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

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

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)**

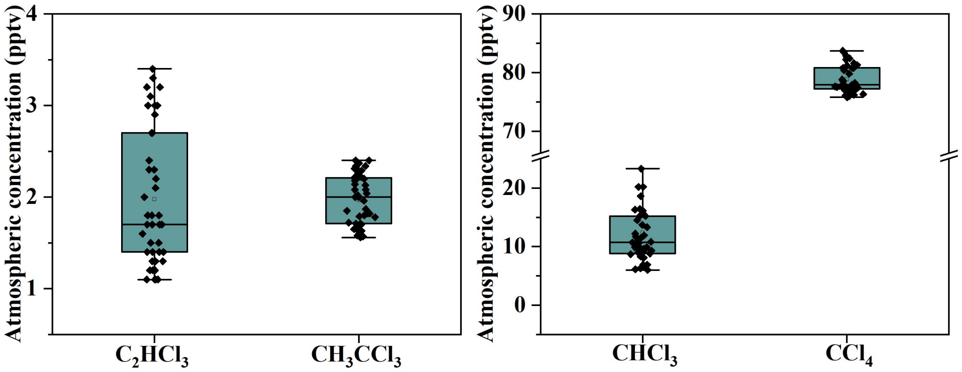

Fig. S3. Boxplots showing the atmospheric concentrations of VCHCs at all sampling locations during the study period.

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).

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

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.

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).

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

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.

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	
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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.

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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)**

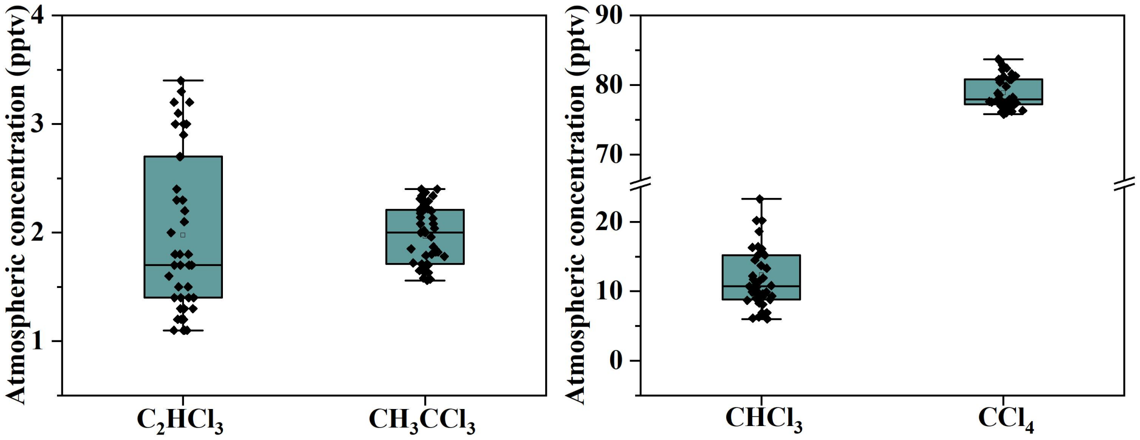

Fig. S3. Boxplots showing the atmospheric concentrations of VCHCs at all sampling locations during the study period.

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.