An itemized response (blue words) to reviewers' comments and suggestions

We sincerely thank the editor and reviewers for their constructive comments on our manuscript entitled "Influence of oceanic ventilation and terrestrial transport on the atmospheric volatile chlorinated hydrocarbons over the Western Pacific" [EGUSPHERE-2025-251]. These thoughtful suggestions have been invaluable in improving the quality of the paper and guiding our future research. In response, we have made every effort to revise and enhance the manuscript, with all changes highlighted in blue. The major corrections and our detailed point-to-point responses are provided below.

Editor's comments:

I noticed that the short summary includes the abbreviation 'CCl_4'. I kindly ask you to adapt your short summary and add the full term to make it better understandable for non-experts. This will require some text adaptation, since the 500-character limit will be exceeded. Currently, your short summary has 497 characters including spaces. You can adjust the short summary during the next revision. 2) For the author list, please use an affiliation numbering of 1, 2, 3,... instead of a, b, c. The two corresponding author are supposed to be added after the affiliations and named separately with their email address (please do not add them in a footer). 3) In the section "Author contributions", please use initials for the respective authors instead of full names.

Reply: **Thank you for your valuable suggestions.**

(1) We have revised the short summary to replace "CCl_4" with "carbon tetrachloride".

(2) We have changed the affiliation numbering to 1, 2, 3,… and listed the two corresponding authors after the affiliations with their emails.

(3) We have updated the "Author contributions" section to use author initials.

Reviewer #1:

General comments

Ocean plays an important role on the biogeochemical cycle of volatile chlorinated hydrocarbons. However, due to scarce data, our understanding is limited about Western Pacific. Quantitative analysis of marine CCl_4 emission or sink help us to narrow or even close the gap of CCl_4, thus the topic of this paper is very important.

This manuscript presents an interesting data set of measurements of $CHCl_3$, C_2HCl_3, CCl_4 and CH_3CCl_3 from both atmosphere and sea water, and present sea-to-air fluxes in globally important region where in addition very little data has been published previously. The manuscript is well structured and generally appropriately written. However, there are a number of problems mainly connected to the data analysis and interpretation that should be addressed first.

Reply: Thank you for your positive assessment of the importance of our study and the value of the data presented. We truly appreciate the constructive comments provided, which have greatly helped improve the quality of our manuscript. Revisions have been made accordingly, with all changes highlighted in blue in the revised manuscript. Below is our point-by-point response.

1. First of all, the variation of atmospheric CCl_4 is with 10% and the atmospheric concentration of CH_3CCl_3 and C_2HCl_3 in only several pptv, so that the quality of sample analysis is essential for this study. The authors presented precision for CCl_4 as 4% and precision of C_2HCl_3 is 3% in the supplement material. Generally, the precision will be much worse if the concentration is smaller. In this study, the concentration of C_2HCl_3 is almost two orders of magnitude lower compared to CCl_4 concentration. I doubt why the precision of C_2HCl_3 are even better than CCl_4. Can the author provide more detailed information how these precisions were achieved?

Reply: We sincerely appreciate the reviewer's careful assessment and insightful comments.

(1) Enhancement of precision evaluation

During the experimental stage, the precision of the target compounds was evaluated using two approaches (a uniform halocarbon concentration and ambient concentration levels). In the original manuscript, considering that most VCHCs occur at relatively low ambient concentrations, a uniform low concentration (5 pptv, prepared by dynamically diluting a 100 ppbv VCHCs standard gas with the Nutech 2202A system) was selected to characterize measurement precision. This approach led to the situation where the reported precision of CCl_4 did not fully correspond to its higher ambient concentration (approximately 80 pptv). However, this discrepancy does not affect data quality, and the ambient concentrations reported in this study remain reliable.

Following the reviewer's suggestion, to more accurately reflect method performance at environmentally relevant levels, we have included precision results for the target compounds at ambient concentrations in the revised manuscript. The updated Table S1 presents these data in full, confirming that at ambient levels the precision of C_2HCl_3 is indeed lower than that of CCl_4, consistent with the reviewer's expectation. In addition, detailed descriptions of the precision testing and calculation methods have been added to the Supplementary Materials. **We wish to emphasize that this correction pertains solely to the presentation of values in Table S1; it does not affect any original sample measurements or the overarching conclusions of our study.**

The updated Table S1 is provided below:

Table S1 The method detection limits (MDL), measurement precision, and atmospheric lifetimes of the selected VCHCs in air.

Compound	**Typical ambient concentration**	**Precision at ambient-relevant concentration**[1]	**MDL**[2]	**Lifetime** [3]
	pptv	**%RSD, n=7**	**pptv**	
$CHCl_3$	10-15	3.2	0.50	178 days
C_2HCl_3	2-5	4.9	0.10	5.6 days
CH_3CCl_3	2-3	6.3	0.20	5 years
CCl_4	80-100	1.1	1.00	30 years

Notes: [1] Precision at ambient-relevant concentrations is expressed as RSD (%), based on seven replicate measurements of mixed standard gases: 2 pptv (C_2HCl_3, CH_3CCl_3), 10 pptv ($CHCl_3$), and 100 pptv (CCl_4).

[2] MDL refers to the method detection limit as determined in accordance with the US EPA procedure (2019).

[3] Atmospheric lifetimes are taken from WMO (2022).

We have added a detailed description of the precision calculation and measurement procedures in the supplementary information, as follows:

"**Text S3 Evaluation indexes in atmospheric VCHCs measurements**

Precision was evaluated in accordance with US EPA (2019) guidelines by conducting seven replicate analyses of standard gas samples prepared at environmentally relevant concentrations. These concentrations reflect typical atmospheric levels of the target VCHCs ($CHCl_3$, C_2HCl_3, CH_3CCl_3, and CCl_4), as referenced in WMO (2022). The test standards were generated by dynamically diluting a 100 ppbv primary mixture (Spectra Gases, USA) with ultra-high-purity nitrogen using a dynamic dilution system (Nutech 2202A). Under consistent analytical conditions, each standard gas sample was measured seven times. Precision was expressed as the relative standard deviation (RSD, %) calculated using Eq. (1).

$$\text{Precision}=\text{RSD}_{(X)}=\frac{\sqrt{\frac{\sum_{i=1}^{n}(X_{(i)}-\bar{X})^2}{n-1}}}{\bar{X}}\times 100\% \quad (1)$$

where $X_{(i)}$ denotes the measured concentration of the target compound in the sample gas derived from a multipoint external calibration curve. $\bar{X}$ is the arithmetic mean of seven replicate measurements, and n=7. The precision results at ambient-relevant concentrations are summarized in Table S1." **(supplementary information Texts S3)**

(2) Supplementary improvements in the methods section:

To enhance the transparency of this study, more detailed descriptions of the experimental procedures have been added in the revised manuscript. In addition, chromatograms of VCHCs at ambient concentration levels (Figures A and B) and a schematic diagram of the sample analysis workflow (Figure C) are provided to clearly demonstrate the applicability and operability of the method. Furthermore, the analytical approach employed in this study is a well-established and reliable technique and widely applied in numerous peer-reviewed studies (Li et al., 1999; Kurihara et al., 2010; Liu et al., 2011; Yokouchi et al., 2013; Cao et al., 2023).

We have added detailed methodological descriptions to the "2.2 Analysis of VCHCs in air" section in the revised manuscript, as follows:

"2.2 Analysis of VCHCs in air

Atmospheric samples were collected by 3 L pre-evacuated stainless-steel Summa polished canisters (SilconCan, Restek Co., Ltd) that were pre-cleaned to measure VCHCs concentrations at ambient pressure. These sampling canisters underwent an intensive cleaning process using an automated cleaning system (Nutech 2010 DS) prior to sample collection. Previous studies have shown that VCHCs remain stable in rigorously pre-cleaned Summa canisters for more than 3 months (Yokouchi et al., 1999; Yokouchi et al., 2013; Yu et al., 2020). To avoid ship exhaust contamination, sampling was conducted upwind on the ship's top deck during low-speed transit. All atmospheric samples were analyzed within 3 months after the collection. Meteorological parameters such as wind speed and direction were recorded by shipboard sensors at a height of 10 m above the sea surface.

The atmospheric concentrations of VCHCs were determined using a three-stage cold-trap preconcentrator (Nutech 8900DS) coupled with a gas chromatography–mass spectrometry (GC–MS) system (Agilent 7890A/5975C). Chromatographic separation was achieved on a DB-624 capillary column (60 m × 0.25 mm × 1.4 µm film thickness) in selective ion monitoring (SIM) mode. Prior to injection, samples (400 mL) were preconcentrated using the three-stage cold-trap system, effectively removing interfering components such as H_2O and CO_2. Target compounds were quantified using a multipoint external calibration method. Calibration curves were established with a 100 ppbv mixed standard gas (Spectra Gases, USA), which was dynamically diluted with ultra-high-purity nitrogen using a mass-flow–controlled dilution system (Nutech 2202A; accuracy ±1%) to achieve ppt–low ppbv concentration levels. Six concentration gradients were prepared, and the diluted standards were analyzed following the same procedures as the field samples. The calibration results showed correlation coefficients for all target compounds are ≥ 0.996. According to the US EPA (2019) procedure, the method detection limits (MDL) of the target compounds ranged from 0.10 to 1.0 pptv. MDL is defined as 3.143 × standard deviation of seven replicates of the low concentration standard gases (5× the expected MDL), where 3.143 represents the t-value at 99% confidence level. Precision in this study was assessed from seven replicate measurements of standard gas samples prepared at environmentally relevant concentrations, with relative standard deviations (RSD) consistently below 7% for all target compounds (Table S1). This method has been validated through comparisons with the China Meteorological Administration Meteorological Observation Centre for independent analysis using an AGAGE-traceable Medusa-GC/MS system (Zhang et al., 2017; Yu et al., 2020; An et al., 2021). Furthermore, it is consistent with previously published methodologies (Zhang et al., 2010; Zheng et al., 2013; Yi et al., 2021; Li et al., 2024). Detailed analytical procedures and data processing methods are provided in the supplementary information (Texts S2 and S3)." **(Lines 197-237)**

We have provided representative GC–MS chromatograms (Fig. A, B), which show clear peak separation and ambient-level detection of all target VCHCs, as follows:

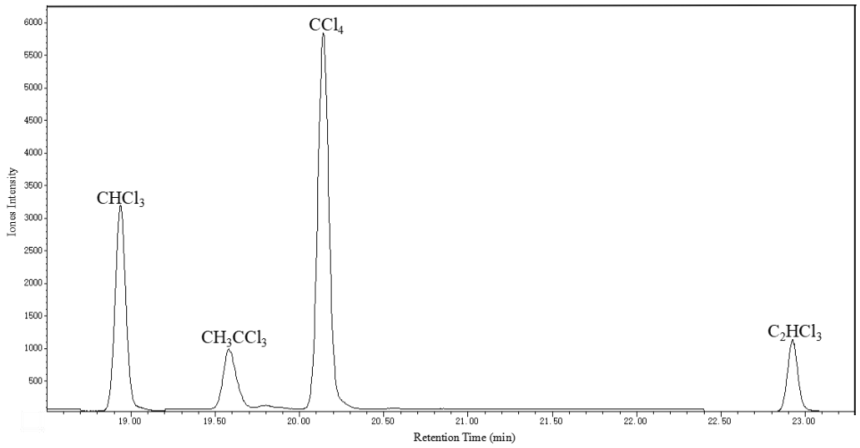


Fig. A Chromatogram from an ambient air sample obtained. X axis: retention time (min). Y axis: ion intensity value without unit.

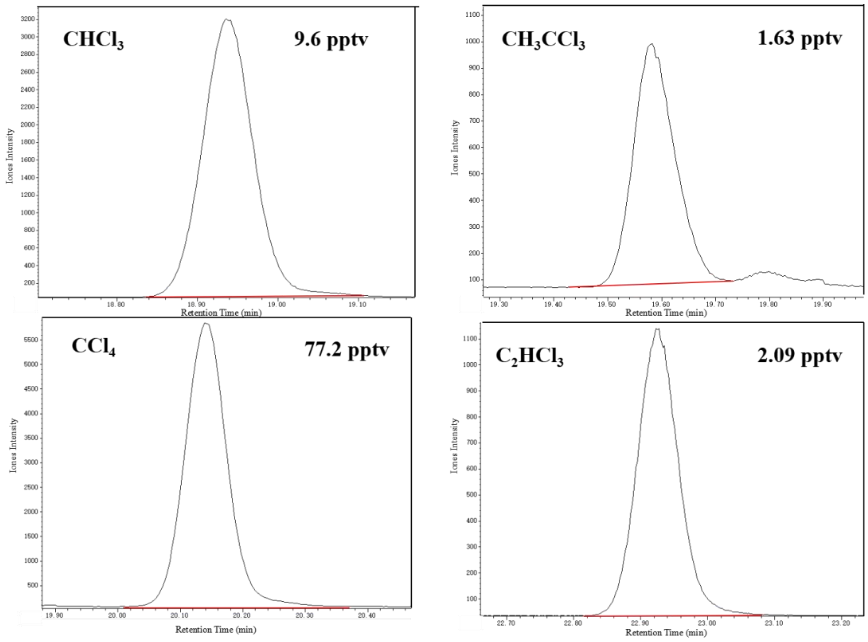
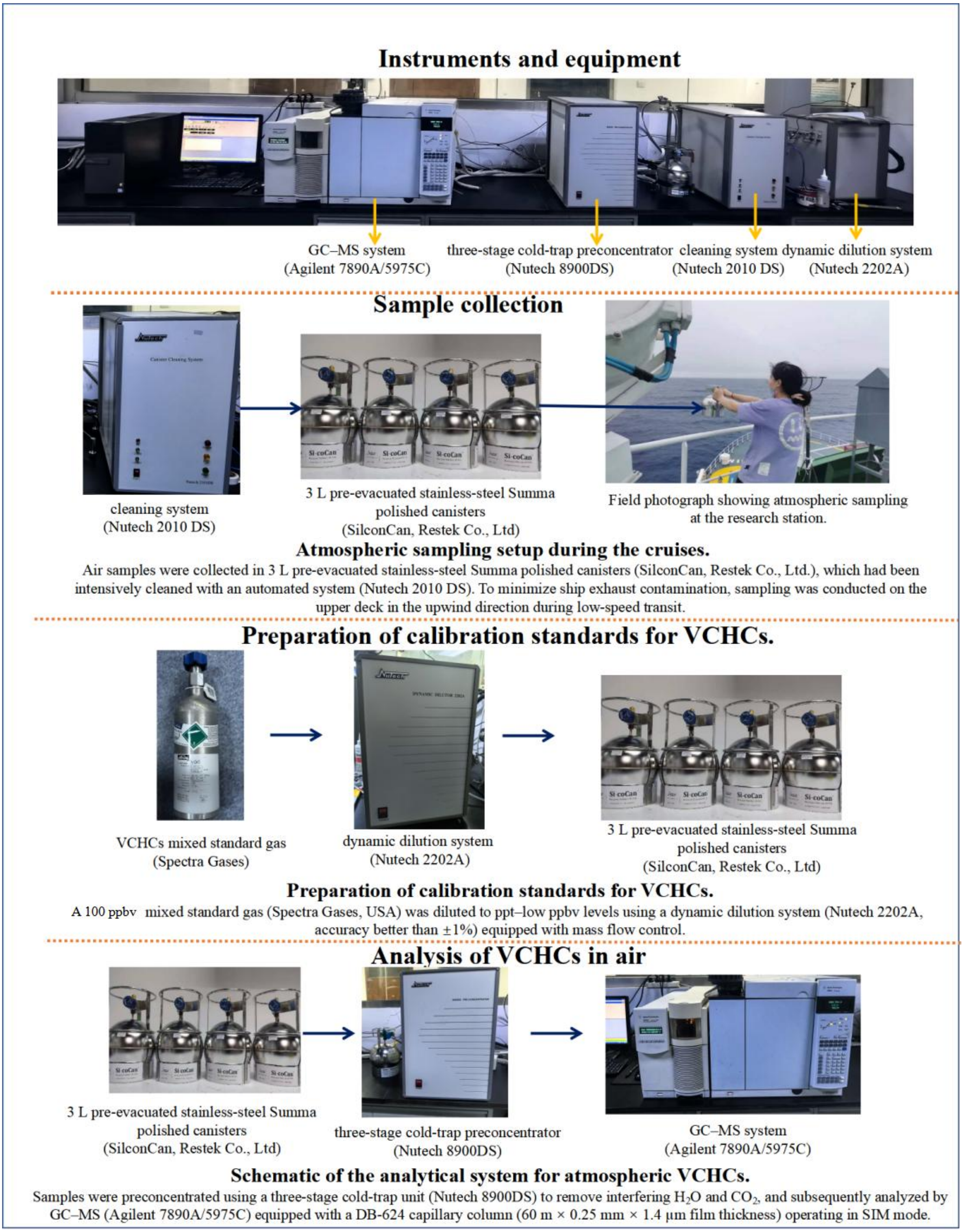


Fig. B. Chromatograms of VCHCs with ambient mole fractions.

A schematic diagram of the sample analysis workflow, as follows:



Atmospheric sampling setup during the cruises.

Air samples were collected in 3 L pre-evacuated stainless-steel Summa polished canisters (SilconCan, Restek Co., Ltd.), which had been intensively cleaned with an automated system (Nutech 2010 DS). To minimize ship exhaust contamination, sampling was conducted on the upper deck in the upwind direction during low-speed transit.

Preparation of calibration standards for VCHCs.

A 100 ppbv mixed standard gas (Spectra Gases, USA) was diluted to ppt–low ppbv levels using a dynamic dilution system (Nutech 2202A, accuracy better than ±1%) equipped with mass flow control.

Schematic of the analytical system for atmospheric VCHCs.

Samples were preconcentrated using a three-stage cold-trap unit (Nutech 8900DS) to remove interfering H_2O and CO_2, and subsequently analyzed by GC–MS (Agilent 7890A/5975C) equipped with a DB-624 capillary column (60 m × 0.25 mm × 1.4 μm film thickness) operating in SIM mode.

Fig. C Sample-analysis workflow diagram.

The related literatures are listed below:

An, M., Western, L. M., Say, D., Chen, L., Claxton, T., Ganesan, A. L., et al. (2021). Rapid increase in dichloromethane emissions from China inferred through atmospheric observations. Nature Communications, 12(1), 7279.

Cao, X., Gu, D., Li, X., Leung, K. F., Sun, H., Mai, Y., et al. (2023). Characteristics and source origin analysis of halogenated hydrocarbons in Hong Kong. Science of the Total Environment, 862, 160504.

Kurihara, M. K., Kimura, M., Iwamoto, Y., Narita, Y., Oohi, A., et al. (2010). Distributions of short-lived iodocarbons and biogenic trace gases in the Open Ocean and atmosphere in the western North Pacific. Marine Chemistry, 118 (3-4), 156-170.

Liu, Y. N., Yvon-Levis, S. A., Hu, L., Salisbury, J. E., O'Hern, J. E. (2011). $CHBr_3$, CH_2Br_2, and $CHClBr_2$ in the U.S. coastal waters during the Gulf of Mexico and East Coast Carbon cruise. Journal of Geophysical Research: Oceans, 116, 1440-1450.

Li, B., Huang, J., Hu, X., Zhang, L., Ma, M., Hu, L., et al. (2024). CCl_4 emissions in eastern China during 2021–2022 and exploration of potential new sources. Nature Communications, 15(1), 1725.

Li, H. J., Yokouchi, Y., Akimoto, H. (1999). Measurement of methyl halides in the marine atmosphere. Atmospheric Environment. 33.12: 1881-1887.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., & Simmonds, P. G. (2008). Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds. Analytical Chemistry, 80(5), 1536-1545.

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., et al. (2000). A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. Journal of Geophysical Research: Atmospheres, 105(D14), 17751-17792.

Yokouchi, Y., Li, H. J., Machida, T., Aoki, S., & Akimoto, H. (1999). Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform. Journal of Geophysical Research: Atmospheres, 104(D7), 8067-8076.

Yokouchi, Y., Inoue, J., & Toom-Sauntry, D. 2013. Distribution of natural halocarbons in marine boundary air over the Arctic Ocean. Geophysical Research Letters, 40, 4086–4091.

Yu, D., Yao, B., Lin, W., Vollmer, M. K, Ge, B., Zhang, G., et al. (2020). Atmospheric CH_3CCl_3 observations in China: historical trends and implications. Atmospheric Research, 231, 104658.

Zhang, G., Yao, B., Vollmer, M. K., Montzka, S. A., Mühle, J., Weiss, R. F., et al. (2017). Ambient mixing ratios of atmospheric halogenated compounds at five background stations in China. Atmospheric Environment, 160, 55–69.

2. For the second, the calibration method described in lines 199-204. How much uncertainties introduced by the dilution? For VCHCs at pptv level, normally calibration scales are applied in calibration to minimize the inconsistent between standards. I also doubt the comparison between this study and AGAGE background is misleading due to the calibration method.

Reply: We thank the reviewer for the insightful comments on calibration uncertainties and the comparability of our data with AGAGE. We have added detailed information demonstrating the reliability of our dilution and calibration procedures, including internal validation and external verification by the China Meteorological Administration laboratory. Moreover, the methodology employed in this study is a

well-established technique that has been widely applied in comparisons with AGAGE data. Therefore, we are confident that the comparisons with AGAGE background data presented in this study are both reliable and valid. Our detailed responses are provided below:

Methodology validation for VCHCs measurements:

(1) Dilution independent verification:

To ensure the accuracy of our calibration procedures, we employed a two-tiered validation approach:

(a) Primary calibration: In this study, a 100 ppbv VCHCs standard gas (Spectra Gases, USA) was dynamically diluted to pptv levels using a mass-flow–controlled dilution system (Nutech 2202A; accuracy ±1%). Six concentration gradients were prepared and analyzed using the same procedures as the field samples. The results showed that the correlation coefficients of the calibration curves for all target compounds are $\geq$ 0.996, indicating excellent linearity and methodological reliability.

(b) Secondary verification: More importantly, to ensure calibration accuracy and international comparability, aliquots of the diluted standard gases were sent to theChina Meteorological Administration Meteorological Observation Centre (CMA-MOC) for independent blind analysis using an AGAGE-traceable Medusa-GC/MS system (Zhang et al., 2017; Yu et al., 2020; An et al., 2021). The results showed the differences between our measurements and CMA-MOC analyses within ±5%, confirming the reliability of our dilution and calibration procedures.

(2) Robustness and comparability with AGAGE data:

The methodology adopted in this study—using a commercial standard gas with dynamic dilution and multipoint calibration—is a well-established and reliable approach for ppt-level VCHCs measurements. It has been widely validated and applied in numerous studies directly comparing with AGAGE background data (e.g., Zhang et al., 2010; Zheng et al., 2013; Yi et al., 2021; Li et al., 2024).

To ensure calibration accuracy and international comparability, aliquots of the diluted standard gases were sent to the CMA-MOC for independent analysis using an AGAGE-traceable Medusa-GC/MS system (Zhang et al., 2017; Yu et al., 2020; An et al., 2021). The CMA-MOC results were reported as dry-air mole fractions on calibration scales established and maintained by the Scripps Institution of Oceanography (SIO) (Prinn et al., 2000; Miller et al., 2008). The intercomparison indicated that the differences between the measurements and those from CMA-MOC for target compounds were within ±5%: $CHCl_3$ (−4.3% to −1.2%), CH_3CCl_3 (+1.5% to +4.6%), and CCl_4 (+1.1% to +3.8%). The independent intercomparison with the CMA laboratory further demonstrated that the concentration differences are small.

These results reinforce the methodological robustness of our approach, ensuring that comparisons with AGAGE background data are both technically sound and scientifically valid.

(3) Supplementary revisions:

In the revised manuscript, we have added the related content of the dilution in the Supplementary Information (Text S2), as follows:

"Text S2 Accuracy of the dynamic dilution system

Calibration curves were established using a 100 ppbv standard mixture gas (Spectra Gases, USA), which was dynamically diluted with ultra-high-purity nitrogen via a mass-flow–controlled dilution system (Nutech 2202A; accuracy ±1%) to achieve ppt–low ppbv concentration levels. Six concentration gradients were prepared, and the diluted standards were analyzed following the same procedures as the field samples. The results showed that the correlation coefficients of the calibration curves for all target compounds are ≥ 0.996, indicating excellent linearity and methodological reliability." **(supplementary information Texts S2)**

The related literatures are listed below:

An, M., Western, L. M., Say, D., Chen, L., Claxton, T., Ganesan, A. L., et al. (2021). Rapid increase in dichloromethane emissions from China inferred through atmospheric observations. Nature Communications, 12(1), 7279.

Li, B., Huang, J., Hu, X., Zhang, L., Ma, M., Hu, L., et al. (2024). CCl_4 emissions in eastern China during 2021–2022 and exploration of potential new sources. Nature Communications, 15(1), 1725.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Greally, B. R., Mühle, J., & Simmonds, P. G. (2008). Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds. Analytical Chemistry, 80(5), 1536-1545.

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., et al. (2000). A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. Journal of Geophysical Research: Atmospheres, 105(D14), 17751-17792.

Yi, L., Wu, J., An, M., Xu, W., Fang, X., Yao, B., et al. (2021). The atmospheric concentrations and emissions of major halocarbons in China during 2009–2019. Environmental Pollution, 284, 117190.

Yu, D., Yao, B., Lin, W., Vollmer, M. K., Ge, B., Zhang, G., et al. (2020). Atmospheric CH_3CCl_3 observations in China: historical trends and implications. Atmospheric Research, 231, 104658.

Zheng, J., Yu, Y., Mo, Z., Zhang, Z., Wang, X., Yin, S., et al. (2013). Industrial sector-based volatile organic compound (VOC) source profiles measured in manufacturing facilities in the Pearl River Delta, China. Science of the Total Environment, 456, 127-136.

Zhang, Y. L., Guo, H., Wang, X.M., Simpson, I. J., Barletta, B., Blake, D. R., et al. (2010). Emission patterns and spatiotemporal variations of halocarbons in the Pearl River Delta region, southern China. Journal of Geophysical Research: Atmospheres, 115(D15).

Zhang, G., Yao, B., Vollmer, M. K., Montzka, S. A., Mühle, J., Weiss, R. F., et al. (2017). Ambient mixing ratios of atmospheric halogenated compounds at five background stations in China. Atmospheric Environment, 160, 55–69.

3. **For the third,** the variation of atmospheric CCl_4 in this study is similar to its analysis precision. So the authors need to prove the changes of atmospheric CCl_4 is not caused by the measurement uncertainties and be aware not to over-interpretation the concentration differences.

Reply: We thank the reviewer for emphasizing the importance of distinguishing real atmospheric signals from analytical uncertainties. We fully agree that this consideration is critical, particularly when the observed variations in trace gas concentrations are close to the analytical precision of the method. It is equally essential to demonstrate that the observed changes in the atmospheric concentration of CCl_4 are not driven by measurement uncertainties. In accordance with the reviewers' suggestions, we have systematically refined our interpretation of concentration variations through the following improvements to avoid over-explaining the differences in concentration: (1) CCl_4 differences exceeding the 3σ analytical precision threshold (3.3%, Table S1) are considered reliable, therefore, only variations greater than 4% above the regional mean were retained for discussion in this study; (2) the observed enhancements show clear spatial consistency, systematically concentrated at nearshore stations influenced by continental air masses rather than random noise; and

(3) these enhancements coincide with elevated concentrations of SF_6, an independent anthropogenic tracer (Ni et al., 2023). Taken together, these multiple lines of evidence indicate that the CCl_4 features reported in the revised manuscript represent real atmospheric signals.

In addition, we have carefully interpreted the concentration differences in the revised manuscript to avoid overstatement.

The corresponding revisions in the revised manuscript are as follows:

"Figure 3 shows the spatial distributions of atmospheric mixing ratios of CCl_4 and CH_3CCl_3. Significant enhancements were observed at nearshore stations (e.g., P1-4, P1-5, P1-7, P1-8 and EQ12). CCl_4 concentrations in these stations were 4–6% higher than the regional average, exceeding its analytical precision threshold of 3σ (3.3%, Table S1). These enhancements exhibited clear spatial consistency, systematically concentrated in nearshore areas influenced by continental air masses (Fig. 1 and Fig. 3). Moreover, the elevated levels coincided with enhanced concentrations of the independent anthropogenic tracer SF_6 (Ni et al., 2023), further corroborating their origin from continental pollution outflows. This result is also consistent with previous studies reporting that elevated CCl_4 and CH_3CCl_3 levels are primarily concentrated in coastal regions (Blake et al., 2003; Zhang et al., 2010)." **(Lines 365-376)**

The related literature is listed below:

Blake, N. J., Blake, D. R., Simpson, I. J., Meinardi, S., Swanson, A. L., Lopez, J. P., et al. (2003). NMHCs and halocarbons in Asian continental outflow during the Transport and Chemical Evolution over the Pacific (TRACE-P) Field Campaign: Comparison with PEM-West B. Journal of Geophysical Research: Atmospheres, 108(D20).

Ni, J., Liu, S. S., Lang, X. P., He, Z., & Yang, G. P. (2023). Sulfur hexafluoride in the marine atmosphere and surface seawater of the Western Pacific and Eastern Indian Ocean. Environmental Pollution, 335, 122266.

Zhang, Y. L., Guo, H., Wang, X. M., Simpson, I. J., Barletta, B., Blake, D. R., et al. (2010). Emission patterns and spatiotemporal variations of halocarbons in the Pearl River Delta region, southern China. Journal of Geophysical Research: Atmospheres, 115(D15).

4. For the fourth, in section 3.1, the authors ascribe the elevated concentrations of VCHCs to the influence of polluted air mass from mainland or east China may not be correct. From Fig. 3 and Fig. 4, the trajectories of air mass with high observed concentration are generally from Siberia and Northeast China, and then pass Japan. However, from the recent publications, these regions are not the major source of VCHCs and there is no report of fluorine/chlorine chemistry located in these regions. It should be noted most of the trajectories in figure 4 did not cover North China or East China mentioned in the references.

Reply: We thank the reviewer for the valuable comment. We acknowledge that our previous attribution of the elevated concentrations to polluted air masses from northern or eastern China was inaccurate. In the revised manuscript, we have adjusted the wording in Section 3.1 to more cautiously describe the possible transport pathways, emphasizing the potential for long-range transport and mixing with polluted air masses from industrialized regions along the route, rather than directly attributing the high concentrations to specific source areas without direct evidence.

The corresponding revisions in the revised manuscript are as follows:

"In this study, the highest atmospheric concentrations of CCl_4 and CH_3CCl_3 were recorded at station P1-4 near Japan. Backward trajectory cluster analysis (Fig. 1c and Fig. S4) indicated that approximately 13% of the air masses originated from short-range transport along the eastern coast of Japan, while the remaining 87% were associated with long-range transport from Siberia and Northeast China and subsequently passed over the eastern coast of Japan. Although Siberia and Northeast China are not typical source regions for halocarbons, previous studies have shown that air masses from these regions may mix with pollution plumes from East Asian industrial areas during long-range transport (Stohl et al., 2002; Blake et al., 2003; Liang et al., 2004; Chang et al., 2022), which could lead to elevated VCHCs concentrations at downwind observation stations. This is corroborated by reports of CCl_4 pollution events at the Shangdianzi (SDZ) regional background station in northern China (117.17°E, 40.65°N, Fig. 1a), with peak mixing ratios reaching 151 pptv (Yi et al., 2023). As anthropogenic compounds, CCl_4 and CH_3CCl_3 are primarily emitted from industrial activities, including chloromethane and perchloroethylene production (Liang et al., 2016; Sherry et al., 2018), as well as unreported releases from chlorine and bleaching processes (estimated up to 10 Gg yr^{-1}). Furthermore, Zheng et al. (2019) and Ou-Yang et al. (2017) reported elevated CCl_4 and CH_3CCl_3 levels in China and Japan, respectively. Lunt et al. (2018) identified continued CCl_4 emissions from Eastern Asia. Collectively, these findings suggested that continental air mass transport was likely the dominant factor driving the elevated CCl_4 and CH_3CCl_3 levels observed at stations P1–4 during the study period."

(Lines 377-399)

"The 96-h backward trajectory cluster analysis revealed that the KEO region is affected by air masses originating from Siberia, Northeast China, Korea, and Japan (Fig. 1c). While Siberia and Northeast China themselves are not recognized as major VCHCs source regions, the long-range air masses from these areas may have entrained polluted plumes during their transport (Section 3.1.1). Indeed, surrounding regions are known to be significant emitters: Feng et al. (2019) reported a marked rise in China's $CHCl_3$ emissions in recent years, and An et al. (2023) further showed that emissions peaked at

193 Gg yr^{-1} in 2017 before declining to 147 Gg yr^{-1} in 2018 and remaining stable thereafter, with eastern China consistently identified as a major contributor. Moreover, Ou-Yang et al. (2017) observed high atmospheric $CHCl_3$ mixing ratios (39 ± 11 pptv) at the Mt. Fuji research station, Japan, in 2015; and in 2017, the highest annual mean $CHCl_3$ (43 ± 18 pptv) was recorded at the Gosan station (GSN, 127.17°E, 33.28°N, 72 m above sea level, a regional baseline station; Fig. 1a) on Jeju Island, South Korea. Furthermore, industrial activities are known sources of $CHCl_3$ and C_2HCl_3 (Montzka et al., 2011; Oram et al., 2017; Zheng et al., 2019). Thus, the elevated $CHCl_3$ and C_2HCl_3 observed in the KEO region were likely related to terrestrial air mass transport and subsequent mixing with polluted plumes during their transit." **(Lines 428-445)**

The following related literature has been added:

Blake, N. J., Blake, D. R., Simpson, I. J., Meinardi, S., Swanson, A. L., Lopez, J. P., et al. (2003). NMHCs and halocarbons in Asian continental outflow during the Transport and Chemical Evolution over the Pacific (TRACE-P) Field Campaign: Comparison with PEM-West B. Journal of Geophysical Research: Atmospheres, 108(D20).

Chang, C. Y., Wang, J. L, Chen, Y. C., Pan, X. X., Chen, W. N., Lin, M. R., et al. (2022). A study of the vertical homogeneity of trace gases in East Asian continental outflow. Chemosphere, 297, 134165.

Liang, Q., Jaeglé, L., Jaffe, D. A., Weiss-Penzias, P., Heckman, A., & Snow, J. A. (2004). Long-range transport of Asian pollution to the northeast Pacific: Seasonal variations and transport pathways of carbon monoxide. Journal of Geophysical Research: Atmospheres, 109(D23).

Stohl, A., Eckhardt, S., Forster, C., James, P., & Spichtinger, N. (2002). On the pathways and timescales of intercontinental air pollution transport. Journal of Geophysical Research: Atmospheres, 107(D23), ACH-6.

Yi, L., An, M., Yu, H., Ma, Z., Xu, L., O'Doherty, S., et al. (2023). In Situ Observations of Halogenated Gases at the Shangdianzi Background Station and Emission Estimates for Northern China. Environmental Science & Technology, 57(18), 7217-7229.

5. Last but not least, both two surveys were conducted in autumn and winter. Concerning the seasonal variation of marine microalgae and seawater temperature, wind speed, the sea-to-air flux obtained by this study might be bias from yearly average.

Reply: We thank the reviewer for this comment. According to your suggestion, we have added the discussion of potential effects of seasonal variations in marine microalgae, seawater temperature, and wind speed on the annual flux estimates in the revised manuscript.

The corresponding revisions in the revised manuscript are as follows:

"It should be noted that the sea–air flux estimates of $CHCl_3$, C_2HCl_3, CCl_4, and CH_3CCl_3 presented in this study are derived exclusively from autumn and winter cruise observations, and thus may not fully represent their annual averages due to seasonal variability. The spatiotemporal patterns of sea–air fluxes are primarily governed by the concentrations of VCHCs in the atmosphere and seawater, SST, and wind speed. In particular, seawater concentrations of $CHCl_3$ and C_2HCl_3 are strongly modulated by biological activity (Section 3.3), while both SST and wind speed exhibit pronounced seasonal variations (Fig. 7a). Moreover, according to AGAGE data (https://agage.mit.edu/), the interannual variability of global atmospheric CCl_4 in 2019 was 2%, with variability at GSN sites of 3% (Fig. 7b), whereas global atmospheric CH_3CCl_3 varied by 13% (Fig. 7c). During the observation period of this study, mean atmospheric concentrations of CCl_4 at GSN sites and globally were 1% lower than their respective annual averages, while the global atmospheric CH_3CCl_3 concentration was

3% lower, indicating that their levels in the western Pacific were generally close to annual averages. In addition, while SST and Chl-*a* in the study region during the observation period were largely consistent with their annual averages, wind speeds were on average 10% higher (Fig. 7a; Tang et al., 2022). Consequently, the flux values reported in this study are likely somewhat higher than the annual mean, primarily due to the elevated wind speeds during the cruises.” **(Lines 683–702)**

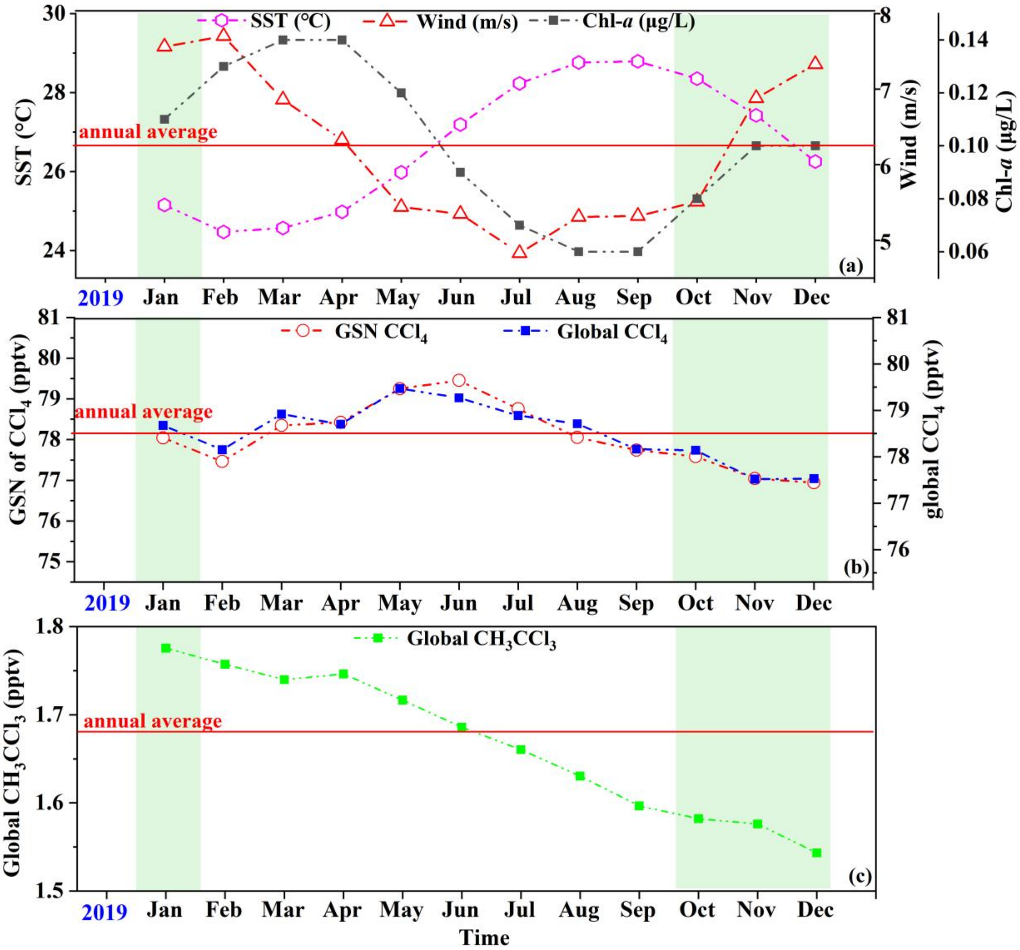


Fig. 7. (a) Interannual variations of wind speed, SST, and Chl-*a* concentration in the study area during 2019. (b) Interannual variability of CCl_4 at the GSN site in 2019 compared with the global mean. (c) Interannual variability of CH_3CCl_3 at the global scale in 2019. Wind speed data were obtained from the ERA5 reanalysis (Hersbach et al., 2020), SST data from the ECCO2 cube92 dataset (Menemenlis et al., 2008), and Chl-*a* data from the NASA Ocean Biology Processing Group (2022). CCl_4 data for the GSN site were retrieved from the AGAGE network (https://agage.mit.edu/). Shaded areas indicate the cruise sampling periods.

Reviewer #2:

General comments

This paper reports the results of two measuring campaigns of selected volatile chlorinated hydrocarbons in the Western Pacific. Air and surface water samples were simultaneously taken to estimate the equilibrium deviation and to calculate fluxes. This is a challenging project that generated a substantial amount of data. It is interesting research, but the manuscript needs some further improvement.

Reply: We are sincerely grateful for your positive assessment of our work on a challenging project that generated a substantial amount of data, as well as for your constructive suggestions for improvement. Revisions have been made accordingly, with all changes highlighted in blue in the revised manuscript. Detailed point-by-point responses to specific comments are provided thereafter.

1. Two sampling campaigns were organized. One from October 31, 2019, to December 1, 2019, and the second from October 3, 2019, to January 5, 2020. Both campaigns roughly cover a 2 - 3 months period in the same season. Therefore, seasonal effects are not included and so, the validity of the results as yearly averages is not guaranteed. In this sense, ln. 716-717 in the conclusions should be interpreted with reticence.

Reply: Thank you for the comment. We agree that seasonal variability was not covered. The conclusion has been revised to reflect that the results represent the observation period, not annual averages.

"This study investigated the seawater and atmospheric concentrations, sea–air fluxes, sources, and control factors of VCHCs in the Western Pacific during October 2019 and January 2020." **(Lines 756–758)**

2. The area covered is about 4500 km S-N and 4000 km E-W at the equator. It would be valuable adding information on the number of sampling locations (they are indicated in Fig. 1 but not always very clear) and the number of samples per location. The distribution of the concentrations is graphically presented in Fig. 3. It would be good adding statistical data on the concentration distributions, e.g., as box plots.

Reply: Thank you for the helpful suggestion.

(1) In the revised manuscript, we have added the number of sampling locations and the number of samples collected per location in the Materials and Methods section.

"A total of 65 stations were surveyed across the study region (Fig. 1a), where seawater samples were collected at all stations and atmospheric samples obtained at 41 stations. Each station provided three replicate surface seawater samples and one atmospheric sample." **(Lines 168–171)**

(2) In addition, following the reviewer's recommendation, we have added box plots (new Fig. S3 in the Supplementary Information) to present the statistical distribution of concentrations for each compound.

"Atmospheric concentrations of CCl_4 and CH_3CCl_3 over the Western Pacific varied from 75.8 to 83.7 pptv (mean: 78.8 pptv) and from 1.6 to 2.4 pptv (mean: 2.0 pptv), respectively (Fig. 3 and Fig. S3)." **(Lines 339–341)**

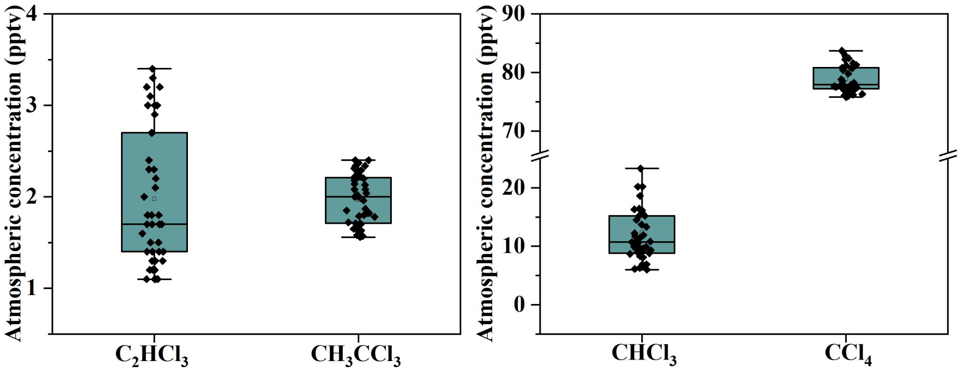


Fig. S3. Boxplots showing the atmospheric concentrations of VCHCs at all sampling locations during the study period.

3. Data for Henry's law constants are taken from Schwardt (2021). Temperature dependence equations are used to correct for the seawater temperature. Schwardt used the EPICS method to determine air/water partitioning using deionized water. It is known that H also depends on salinity. Data from the literature show a 30% in H for tetrachloromethane when salinity increases from 0 to 35 ppt at 25 °C. Reported salinity of the samples in the study is roughly 35 ppt (Fig. 2). So, is salinity considered, if not what would be the effect on the calculated fluxes by increasing H values with 30 %?

Reply: We thank the reviewer for the constructive comment. In response to your suggestion regarding the influence of salinity on Henry's law constants (*H*) and flux estimates, we have refined the calculation approach in the revised manuscript:

(1) Updated equation sources: For $CHCl_3$, C_2HCl_3, and CCl_4, we replaced the original equations with seawater-based temperature–*H* parameterizations (Moore, 2000; Hunter-Smith et al., 1983). These inherently account for the salinity effect at S=35‰, thus no additional correction is required.

(2) Salinity correction for freshwater data: For CH_3CCl_3, we retained the freshwater equation from Schwardt et al. (2021) but explicitly applied the Sechenov "salting-out" correction (Gossett, 1987), resulting in a 30.5% increase (factor 1.305) at S =35 ‰.

(3) Impact on results: The absolute values of the flux estimates for CH_3CCl_3 and CCl_4 decreased by approximately 20-50% compared to the original manuscript, while those for $CHCl_3$ and C_2HCl_3 changed minimally. These adjustments do not affect the overall conclusion that, during the cruise periods, the Western Pacific acted as a source of $CHCl_3$ and C_2HCl_3 and as a sink for CH_3CCl_3 and CCl_4.

The corresponding revisions in the revised manuscript are as follows:

"Specifically, the *H* values for $CHCl_3$ and C_2HCl_3 were derived from seawater-based temperature–*H* parameterizations reported by Moore (2000). The *H* value for CCl_4 was obtained from the seawater-based equation of Hunter-Smith et al. (1983). For CH_3CCl_3, the temperature dependence was taken from the freshwater measurements of Schwardt et al. (2021) and subsequently adjusted to seawater conditions using the Sechenov “salting-out” relationship, with the salting-out coefficient (k_s) reported by Gossett (1987). The corresponding equations are:

$$H(CHCl_3) = \exp(13.10 - 4377 \cdot T^{-1}) \quad (2)$$

$$H(C_2HCl_3) = \exp(14.88 - 4624 \cdot T^{-1}) \quad (3)$$

$$H(CCl_4) = \exp(11.27 - 3230 \cdot T^{-1}) \quad (4)$$

$$H(CH_3CCl_3) = \exp(459.80 - 23465\ T^{-1} - 66.96\ \mathrm{Ln}(T)) \cdot 1.305 \quad (5)”$$

(Lines 279–293)

The related literatures are listed below:

Gossett, J. M. (1987). Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons. Environmental Science & Technology, 21(2), 202-208.

Hunter-Smith, RJ, Balls, P. W, & Liss, P. S. (1983). Henry's law constants and the air-sea exchange of various low molecular weight halocarbon gases. Tellus B: Chemical and Physical Meteorology, 35(3), 170-176.

Moore, R. M. (2000). The solubility of a suite of low molecular weight organochlorine compounds in seawater and implications for estimating the marine source of methyl chloride to the atmosphere. Chemosphere-Global Change Science, 2(1), 95-99.

Schwardt, A., Dahmke, A., & Köber, R. (2021). Henry’s law constants of volatile organic compounds between 0 and 95 °C–Data compilation and complementation in context of urban temperature increases of the subsurface. Chemosphere, 272, 129858.

4. The analytical methods are described. However, some detailed but relevant information is not reported: argumentation on why using GC-MS for air samples and GC-ECD for water samples; type of GC column used for air samples; number of data points on which calibration curves and RSBs are calculated. In Table S3 information about MDL is given. The definition of MDL as used here is not reported. Is it the instrumental MDL or the overall method (including, sampling, transportation, storage sample preparation) MDL. RSDs on MDL are all below 10% even 3%. So, this looks more like instrumental MDL. The difference is important because this affects results of equation 9 and so the calculated fluxes.

Reply: We appreciate the reviewer's valuable comments. Our detailed responses to each point are as follows:

(1) Rationale for analytical methods:

For seawater analysis, halogenated compounds are prone to degradation and volatilization during storage and transport, necessitating immediate onboard measurements. GC–ECD was employed because its compact design, operational simplicity, and high sensitivity to halogenated compounds make it well suited for shipboard deployment, as demonstrated in previous field studies (Abrahamsson et al., 2004; Richter and Wallace, 2004; Chuck et al., 2005; Smythe-Wright et al., 2006; Quack et al., 2007).

In contrast, atmospheric samples were collected in pre-cleaned Summa canisters, which can preserve stability for more than 3 months (Yokouchi et al., 1999; Yokouchi et al., 2013; Yu et al., 2020), thereby ensuring safe transport to the laboratory. Given that the atmospheric sample matrix is more complex, GC–MS was employed owing to its high selectivity and reliable compound identification. This approach represents a classical, robust, and widely applied analytical method, as demonstrated in numerous studies (Li et al., 1999; Kurihara et al., 2010; Liu et al., 2011; Yokouchi et al., 2013; Yu et al., 2020; Cao et al., 2023). Although shipborne mass spectrometers have been applied in marine monitoring, they require costly modifications and maintenance (e.g., anti-magnetic interference, vibration damping, temperature/humidity control) and generally perform at a slightly lower level than laboratory-based instruments. Considering that the collected samples can be stably preserved in canisters, it is more practical and reliable to transport them back to the laboratory for subsequent analysis.

The related literatures are listed below:

For seawater analysis:

Abrahamsson, K., Bertilsson, S., Chierici, M., Fransson, A., Froneman, P. W., Lorén, A., & Pakhomov, E. A. (2004). Variations of biochemical parameters along a transect in the Southern Ocean, with special emphasis on volatile halogenated organic compounds. Deep Sea Research Part II: Topical Studies in Oceanography, 51(22-24), 2745-2756.

Chuck, A. L., Turner, S. M., & Liss, P. S. (2005). Oceanic distributions and air-sea fluxes of biogenic halocarbons in the open ocean. Journal of Geophysical Research: Oceans, 110(C10).

Quack, B., Peeken, I., Petrick, G., & Nachtigall, K. (2007). Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling. Journal of Geophysical Research: Oceans, 112(C10), 1-13.

Richter, U., & Wallace, D. W. R. (2004). Production of methyl iodide in the tropical Atlantic Ocean. Geophysical Research Letters, 31, 1-4.

Smythe-Wright, D., BoSSWell, S., Breithaupt, P., Davidson, R., Dimmer, C., & Eiras Diaz, L. (2006). Methyl iodide production in the ocean: Implications for climate change. Global Biogeochemical Cycles, 20(3), 1-9.

For atmosphere analysis:

Cao, X., Gu, D., Li, X., Leung, K. F., Sun, H., Mai, Y., et al. (2023). Characteristics and source origin analysis of halogenated hydrocarbons in Hong Kong. Science of the Total Environment, 862, 160504.

Kurihara, M. K., Kimura, M., Iwamoto, Y., Narita, Y., Oohi, A., et al. (2010). Distributions of short-lived iodocarbons and biogenic trace gases in the Open Ocean and atmosphere in the western North Pacific. Marine Chemistry, 118 (3-4), 156-170.

Liu, Y. N, Yvon-Levis, S. A., Hu, L., Salisbury, J. E., & O'Hern, J. E. (2011). $CHBr_3$, CH_2Br_2, and $CHClBr_2$ in the U.S. coastal waters during the Gulf of Mexico and East Coast Carbon cruise. Journal of Geophysical Research: Oceans, 116, 1440-1450.

Li, H. J., Yokouchi, Y., & Akimoto, H. (1999). Measurement of methyl halides in the marine atmosphere. Atmospheric Environment. 33.12, 1881-1887.

Yokouchi, Y., Li, H. J., Machida, T., Aoki, S., & Akimoto, H. (1999). Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform. Journal of Geophysical Research: Atmospheres, 104(D7), 8067-8076.

Yokouchi, Y., Inoue, J., & Toom-Sauntry, D. (2013). Distribution of natural halocarbons in marine boundary air over the Arctic Ocean. Geophysical Research Letters, 40, 4086–4091.

Yu, D., Yao, B., Lin, W., Vollmer, M. K, Ge, B., Zhang, G., et al. (2020). Atmospheric CH_3CCl_3 observations in China: historical trends and implications. Atmospheric Research, 231, 104658.

(2) Instrument parameters: For air samples, chromatographic separation was performed on a DB-624 capillary column (60 m × 0.25 mm × 1.4 μm film thickness); for seawater samples, a DB-624 capillary column (60 m × 0.53 mm × 3.0 μm film thickness) was used.

(3) Calibration details: Calibration curves were established using six concentration levels, each analyzed in triplicate. Relative standard deviations (RSD) were determined from seven replicate measurements. The detailed measurement and calculation procedures have been added to the Supplementary Information (Text S3).

(4) Definition of MDL: MDL is defined as 3.143 × standard deviation of seven replicates of the low concentration standard gases (5× the expected MDL), where 3.143 represents the t-value at 99% confidence level. It was determined following the US EPA (2019) procedure, which includes standard gas preparation, preconcentration, injection, chromatographic separation, and detection. According to the US EPA (2019), these steps are used to characterize the method detection limit. Although this procedure (US EPA (2019)) does not explicitly cover sampling and transport, previous studies have shown that VCHCs remain stable in rigorously pre-cleaned Summa canisters for more than 3 months (Yokouchi et al., 1999; Yokouchi et al., 2013; Yu et al., 2020). In this study, all samples were analyzed within 3 months of collection, within the stability period, so uncertainties from sampling, storage, and transport are negligible compared to those from the analytical procedure itself. Therefore, the MDL reported here can be regarded as effectively representing the full-method detection capability, covering the entire process from sampling through analysis. Moreover, since all ambient concentrations of target compounds were far above their respective MDL (typically >10×), the quantitative results, including flux estimates, are robust and reliable.

The revised method description has been updated in the manuscript as follows:

"Atmospheric samples were collected by 3 L pre-evacuated stainless-steel Summa polished canisters (SilconCan, Restek Co., Ltd) that were pre-cleaned to measure VCHCs concentrations at ambient pressure. These sampling canisters underwent an intensive cleaning process using an automated cleaning system (Nutech 2010 DS) prior to sample collection. Previous studies have shown that VCHCs remain stable in rigorously pre-cleaned Summa canisters for more than 3 months (Yokouchi et al., 1999; Yokouchi et al., 2013; Yu et al., 2020). To avoid ship exhaust contamination, sampling was conducted upwind on the ship's top deck during low-speed transit. All atmospheric samples were analyzed within 3 months after the collection. Meteorological parameters such as wind speed and direction were recorded by shipboard sensors at a height of 10 m above the sea surface.

The atmospheric concentrations of VCHCs were determined using a three-stage cold-trap preconcentrator (Nutech 8900DS) coupled with a gas chromatography–mass spectrometry (GC–MS) system (Agilent 7890A/5975C). Chromatographic separation was achieved on a DB-624 capillary column (60 m × 0.25 mm × 1.4 µm film thickness) in selective ion monitoring (SIM) mode. Prior to injection, samples (400 mL) were preconcentrated using the three-stage cold-trap system, effectively removing interfering components such as H_2O and CO_2. Target compounds were quantified using a multipoint external calibration method. Calibration curves were established with a 100 ppbv mixed standard gas (Spectra Gases, USA), which was dynamically diluted with ultra-high-purity nitrogen using a mass-flow–controlled dilution system (Nutech 2202A; accuracy ±1%) to achieve ppt–low ppbv concentration levels. Six concentration gradients were prepared, and the diluted standards were analyzed following the same procedures as the field samples. The calibration results showed correlation coefficients for all target compounds are ≥ 0.996. According to the US EPA (2019) procedure, the method detection limits (MDL) of the target compounds ranged from 0.10 to 1.0 pptv. MDL is defined as 3.143 × standard deviation of seven replicates of the low concentration standard gases (5× the expected MDL), where 3.143 represents the t-value at 99% confidence level. Precision in this study was assessed from seven replicate measurements of standard gas samples prepared at environmentally relevant concentrations, with relative standard deviations (RSD) consistently below 7% for all target compounds (Table S1). This method has been validated through comparisons with the China Meteorological Administration Meteorological Observation Centre for independent analysis using an AGAGE-traceable Medusa-GC/MS system (Zhang et al., 2017; Yu et al., 2020; An et al., 2021). Furthermore, it is consistent with previously published methodologies (Zhang et al., 2010; Zheng et al., 2013; Yi et al., 2021; Li et al., 2024). Detailed analytical procedures and data processing methods are provided in the supplementary information (Texts S2 and S3)." **(Lines 197–237)**

"Surface seawater (5 m) was collected using a 12 L Niskin sampler equipped with a temperature-salinity-depth probe (CTD) for concurrent temperature and salinity measurements. Samples were transferred into 100 mL airtight glass syringes without headspace, stored in the dark at 4°C, and analyzed within 4 h of collection. To minimize compound degradation, VCHCs were analyzed immediately onboard using a cold trap purge-and-trap gas chromatograph with an electron capture detector (GC–ECD, Agilent 6890A)." **(Lines 239–246)**

The detailed measurement and calculation procedures have been added to the Supplementary Information (Text S3), as follows:

"**Text S3 Evaluation indexes in atmospheric VCHCs measurements**

Precision was evaluated in accordance with US EPA (2019) guidelines by conducting seven replicate analyses of standard gas samples prepared at environmentally relevant concentrations. These concentrations reflect typical atmospheric levels of the target VCHCs ($CHCl_3$, C_2HCl_3, CH_3CCl_3, and CCl_4), as referenced in WMO (2022). The test standards were generated by dynamically diluting a 100 ppbv primary mixture (Spectra Gases, USA) with ultra-high-purity nitrogen using a dynamic dilution system (Nutech 2202A). Under consistent analytical conditions, each standard gas sample was measured seven times. Precision was expressed as the relative standard deviation (RSD, %) calculated using Eq. (1).

$$\text{Precision}=\text{RSD}_{(X)}=\frac{\sqrt{\frac{\sum_{i=1}^{n}(X_{(i)}-\bar{X})^2}{n-1}}}{\bar{X}}\times 100\% \qquad (1)$$

where $X_{(i)}$ denotes the measured concentration of the target compound in the sample gas derived from a multipoint external calibration curve. $\bar{X}$ is the arithmetic mean of seven replicate measurements, and n=7. The precision results at ambient-relevant concentrations are summarized in Table S1.

In this study, the method detection limits (MDL) of atmospheric target compounds were determined in strict accordance with the U.S. Environmental Protection Agency (US EPA, 2019) procedure. Specifically, low-concentration standard gases at approximately five times the expected MDL were prepared using a dynamic dilution system, and seven complete analytical runs—including standard gas preparation, preconcentration, injection, chromatographic separation, and mass spectrometric detection—were conducted. MDL was calculated as MDL = t × S, where S is the standard deviation of seven replicate measurements and t is the student’s t-value at the 99% confidence level with six degrees of freedom (3.143). The MDL for each target compound is listed in Table S1.”

The updated Table S1 is provided below:

Table S1 The method detection limits (MDL), measurement precision, and atmospheric lifetimes of the selected VCHCs in air.

Compound	**Typical ambient concentration**	**Precision at ambient-relevant concentration**[1]	**MDL**[2]	**Lifetime** [3]
	pptv	**%RSD, n=7**	**pptv**	
$CHCl_3$	10-15	3.2	0.50	178 days
C_2HCl_3	2-5	4.9	0.10	5.6 days
CH_3CCl_3	2-3	6.3	0.20	5 years
CCl_4	80-100	1.1	1.00	30 years

Notes: [1] Precision at ambient-relevant concentrations is expressed as RSD (%), based on seven replicate measurements of mixed standard gases: 2 pptv (C_2HCl_3, CH_3CCl_3), 10 pptv ($CHCl_3$), and 100 pptv (CCl_4).

[2] MDL refers to the method detection limit as determined in accordance with the US EPA procedure (2019).

[3] Atmospheric lifetimes are taken from WMO (2022).

The related literature is listed below:

US EPA. (2019). Method TO-15A: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography–Mass Spectrometry (GC-MS). https://nepis.epa.gov/Exe/ZyNET.exe/P100YDPO.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2016+Thru+2020&Docs=&Quer

Yokouchi, Y., Li, H. J., Machida, T., Aoki, S., & Akimoto, H. (1999). Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform. Journal of Geophysical Research: Atmospheres, 104(D7), 8067-8076.

Yokouchi, Y., Inoue, J., & Toom-Sauntry, D. (2013). Distribution of natural halocarbons in marine boundary air over the Arctic Ocean. Geophysical Research Letters, 40, 4086–4091.

Yu, D., Yao, B., Lin, W., Vollmer, M. K, Ge, B., Zhang, G., et al. (2020). Atmospheric CH_3CCl_3 observations in China: historical trends and implications. Atmospheric Research, 231, 104658.

Detailed comments

1. p.3 ln 51. My suggestion is avoiding subjective phrasing "very short-lived" (less than six months). Compared with CCl_4 this lifetime is short but not in absolute terms. As an example, isoprene about 1 h; aromatic hydrocarbons in the order of days.

Reply: Thank you for your comment. We would like to clarify that "very short-lived substances (VSLSs)" is not a subjective term, but an official classification defined by the WMO (2007) for halogenated compounds with atmospheric lifetimes less than six months. To avoid confusion, we have revised the sentence to explicitly reference this definition.

"In contrast, short-lived species such as C_2HCl_3 and $CHCl_3$ are classified as halogenated very short-lived substances (VSLSs), with typical atmospheric lifetimes of less than six months (WMO, 2007), and are currently not regulated under the Montreal Protocol."

(Lines 55–58)

The related literature is listed below:

WMO (World Meteorological Organization). (2007). Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project-Report No. 50, 572 pp., Geneva, Switzerland.

2. ln 55. "disproportionately" compared with what?

Reply: Thank you for the comment. We agree that the reference point for "disproportionately" was unclear. In the revised manuscript, we clarify that the

radiative and ozone impacts of VSLSs are disproportionately large relative to their relatively low atmospheric concentrations and short lifetimes. The sentence has been revised accordingly to improve clarity.

"Although present at low concentrations, VSLSs exert disproportionately large impacts on radiative forcing and climate through ozone depletion, particularly due to their breakdown in the lower atmosphere, which is more sensitive to climate change (Hossaini et al., 2015; 2017; An et al., 2023; Saiz-Lopez et al., 2023)." **(Lines 60–64)**

3. Ln. 100-102. Li et al. (2024) Is this statement general or specific for Eastern China? The concentration distribution in Fig. 4 in that reference paper (comparing sectors) is highly skewed, with mean values highly influenced by a few large concentrations. I suggest drawing the readers attention to this point to avoid pointing too fast to some specific sectors.

Reply: We thank the reviewer for this crucial and insightful comment. We fully agree. The findings of Li et al. (2024) are specific to Eastern China, and their data distribution is indeed highly skewed. We have rewritten the sentence to explicitly emphasize both of these points to prevent any potential misinterpretation by the readers.

The revised sentence now reads:

"Additionally, Li et al. (2024) identified potential CCl_4 sources in eastern China, including the manufacture of general-purpose machinery, raw chemical materials, and chemical products." **(Lines 106–108)**

4. Ln. 202 Please add the number of concentration levels for the calibration curves.

Reply: Thank you for this valuable suggestion. We have added that the calibration curves were constructed using six concentration levels (Lines 220–223).

“Six concentration gradients were prepared, and the diluted standards were analyzed following the same procedures as the field samples. The calibration results showed correlation coefficients for all target compounds are ≥ 0.996.”

5. Ln. 207 S3. Please add the number of data to calculate RSD. Which definition of MDL was used and check layout of the Table.

Reply: We thank the reviewer for raising these critical points regarding methodological detail. We have added that the RSD were calculated from seven replicate measurements. Method detection limits (MDL) are defined as 3.143 × standard deviation of seven replicates of the low concentration standard gases (5× the expected MDL), where 3.143 represents the t-value at 99% confidence level. In the revised manuscript, we have added the definition of MDL in the analytical methodology section to enhance clarity and corrected the Table.

The corresponding revisions in the revised manuscript are as follows:

“**Text S3 Evaluation indexes in atmospheric VCHCs measurements**

Precision was evaluated in accordance with US EPA (2019) guidelines by conducting seven replicate analyses of standard gas samples prepared at environmentally relevant concentrations. These concentrations reflect typical atmospheric levels of the target VCHCs ($CHCl_3$, C_2HCl_3, CH_3CCl_3, and CCl_4), as referenced in WMO (2022). The test standards were generated by dynamically diluting a 100 ppbv primary mixture (Spectra Gases, USA) with ultra-high-purity nitrogen using a dynamic dilution system (Nutech 2202A). Under consistent analytical conditions, each standard gas sample was measured seven times. Precision was expressed as the relative standard deviation (RSD, %) calculated using Eq. (1).

$$\text{Precision}=\text{RSD}_{(X)}=\frac{\sqrt{\frac{\sum_{i=1}^{n}(X_{(i)}-\bar{X})^2}{n-1}}}{\bar{X}}\times 100\% \qquad (1)$$

where $X_{(i)}$ denotes the measured concentration of the target compound in the sample gas derived from a multipoint external calibration curve. $\bar{X}$ is the arithmetic mean of seven replicate measurements, and n=7. The precision results at ambient-relevant concentrations are summarized in Table S1.

In this study, the method detection limits (MDL) of atmospheric target compounds were determined in strict accordance with the U.S. Environmental Protection Agency (US EPA, 2019) procedure. Specifically, low-concentration standard gases at approximately five times the expected MDL were prepared using a dynamic dilution system, and seven complete analytical runs—including standard gas preparation, preconcentration, injection, chromatographic separation, and mass spectrometric detection—were conducted. MDL was calculated as MDL = t × S, where S is the standard deviation of seven replicate measurements and t is the Student's t-value at the 99% confidence level with six degrees of freedom (3.143). The MDL for each target compound are listed in Table S1." **(Supplementary information Text S3)**

The updated Table S1 is provided below:

Table S1 The method detection limits (MDL), measurement precision, and atmospheric lifetimes of the selected VCHCs in air.

Compound	**Typical ambient concentration**	**Precision at ambient-relevant concentration**[1]	**MDL**[2]	**Lifetime** [3]
	pptv	**%RSD, n=7**	**pptv**	
$CHCl_3$	10-15	3.2	0.50	178 days
C_2HCl_3	2-5	4.9	0.10	5.6 days
CH_3CCl_3	2-3	6.3	0.20	5 years
CCl_4	80-100	1.1	1.00	30 years

Notes: [1] Precision at ambient-relevant concentrations is expressed as RSD (%), based on seven replicate measurements of mixed standard gases: 2 pptv (C_2HCl_3, CH_3CCl_3), 10 pptv ($CHCl_3$), and 100 pptv (CCl_4).

[2] MDL refers to the method detection limit as determined in accordance with the US EPA procedure (2019).

[3] Atmospheric lifetimes are taken from WMO (2022).

The related literature is listed below:

US EPA. (2019). Method TO-15A: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography–Mass Spectrometry (GC-MS). https://nepis.epa.gov/Exe/ZyNET.exe/P100YDPO.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2016+Thru+2020&Docs=&Quer

Yokouchi, Y., Li, H. J., Machida, T., Aoki, S., & Akimoto, H. (1999). Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform. Journal of Geophysical Research: Atmospheres, 104(D7), 8067-8076.

Yokouchi, Y., Inoue, J., & Toom-Sauntry, D. (2013). Distribution of natural halocarbons in marine boundary air over the Arctic Ocean. Geophysical Research Letters, 40, 4086–4091.

Yu, D., Yao, B., Lin, W., Vollmer, M. K, Ge, B., Zhang, G., et al. (2020). Atmospheric CH_3CCl_3 observations in China: historical trends and implications. Atmospheric Research, 231, 104658.

6. Ln. 209. Were seawater samples taken always at the same depth? If so, which? A bit confusing that in this line there is (0-5 m).

Reply: We apologize for the confusion. All seawater samples in this study were collected at a fixed depth of 5 m below the surface using a 12 L Niskin sampler equipped with a CTD. The notation "0–5 m" in the original text has been revised to "5 m" in the manuscript for clarity.

"Surface seawater (5 m) was collected using a 12 L Niskin sampler equipped with a temperature-salinity-depth probe (CTD) for concurrent temperature and salinity measurements." **(Lines 239–241)**

7. Ln. 216 For water sample analysis a GC-ECD method is used while for air it is GC-MS. Any specific reasons? For the water sample analysis, the type of GC column is specified but not for air samples. Was the same GC column used. If not, please add information on the GC column used for air sample analysis.

Reply: We sincerely thank the reviewer for this valuable comment.

(1) The reasons for GC–ECD for shipboard seawater analysis

Halogenated compounds in seawater samples are prone to degradation during storage and transport, making immediate onboard analysis essential. GC–ECD offers a compact design, operational simplicity, and high sensitivity to halogenated compounds, which makes it well-suited for shipboard deployment. Its reliability in field measurements has been well demonstrated in previous studies (Abrahamsson et al., 2004; Richter and Wallace, 2004; Chuck et al., 2005; Smythe-Wright et al., 2006; Quack et al., 2007).

The related literature is listed below:

Abrahamsson, K., Bertilsson, S., Chierici, M., Fransson, A., Froneman, P. W., Lorén, A., & Pakhomov, E. A. (2004). Variations of biochemical parameters along a transect in the Southern Ocean, with special emphasis on volatile halogenated organic compounds. Deep Sea Research Part II: Topical Studies in Oceanography, 51(22-24), 2745-2756.

Chuck, A. L., Turner, S. M., & Liss, P. S. (2005). Oceanic distributions and air-sea fluxes of biogenic halocarbons in the open ocean. Journal of Geophysical Research: Oceans, 110(C10).

Quack, B., Peeken, I., Petrick, G., & Nachtigall, K. (2007). Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling. Journal of Geophysical Research: Oceans, 112(C10), 1-13.

Richter, U., & Wallace, D. W. R. (2004). Production of methyl iodide in the tropical Atlantic Ocean. Geophysical Research Letters, 31, 1-4.

Smythe-Wright, D., BoSSWell, S., Breithaupt, P., Davidson, R., Dimmer, C., & Eiras Diaz, L. (2006). Methyl iodide production in the ocean: Implications for climate change. Global Biogeochemical Cycles, 20(3), 1-9.

(2) Stability of air samples and GC–MS analysis

Atmospheric samples were collected in pre-cleaned Summa canisters, which can maintain sample stability for more than 3 months, as confirmed by previous literature (Yokouchi et al., 1999; Yokouchi et al., 2013; Yu et al., 2020) and our own tests, allowing safe transportation back to the laboratory. Given the more complex atmospheric matrix, GC–MS provides higher selectivity and more unambiguous compound identification compared with GC–ECD, and is therefore the more appropriate choice for air sample analysis (Li et al., 1999; Kurihara et al., 2010; Liu et al., 2011; Yokouchi et al., 2013; Cao et al., 2023). Although shipborne mass spectrometers have been applied in marine monitoring, they require costly modifications and maintenance (e.g., anti-magnetic interference, vibration damping, temperature/humidity control) and generally perform at a slightly lower level than laboratory-based instruments. Considering that the collected samples can be stably preserved in canisters, it is more practical and reliable to transport them back to the laboratory for subsequent analysis.

The related literatures are listed below:

Cao, X., Gu, D., Li, X., Leung, K. F., Sun, H., Mai, Y., et al. (2023). Characteristics and source origin analysis of halogenated hydrocarbons in Hong Kong. Science of the Total Environment, 862, 160504.

Kurihara, M. K., Kimura, M., Iwamoto, Y., Narita, Y., Oohi, A., et al. (2010). Distributions of short-lived iodocarbons and biogenic trace gases in the Open Ocean and atmosphere in the western North Pacific. Marine Chemistry, 118 (3-4), 156-170.

Liu, Y. N, Yvon-Levis, S. A., Hu, L., Salisbury, J. E., & O'Hern, J. E. (2011). $CHBr_3$, CH_2Br_2, and $CHClBr_2$ in the U.S. coastal waters during the Gulf of Mexico and East Coast Carbon cruise. Journal of Geophysical Research: Oceans, 116, 1440-1450.

Li, H. J., Yokouchi, Y., & Akimoto, H. (1999). Measurement of methyl halides in the marine atmosphere. Atmospheric Environment. 33.12: 1881-1887.

Yokouchi, Y., Li, H. J., Machida, T., Aoki, S., & Akimoto, H. (1999). Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide and bromoform. Journal of Geophysical Research: Atmospheres, 104(D7), 8067-8076.

Yokouchi, Y., Inoue, J., & Toom-Sauntry, D. (2013). Distribution of natural halocarbons in marine boundary air over the Arctic Ocean. Geophysical Research Letters, 40, 4086–4091.

Yu, D., Yao, B., Lin, W., Vollmer, M. K, Ge, B., Zhang, G., et al. (2020). Atmospheric CH_3CCl_3 observations in China: historical trends and implications. Atmospheric Research, 231, 104658.

(3) Clarifications in the revised manuscript

To avoid ambiguity, we have added detailed information on the chromatographic column used for air sample analysis in the revised methods section and clarified the rationale for selecting different analytical instruments according to sample matrices.

"The atmospheric concentrations of VCHCs were determined using a three-stage cold-trap preconcentrator (Nutech 8900DS) coupled with a gas chromatography–mass spectrometry (GC–MS) system (Agilent 7890A/5975C). Chromatographic separation was achieved on a DB-624 capillary column (60 m × 0.25 mm × 1.4 μm film thickness) in selective ion monitoring (SIM) mode." **(Lines 209–213)**

"Surface seawater (5 m) was collected using a 12 L Niskin sampler equipped with a temperature-salinity-depth probe (CTD) for concurrent temperature and salinity measurements. Samples were transferred into 100 mL airtight glass syringes without headspace, stored in the dark at 4°C, and analyzed within 4 h of collection. To minimize compound concentration changes, Samples for VCHCs were analyzed immediately onboard using a cold trap purge-and-trap gas chromatograph equipped with an electron capture detector (GC–ECD, Agilent 6890A)." **(Lines 239–246)**

8. Ln. 205-252. I assume that Henry's constant is dimensionless. Please specify. Why using concentrations in pmol/L which is equal to nmol/m^3 ? I prefer the latter because then it fits better with the equation where F is given as nmol m^{-2} d^{-1}.

Reply: We thank the reviewer for the comment. In the revised manuscript, we have specified that the Henry's constant used here is dimensionless. Regarding the

concentration units, we note that pmol L^{-1} is equivalent to nmol m^{-3}. To ensure consistency with previously published datasets and facilitate comparison, we retained pmol L^{-1} for seawater data in the manuscript. To avoid ambiguity, we have deleted the redundant unit description at this point. It should be emphasized that pmol L^{-1} can be directly converted to nmol m^{-3}, and thus the flux calculations (with F expressed in nmol m^{-2} d^{-1}) are not affected.

"C_w and C_a are the concentrations of VCHCs in surface seawater and the atmosphere, respectively. H is the dimensionless Henry's Law constant, calculated as an equation of seawater temperature (T, in Kelvin)." **(Lines 279–282)**

9. Fig. 3. A large amount of information is presented in this figure. Maybe it would be good mentioning the different concentration scales and units. CCl_4 from 74-84 pptv: CH_3CCl_3 from 1.6-2.6 pptv. Because the same-colored dot stands for quite different concentrations. Or even better to report boxplots for the concentration distributions, e.g., as supplementary material.

Reply: We thank the reviewer for this excellent and constructive suggestion. We fully agree that while a shared color scale facilitates spatial comparison, it may obscure the significant differences in absolute concentrations between compounds. In the revised manuscript, we have improved the figure presentation based on your advice.

"Atmospheric concentrations of CCl_4 and CH_3CCl_3 over the Western Pacific varied from 75.8 to 83.7 pptv (mean: 78.8 pptv) and from 1.6 to 2.4 pptv (mean: 2.0 pptv), respectively (Fig. 3 and Fig. S3)." **(Lines 339–341)**

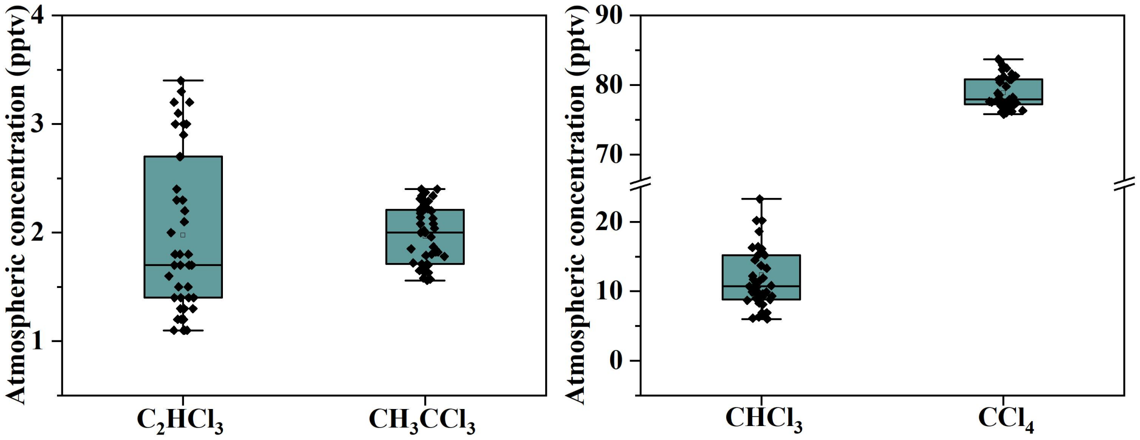


Fig. S3. Boxplots showing the atmospheric concentrations of VCHCs at all sampling locations during the study period.

In short, we have carefully considered the reviewers' comments and suggestions and conducted the revision seriously. We are very thankful to the reviewer for all the valuable comments and helpful suggestions to improve this manuscript.