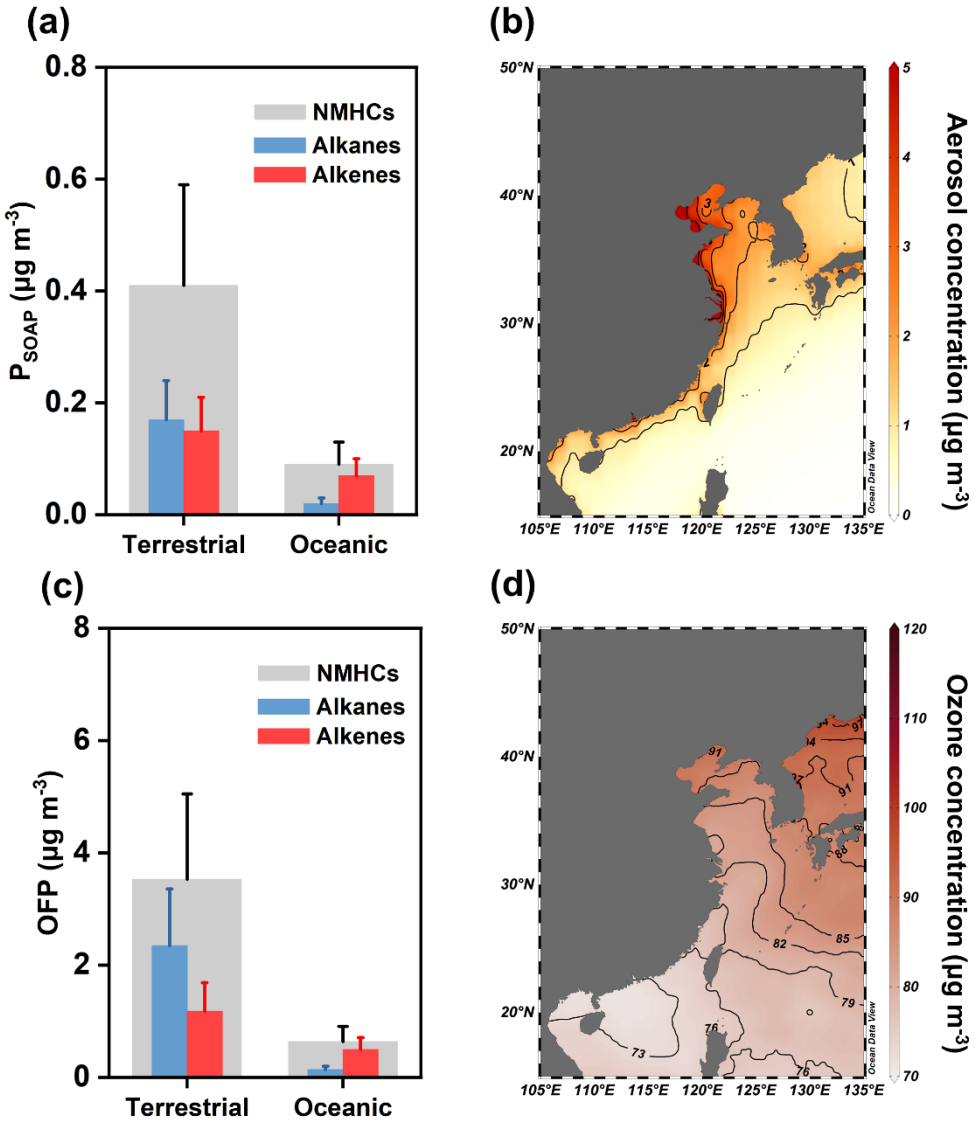

Figure 8 OFP (panel a), P_{SOAP} (panel c) of NMHCs and averaged concentration of troposphere aerosol (panel b), ozone (panel d) during the investigation period over the

Chinese marginal seas. Data of aerosol and ozone were downloaded from GES DISC (https://goldsmr5.gesdisc.eosdis.nasa.gov/data/MERRA2/M2I3NPASM.5.12.4).

Reference:

Carter, W. P. L.: Development of a condensed SAPRC-07 chemical mechanism, Atmos. Environ., 44, 5336-5345, https://doi.org/10.1016/j.atmosenv.2010.01.024, 2010.

Conley, S. A., Faloona, I. C., Lenschow, D. H., Campos, T., Heizer, C., Weinheimer, A., Cantrell, C. A., Mauldin, R. L., Hornbrook, R. S., Pollack, I., and Bandy, A: A complete dynamical ozone budget measured in the tropical marine boundary layer during PASE, J. Atmos. Chem., 66, 55-70, https://doi.org/10.1007/s10874-011-9195-0, 2011.

Grosjean, D. and Seinfeld, J.H.: Parameterization of the formation potential of secondary organic aerosols. Atmos. Environ. 23, 1733–1747, https://doi.org/10.1016/0004-6981(89)90058-9, 1989.

Monks, P. S., Carpenter, L. J., Penkett, S. A., Ayers, G. P., Gillett, R. W., Galbally, I. E., and Meyer, C. P.: Fundamental ozone photochemistry in the remote marine boundary layer: the soapex experiment, measurement and theory, Atmos. Environ., 32, 3647-3664, https://doi.org/10.1016/S1352-2310(98)00084-3, 1998.

Table S11 Parameters and results of ozone formation potential (OFP) and secondary organic aerosol formation potential (P_{SOAP}) for non-methane hydrocarbons (NMHCs)

Species	Mean conc. of NMHCs (ppb)	MIR ($gO_3\ gVOC^{-1}$)	SOAP	M ($g\ mol\ L^{-1}$)	OFP ($\mu g\ m^{-3}$)				P_{SOAP} ($\mu g\ m^{-3}$)			
					Industrial activities	Exhaust emissions	Ocean emissions	Terrestrial vegetation emissions	Industrial activities	Exhaust emissions	Ocean emissions	Terrestrial vegetation emissions
Ethane	1.21	0.28	0.1	30.07	0.17	0.16	0.08	0.02	0.03	0.03	0.02	0.01
Propane	0.769	0.49	-	44.1	0.51	0.10	0.05	0.04	-	-	-	-
i-butane	0.288	1.23	-	58.12	0.52	0.04	0.01	0.03	-	-	-	-
n-butane	0.234	1.15	0.3	58.12	0.68	0.04	0	0.04	0.08	0.01	0	0.01
Ethylene	0.145	9.00	1.3	28.05	0.47	0.46	0.45	0	0.04	0.04	0.04	0
Propylene	0.033	1.66	1.6	42.08	0.05	0.03	0.03	0.02	0.01	0.02	0.02	0.01
Isoprene	0.008	10.61	1.9	68.12	0.01	0.02	0.02	0.12	0.01	0.01	0.01	0.01

Specific comments

Line 57-60: There are several more recent studies that provide higher/different global VOC ocean emission estimates than Guenther et al. (1995). Suggest providing a range here to expand the literature review and also highlight how uncertain these fluxes here.

Reply: Thanks for your suggestion. We have updated the range of VOCs emissions and highlighted their uncertainties, as indicated below:

Line 57-61:

"Despite the uncertainties in the global flux of VOCs, substantial evidence indicates a significant discrepancy between terrestrial emissions (660-1146 Tg C yr^{-1}) (Guenther et al., 1995, 2012; Messina et al., 2016; Sindelarova et al., 2014; Singh and Zimmerman, 1992) and marine emissions (5-36 Tg C yr^{-1}) (Guenther et al., 1995; Singh and Zimmerman, 1992)."

Reference:

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global-model of natural volatile organic-compound emissions, J. Geophys. Res.-Atmos., 100, 8873-8892, https://doi.org/10.1029/94JD02950, 1995.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471–1492, https://doi.org/10.5194/gmd-5-1471-2012, 2012.

Messina, P., Lathière, J., Sindelarova, K., Vuichard, N., Granier, C., Ghattas, J., Cozic, A., and Hauglustaine, D. A.: Global biogenic volatile organic compound emissions in the ORCHIDEE and MEGAN models and sensitivity to key parameters, Atmos. Chem. Phys., 16, 14169–14202, https://doi.org/10.5194/acp-16-14169-2016, 2016.

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., Müller, J.-F., Kuhn, U., Stefani, P., and Knorr, W.: Global data set of biogenic VOC emissions calculated by the

MEGAN model over the last 30 years, Atmos. Chem. Phys., 14, 9317–9341, https://doi.org/10.5194/acp-14-9317-2014, 2014.

Singh, H. B. and Zimmerman, P.: Atmospheric distributions and sources of non-methane hydrocarbons, Nriagu, J. O. (Ed.), Gaseous Pollutants: Characterisation and Cycling, Wiley, New York, p. 235, 1992.

Section 2.7: More detail is needed here to explain the PMF model set-up and what is meant by the scaled residuals shown in Fig. S1.

Reply: Thanks for your suggestion. We have added a more detailed explanation of the PMF model and provided further clarification on the meaning of Fig. S1, as indicated below:

Line 235-248:

"PMF model introduced in detail in the study of Paatero and Trapper (1994) was applied to analyze the data of atmospheric NMHCs in the Yellow Sea and the East China Sea. Based on a matrix consisting of the concentrations of diverse chemical species, the objective of PMF is to determine the number of NMHCs source factors, the chemical composition profile of each factor, and the contribution of each factor to species. The matrix representation of this model is defined as Eq. (10).

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (10)$$

Where x_{ij} represents the concentration of species j measured on sample i, p denotes the number of factors facilitating the samples. f_{kj} represents the concentration of species j in factor profile k, g_{ik} denotes the relative contribution of factor k to sample i, and e_{ij} represents the PMF model error of species j measured on sample i. The factors resolved by PMF are typically interpreted as sources. The objective of this algorithm is to find the values of f_{kj}, g_{ik}, and p that best reproduce x_{ij}, continuously adjusting f_{kj} and g_{ik} until the minimum Q value for a given p is attained. Q is defined as Eq. (11).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{\sigma_{ij}}\right)^2 \quad (11)$$

Where σ_{ij} represents the uncertainty of the concentration of the species *j* in sample *i*, n is the number of samples, and m is the number of species."

Line 253-257:

"Additionally, scaled residuals are instrumental in assessing the fit of the PMF model to the observed data. They represent the difference between the observed and modeled data, scaled by the uncertainty in the observed data. In this PMF analysis, approximately 94 % of the scaled residuals ranged from -3 to 3 (Fig. S1), suggesting a reasonable fit of the model result."

Lines 338-334: This analysis is interesting—were there also any temperature and/or windspeed differences within and beyond 100 km from shore? Also, could the authors find a way to reference Fig 5a and b here, rather than just listing the total (alkanes+alkenes) emissions in text? It's a nice figure and I find it easier to digest than the numbers in Table 1, but right now I don't think those panels are actually referenced in the document.

Reply: Thanks for your suggestion. The temperature/windspeed within and beyond 100 km from the shore has been presented in the manuscript, with a discussion about their effects on NMHCs emissions. Besides, Fig. 5a/b has been referenced in the text, as indicated below:

Line 385-390:

"The averaged sea-to-air fluxes of alkanes and alkenes within 100 km from the coastline were 147 ± 116 and 551 ± 497 nmol m^{-2} d^{-1}, respectively, which were relatively higher than those beyond 100 km (Fig. 5a, b). Since there were no significant differences in surface seawater temperature and 10 m wind speed between regions within and beyond

100 km from the coastline (Fig. S5), the discrepancy in fluxes might not be driven by physical processes."

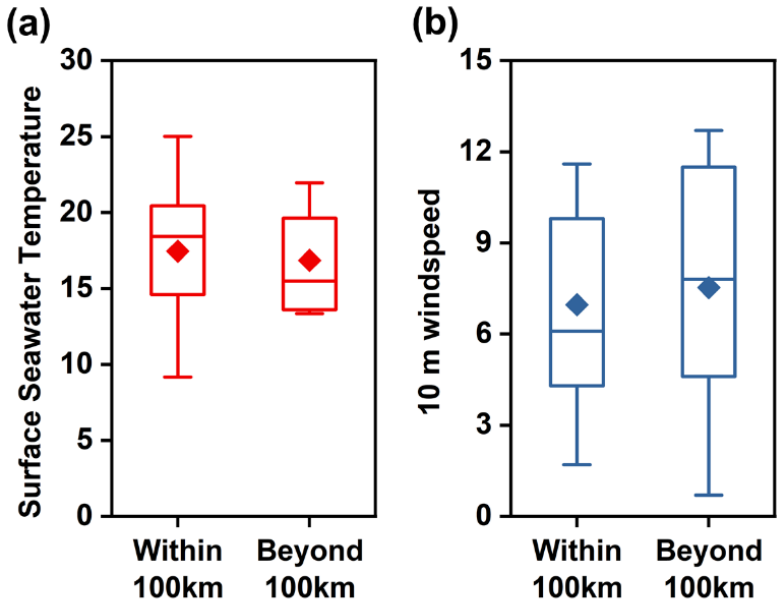

Figure S5 Comparison in surface seawater temperature (panel a) and wind speed (panel b) between regions within/beyond 100 km from the coastline. Boxes span the interquartile range, with lines at the median. Diamonds indicate mean values, and whiskers span the 5-95 percentiles.

Technical comments:

Line 45: suggest deleting the word "second" before "organic"

Reply: Thanks for your suggestion. We have deleted the word "second", as indicated below:

Line 45:

"Non-methane hydrocarbons (NMHCs), a significant subset of volatile organic compounds (VOCs), are acknowledged as key precursors to tropospheric ozone formation (Houweling et al., 1998; Solomon et al., 2005) and organic aerosol generation (Hallquist et al., 2009; Wu and Xie, 2018), playing a pivotal role in atmospheric chemistry."

Line 108: Tables are being referenced out of order here. Suggest reordering to avoid this.

Reply: We apologize for any confusion caused by the tables that are out of order. We have reordered table reference in the text, as indicated below:

Line 108:

"Sampling details for urban (Table S4) and marine samples (Table S5) are shown in supplementary tables."

Line 177: "analyzed" should be "analyze"

Reply: We apologize for the grammar errors. It has been revised in the text, as indicated below:

Line 192:

"A novel approach was employed to analyze the correlation between the concentrations of various NMHCs and their sea-to-air fluxes."

Line 181: "yield" should be "yielding"

Reply: We apologize for the grammar errors. It has been revised in the text, as indicated below:

Line 196:

"This was achieved by dividing the concentration of each NMHCs by its corresponding atmospheric •OH lifetime, yielding a "lifetime-weighted concentration" for each NMHCs (C_{life-i}) (Eq. 6)."

Line 359-361: this sentence is awkward, consider revising.

Reply: We apologize for any confusion caused by this awkward sentence. It has been revised in the text, as indicated below:

Line 411-412:

"The relatively long atmospheric residence time of ethane facilitates its accumulation in the atmosphere."

Line 364: "life-weighted" should be "lifetime-weighted"

Reply: Thanks for your suggestion. It has been revised in the text, as indicated below:

Line 415:

"Thus, to mitigate the impact of varying reactivity among the different gas species, we calculated the lifetime-weighted concentrations of each NMHCs according to their atmospheric lifetime (introduced in section 2.5)."

Line 366: "acknowledging" should be "acknowledges"

Reply: We apologize for the grammar errors. It has been revised in the text, as indicated below:

Line 417:

"This novel method is more nuanced to assess the impact of oceanic emission on atmospheric NMHCs, as it acknowledges not only their abundance but also their residence in the atmosphere."

Line 399: "NHMCs" should be "NMHCs"

Reply: We apologize for the spelling errors. It has been revised in the text, as indicated below:

Line 450:

"Conversely, the lower ratios indicate the importance of tropical forest fires (0.43-0.57) (Andreae and Merlet, 2001; Rossabi and Helmig, 2018), natural and oil gas operations (0.81-1.1) (Gilman et al., 2013; Swarthout et al., 2013), and marine vessel exhaust (1.59-1.71) (Bourtsoukidis et al., 2019) in controlling the chemical composition of NMHCs"

Figure 5e and f: "Slpoe" should be "Slope" in these two panels

Reply: We apologize for the spelling errors. It has been revised in the Figure, as indicated below:

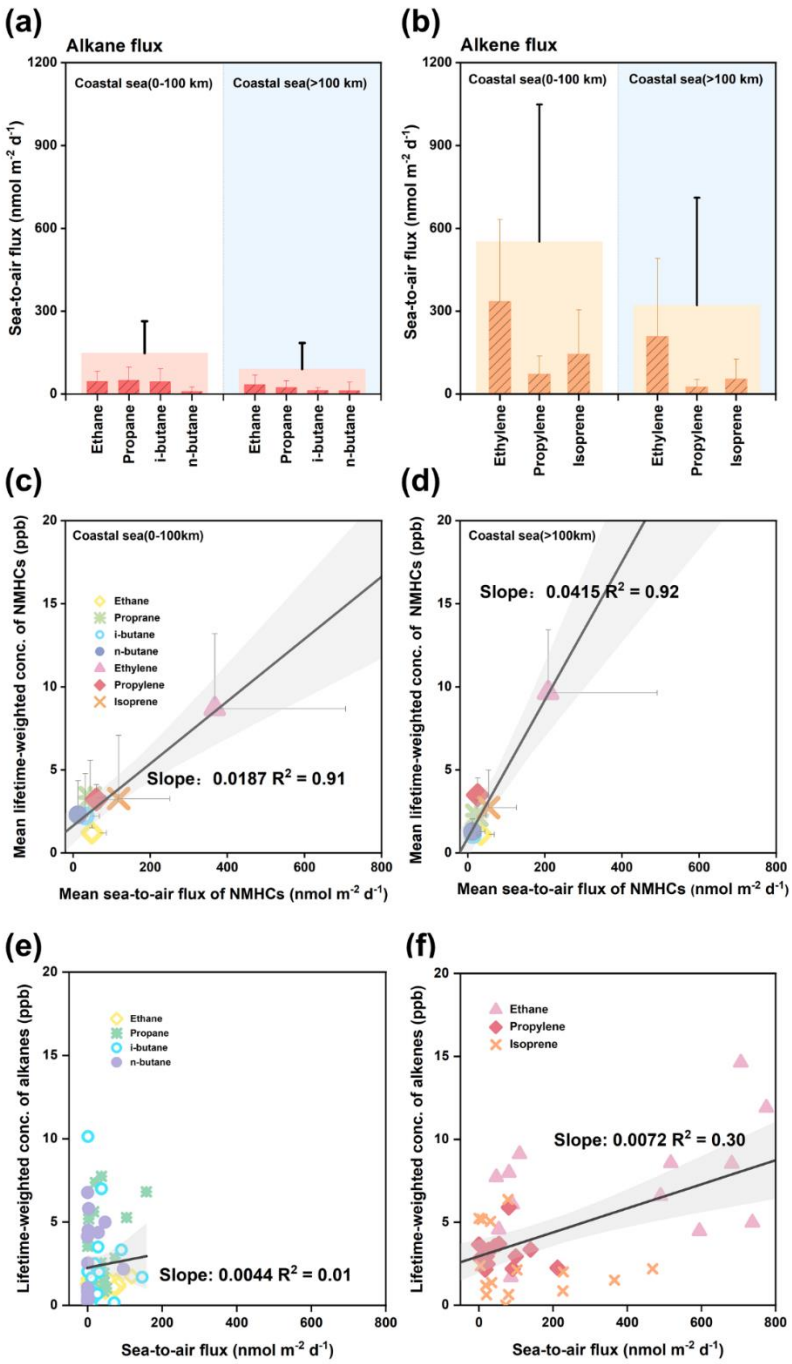

Figure 5 Means of sea-to-air fluxes of alkanes (panel a) and alkenes (panel b) in sea areas within 100 km (n = 10) and beyond 100 km (n = 9) from the nearshore land. The wider columns represent the sum of alkanes or alkenes. Panel c or d shows the means of lifetime-weighted concentrations of NMHCs plotted against the means of their mean sea-to-air fluxes in the area within 100 km or beyond 100 km from the coastline. Specific lifetime-weighted concentrations of alkanes (panel e) and alkenes (panel f) plotted against sea-to-air fluxes in the whole coastal sea region. The black, blue or red line is the best linear fitting for each dataset and the shadowed area represents the confidence band at a 95 % confidence level.

Figure S2: Suggest changing the panel titles to eliminate the "@Dummy=first"

Reply: Thanks for your suggestion. We have revised the title of Figure S2, as indicated below:

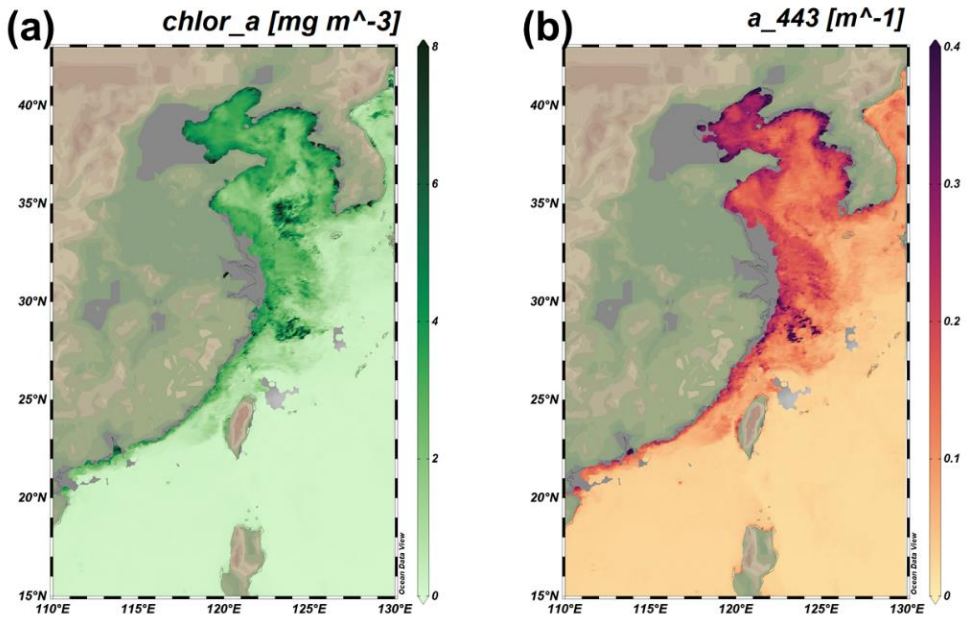

Figure S2 Romte sensing monthly Chl-*a* concentration (panel a) and total absorption coefficient at 443 nm (panel b) in April 2021. Data of Aqua-MODIS at resolution of 9 km were downloaded from https://oceancolor.gsfc.nasa.gov/