

**Influence of oceanic ventilation and terrestrial transport on the atmospheric
volatile chlorinated hydrocarbons over the Western Pacific**

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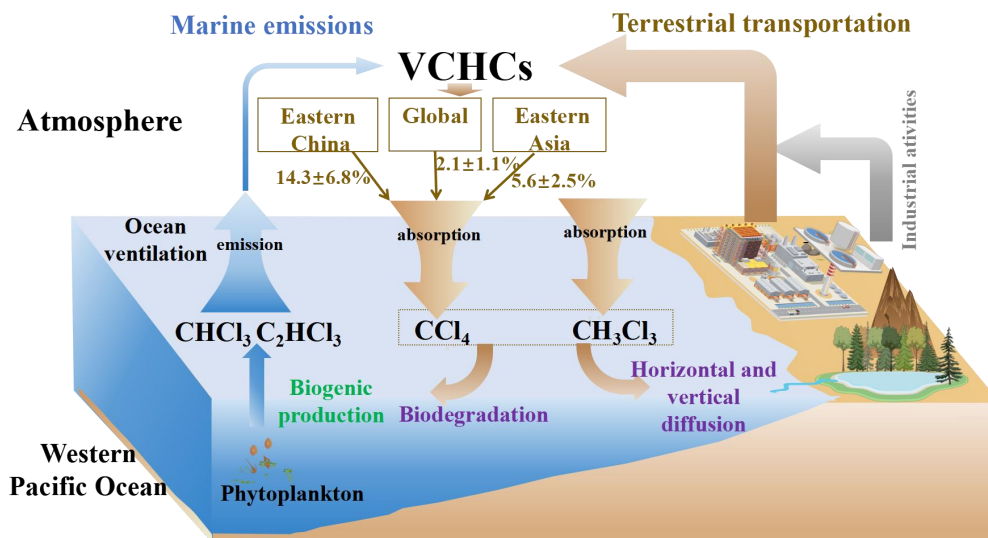
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Abstract

Volatile chlorinated hydrocarbons (VCHCs), key ozone-depleting substances
and greenhouse gases, depend on oceanic emission and uptake for their
atmospheric budget. However, data on VCHCs in the Western Pacific remain
limited. This study investigated the distribution and sources of VCHCs (CHCl₃,
C₂HCl₃, CCl₄, and CH₃CCl₃) in the Western Pacific during 2019-2020. Elevated
seawater concentrations of CHCl₃ and C₂HCl₃ in the Kuroshio-Oyashio Extension
were driven by mesoscale eddies enhancing primary productivity, while CCl₄ and
CH₃CCl₃ concentrations were mainly influenced by atmospheric inputs.

Atmospheric concentrations of VCHCs decreased from coastal to open ocean areas, with terrestrial air masses contributing significantly. Additionally, positive saturation anomalies and correlations with chlorophyll-*a* indicated the marine biological source for atmospheric CHCl₃ and C₂HCl₃. However, the atmospheric concentration variability of these gases was not fully consistent with oceanic emissions indicators (saturation anomalies and sea–air fluxes) and showed strong correlations with terrestrial tracers, indicating that land-derived atmospheric transport primarily influenced atmospheric CHCl₃ and C₂HCl₃. The estimated sea–air flux indicated that the Western Pacific acted as a source for CHCl₃ and C₂HCl₃ but a sink for CCl₄ and CH₃CCl₃, with the potential to absorb $14.3 \pm 6.8\%$ of CCl₄ emissions from Eastern China, $5.6 \pm 2.5\%$ from Eastern Asia, and $2.1 \pm 1.1\%$ of global emissions. Additionally, this region accounted for $6.3 \pm 2.8\%$ of the global oceanic absorption of CCl₄. These findings underscore the Western Pacific’s key role in regulating atmospheric CCl₄ concentrations and mitigating its accumulation in Eastern Asia, providing essential data for global VCHCs emission and uptake estimates.

42 **Graphical abstract**



44 **Introduction**

45 Volatile halocarbons (VHCs) are ozone-depleting substances and
 46 greenhouse gases (Abrahamsson et al., 1995; Abrahamsson and Edkahl, 1996). As
 47 an important component of VHCs, volatile chlorinated hydrocarbons (VCHCs) are
 48 believed to be important carriers of chlorine to the stratosphere. Among them,
 49 carbon tetrachloride (CCl_4), chloroform (CHCl_3), methyl chloroform (CH_3CCl_3),
 50 and trichloroethene (C_2HCl_3) account for an estimated 11% of the total organic
 51 chlorine in the troposphere (WMO, 2022). Long-lived compounds such as CCl_4
 52 and CH_3CCl_3 , which have atmospheric lifetimes exceeding six months, are
 53 well-mixed in the troposphere except where there are local sources. They are
 54 major contributors to both the greenhouse effect and ozone depletion, and their
 55 usage and emissions are subject to regulation under the Montreal Protocol (1987).
 56 In contrast, short-lived species such as C_2HCl_3 and CHCl_3 are classified as
 57 halogenated very short-lived substances (VSLs), with typical atmospheric
 58 lifetimes of less than six months (WMO, 2007), and are currently not regulated
 59 under the Montreal Protocol. Nevertheless, a significant portion of VSLs and

their degradation products reach the stratosphere, with over 80% of chlorinated VSLs estimated to reach these altitudes (Carpenter et al., 2014). Although present at low concentrations, VSLs 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).

The oceans, acting as source and sink of VCHCs (C_2HCl_3 , $CHCl_3$, CCl_4 , and CH_3CCl_3), play a significant role in the biogeochemical cycling of VCHCs (Blake et al., 2003; Karlsson et al., 2008; Butler et al., 2016). $CHCl_3$ and C_2HCl_3 in the oceans come from both anthropogenic and natural sources (Abrahamsson and Edkahl, 1996; Moore, 2003; Karlsson et al., 2008; He et al., 2013c). Previous studies have revealed that marine microalgae (Scarratt et al., 1999; Lim et al., 2018), macroalgae (Gschwend et al., 1985; Abrahamsson et al., 1995), and various other marine organisms (Khan et al., 2011) act as natural sources of $CHCl_3$ and C_2HCl_3 . The tropical diatoms, the cyanobacterium *Synechococcus* and the chlorophyte *Parachlorella*, and purple sulfur bacteria, have been shown to produce $CHCl_3$ (Scarratt et al., 1999; Plummer et al., 2002; Lim et al., 2018). Moreover, $CHCl_3$ emissions have also been found in regions like the Antarctic tundra (Zhang et al., 2021), Dead Sea landscapes (Shechner et al., 2019), and coastal wetlands affected by sea level rise (Jiao et al., 2018), entering the ocean via land runoff and atmospheric deposition. Abrahamsson et al. (1995) argued that C_2HCl_3 emissions from algae to the atmosphere are present in non-negligible amounts within the global atmospheric chlorine budget. Anthropogenic emissions of $CHCl_3$ mainly come from its use as a raw material in refrigerant hydrochlorofluorocarbon-22 (HCFC-22) production and as a byproduct of the water chlorination and bleaching

processes in the pulp and paper industry (McCulloch, 2003). C_2HCl_3 is also emitted from its use as a solvent and as feedstock in producing HFCs and other chemicals (Chipperfield et al., 2020). Notably, while the Montreal Protocol regulates the use of HCFC-22 in dispersive applications, demand for the refrigerant as a feedstock in the manufacture of fluoropolymers is surging (Say et al., 2020). These anthropogenic $CHCl_3$ and C_2HCl_3 ultimately enter the ocean through land runoff and atmospheric deposition, especially in coastal and estuarine regions (Yokouchi et al., 2005). In contrast, oceanic CH_3CCl_3 and CCl_4 are largely from anthropogenic sources (Butler et al., 2016; WMO, 2022). As a primary component of cleaning agents, dry-cleaning solvents, and degreasing agents, CH_3CCl_3 previously saw widespread use (Wang et al., 1995). CCl_4 was previously extensively used in chlorine gas production, industrial bleaching, organic chemical solvents, and fire extinguisher production (Rigby et al., 2014). Moreover, these two gases are used as solvents and feedstock chemicals in producing HFCs and other chemicals (Chipperfield et al., 2020). Although their usage is banned in the Montreal Protocol (1987) and its amendments and adjustments, unregulated emissions persist from specific manufacturing activities. For example, Liang et al. (2016) and Sherry et al. (2018) showed that CCl_4 production is linked to non-feedstock emissions associated with chloromethane and perchloroethylene manufacturing facilities. They also demonstrated that up to 10 Gg yr^{-1} of CCl_4 emissions may be produced by unreported, unintentional release during chlorine production, including emissions from chlor-alkali plants and their use in industrial and domestic bleaching. 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.

Substantial spatial and temporal variabilities characterize the distributions of VCHCs in oceans, with higher concentrations in estuaries than nearshore zones, and higher concentrations in nearshore zones than in the open ocean. These distributions are mainly influenced by anthropogenic emissions from terrestrial sources (Yokouchi et al., 2005; Bravo-Linares et al., 2007; Liang et al., 2014) and by the biological processes of algae in nearshore zones (Christof et al., 2002; Karlsson et al., 2008; Yang et al., 2015). In addition, the distributions of VCHCs are related to various factors, including source strength, season, topography, tides, and water masses (Yang et al., 2015; Liu et al., 2021). Previous studies have pointed out that land-based inputs have significant impacts on the distributions of marine VCHCs because VCHCs from human activities exceed marine emissions (Lunt et al., 2018; Fang et al., 2019; An et al., 2021; Yi et al., 2023). For example, persistent large emissions of CCl_4 from Eastern Asia, accounting for approximately 40% of global emissions (Lunt et al., 2018), coincided with a global increase in CCl_4 mole fractions between 2010 and 2015, as noted by Fang et al. (2019). This growth, notably driven by eastern China, has potential implications for Antarctic ozone layer recovery. However, according to the latest data from WMO (2022), the CCl_4 emissions from eastern China showed a significant decline from 2016 to 2019, dropping from $11.3 \pm 1.9 \text{ Gg yr}^{-1}$ in 2016 to $6.3 \pm 1.1 \text{ Gg yr}^{-1}$ in 2019. Similarly, An et al. (2023) reported a decline in CHCl_3 emissions from China, which peaked at 193 Gg yr^{-1} in 2017 and decreased to 147 Gg yr^{-1} by 2018, where, as of 2020, it has remained relatively constant. Yu et al. (2020) demonstrated a successful reduction in China CH_3CCl_3 emissions from 1.6 Gg yr^{-1} in 2007 to 0.3 Gg yr^{-1} in 2013, demonstrating compliance with the Montreal Protocol. Despite these declines in VCHCs emissions, Eastern Asia continues to be

an important source of global VCHCs emissions (WMO, 2022).

The Western Pacific exerts a profound influence on sea–air exchanges and the global biogeochemical cycles of materials (Tsunogai, 2002; Shi et al., 2022). The dynamic western boundary currents, equatorial Pacific circulation systems, and the expansive Western Pacific Warm Pool play pivotal roles in vertical water mass transport and material/heat exchange between the equatorial and subtropical Pacific regions (Hu et al., 2015). These oceanic processes likely impact the variations in emissions of VCHCs in the Western Pacific. Additionally, owing to its proximity to land, encompassing regions such as the Philippines and Japan, atmospheric vertical diffusion and pollutant transport from land may significantly influence atmospheric VCHCs levels over the Western Pacific (Lunt et al., 2018). While a few studies have observed seawater and atmospheric VCHCs in the Western Pacific (Quack and Suess, 1999; Liu et al., 2021), comprehensive data on atmospheric and seawater VCHCs in the Western Pacific remain scarce. Consequently, substantial uncertainties persist in estimates of oceanic sources and sinks of VCHCs (Blake et al., 2003; Butler et al., 2016). A noticeable research gap exists concerning our understanding of VCHCs in the Western Pacific. Furthermore, the lack of comprehensive knowledge regarding the biogeochemical factors that control VCHCs concentrations and sea–air fluxes produces uncertainties in global emission estimates.

In this study, a comprehensive field investigation was carried out in the Western Pacific with two primary objectives. Firstly, the study aimed to understand how oceanic physical and biogeochemical processes influence the distributions and emissions of these climatic VCHCs by examining various sources. Secondly, the study sought to ascertain the influence of the Western

Pacific on the levels of volatile VCHCs in the atmosphere, evaluating whether it acts primarily as a source or sink of these VCHCs. Investigating the distributions of VCHCs in both the seawater and the atmosphere, along with determining their sea-air fluxes, is essential for evaluating their potential impacts on the global halogen cycle.

2 Materials and methods

2.1 Study area

Our measurements were conducted on board the R/V “Dongfanghong 3” from October 31 to December 1, 2019, and the R/V “Science” from October 3, 2019, to January 5, 2020. 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. The Western Pacific survey area was divided into the Kuroshio-Oyashio Extension (KOE), North Pacific Subtropical Gyre (NPSG), and Western Pacific Warm Pool (WPWP) based on oceanographic features (supplementary information, Text S1), including seawater temperature, salinity, nutrient concentrations, and Chl-*a* concentrations observed in this study (Fig. S1 and Fig. S2).

The cruises encompassed a broad geographic range, extending from coastal to open-ocean areas and from tropical to subtropical latitudes. Data were collected along multiple transects, summarized here along two primary directions: the South-North (S-N) direction (from 1°S to 40°N) and the East-West (E-W) direction (from 130°E to 165°E). The circulation patterns of the Western Pacific, depicted in Fig. 1b, are intricate and encompass multiple oceanic currents, including the Oyashio Current (OC), the North Equatorial Current (NEC), the

North Equatorial Counter Current (NECC), the Mindanao Current (MC), and the Kuroshio Current (KC). This intricate marine circulation system and the intense ocean-atmosphere interactions bestow the Western Pacific with a pivotal role in oceanic environmental changes, water mass exchanges, nutrient and heat transport, global biogeochemical cycles, and climatic transitions (Hu et al., 2020). Further, with the planet's largest warm pool and most robust tropical convection, the WPWP area is a critical player in global sea-air substance exchange. Meteorological patterns in this area are also significantly influenced by the Indo-Australian monsoon (Wang et al., 2004; Li et al., 2019). Thus, the combined forces of the NEC-MC-KC system and the region's distinct meteorological conditions inevitably modulate the biogeochemical cycling of VCHCs in both seawater and the atmosphere.

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 H₂O and CO₂. 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 pptv–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).

2.3 Analysis of VCHCs in seawater

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). Briefly, seawater samples (100 mL) were transferred to a purge-and-trap apparatus and purged with high-purity nitrogen at a flow rate of 60 mL min⁻¹ for 14 min. The purged VCHCs were sequentially passed through glass tubes containing magnesium perchlorate (MgClO₄) and sodium hydroxide (NaOH) for drying and CO₂ removal, followed by enrichment onto a trap column (length: 30 cm; diameter: 0.8 mm) immersed in liquid nitrogen. After trapping, the trap was subsequently heated with boiling water, and the desorbed gases were introduced into the GC using high-purity nitrogen. Separation was performed on a DB-624 capillary column (60 m × 0.53 mm × 3.0 µm film thickness) with the following temperature program: 45 °C (hold 10 min), ramp to 200 °C at 15 °C min⁻¹, and hold for 5 min. The inlet and detector temperatures were 110 °C and 275 °C, respectively, and the carrier gas (ultrapure N₂) flow rate was 2.1 mL min⁻¹.

Identification and quantification of the VCHCs in seawater were based on retention times and liquid standards purchased from o2si in the US (purity > 99%).

The liquid standards were diluted twice with methanol (Merck, Darmstadt, Germany, suitable for purging and analysis) to obtain the desired standard concentrations. Using the same analytical method as for the surface seawater samples, the deep seawater (5000 m) was purged with high-purity N₂ to remove the background VCHCs, and standard curves were established by diluting VCHCs standards in series (correlation coefficients > 0.995). The detection limits for target compounds in this method ranged between 0.05 pmol L⁻¹ and 0.50 pmol L⁻¹ with a relative standard deviation of 3% to 9% (He et al., 2013b, 2013c).

2.4 Determination of chlorophyll *a* (Chl-*a*) in seawater

For the analysis of Chl-*a*, seawater samples (500 mL) were vacuum-filtered through a 0.7 µm Whatman GF/F glass fiber filter (diameter: 47 mm) and stored in the dark at -20 °C. Upon transport to the laboratory, the samples were extracted in the dark with 10 mL of 90% acetone for 24 h and centrifuged at 4000 rpm for 10 min. The supernatant was then analyzed using a fluorescence spectrophotometer (F-4500, Hitachi), achieving a detection limit of 0.01 µg L⁻¹.

2.5 Calculation of sea–air fluxes and saturation anomalies

The sea-air fluxes of VCHCs, denoted by F (nmol m⁻² d⁻¹), were calculated according to the following equation.

$$F = k_w (C_w - C_a/H) \quad (1)$$

Where k_w (m d⁻¹) is the gas exchange constant. 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 the equation of seawater temperature (T , in Kelvin). Specifically, the H values for CHCl₃ and C₂HCl₃ were derived from seawater-based temperature– H parameterizations reported by Moore (2000). The H value for CCl₄ was obtained from the seawater-based equation of

Hunter-Smith et al. (1983). For CH₃CCl₃, 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:

$$H(\text{CHCl}_3) = \exp (13.10 - 4377 \text{ T}^{-1}) \quad (2)$$

$$H(\text{C}_2\text{HCl}_3) = \exp (14.88 - 4624 \text{ T}^{-1}) \quad (3)$$

$$H(\text{CCl}_4) = \exp (11.27 - 3230 \text{ T}^{-1}) \quad (4)$$

$$H(\text{CH}_3\text{CCl}_3) = \exp (459.80 - 23465 \text{ T}^{-1} - 66.96 \text{ Ln}(\text{T})) 1.305 \quad (5)$$

k_w is calculated using the following equation by Wanninkhof (2014):

$$k_w = 0.251 u^2 (Sc / 660)^{-1/2} \quad (6)$$

Where u is the wind speed and Sc is the Schmidt constant. The Sc values of VCHCs were calculated using the equation proposed by Khalil et al. (1999):

$$Sc = 335.6 M^{1/2} \times (1 - 0.065 t + 0.002043 t^2 - 2.6 \times 10^{-5} t^3) \quad (7)$$

where t (°C) represents the temperature of the surface seawater and M is the molecular weight of VCHCs.

Saturation anomalies Δ (%) were calculated as the departure of the observed dissolved amount from equilibrium with air according to the following equation (Kurihara et al., 2010).

$$\Delta\% = 100 (C_w - C_a/H) / C_a/H \quad (8)$$

A positive saturation anomaly implies a net flux from the ocean to the air.

The uncertainty of the sea-air fluxes obtained in this study arises from both systematic and random measurement errors. Propagation of error analysis was conducted to quantify the uncertainty of the calculated sea-air fluxes, following the method outlined by Shoemaker et al. (1974).

$$\sigma^2 F = \left(\frac{\partial F}{\partial k_w} \right)^2 (\sigma k_w)^2 + \left(\frac{\partial F}{\partial C_w} \right)^2 (\sigma C_w)^2 + \left(\frac{\partial F}{\partial C_a} \right)^2 (\sigma C_a)^2 + \left(\frac{\partial F}{\partial H} \right)^2 (\sigma H)^2 \quad (9)$$

The precision of VCHCs measurements was under 9%, determined based on repeated sample injections. The overall error was calculated at approximately 20%, primarily due to the value of 20% from Wanninkhof (2014) for uncertainty in k_w , influenced by wind speed and Sc variabilities. Also, while a single Henry's Law calculation was done, there is uncertainty in both the determination of H and the temperature dependence. Thus, the error of the flux estimate in this study was determined to be $> 20\%$.

2.6 Data analysis

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, provided by the National Oceanic and Atmospheric Administration (NOAA) (<http://www.arl.noaa.gov/ready.php>), was employed to generate 96 h backward trajectories for air masses. The Matlab software was used to compile and analyze all survey station back trajectories. The TrajStat module for the MeteoInfo software was applied for trajectory analysis, enabling the clustering of trajectories based on geographic origins and historical paths identified in a previous study (Squizzato and Masiol, 2015). Following convention (Byčenkienė et al., 2014; Liu et al., 2017), these trajectories were initialized 100 m above sea level. Meteorological data were obtained from the Global Data Assimilation System (GDAS) dataset (<http://ready.arl.noaa.gov/archives.php>).

3 Results and discussion

3.1 Variability of the overlying atmospheric VCHCs concentrations

The atmospheric mixing ratios of the four VCHCs over the Western Pacific are summarized in Fig. 2, Fig. 3, and Fig. S3. The results indicated that the

distributions of the selected VCHCs were correlated with both source strength and prevailing meteorological conditions. To clarify the drivers behind the observed concentration fluctuations and spatial patterns, the trace gases were classified into two groups based on their molecular lifetimes (Table S1).

3.1.1 CCl₄ and CH₃CCl₃

Atmospheric concentrations of CCl₄ and CH₃CCl₃ 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). The concentration of CCl₄ was similar to the average background mixing ratio of 78.5 pptv in the Northern Hemisphere during a survey from October 2019 to January 2020, as reported by the AGAGE network (<https://agage.mit.edu/>). However, it was considerably lower than the concentrations reported by Blake et al. (2003) for the Pacific Ocean (108.7 pptv) from February 24 to April 10, 2001, the measurements by Zhang et al. (2010) in 2007 for the Pearl River Delta region (116 pptv), those by Ou-Yang et al. (2017) in 2015 for the Mt. Fuji Research Station in Japan (84 pptv), and by Zheng et al. (2019) in 2015 at the Yellow River delta in China (109 pptv). Similarly, the mean CH₃CCl₃ concentration in this study (2.0 pptv) exceeded the average background mixing ratio of 1.67 pptv in the Northern Hemisphere during a survey from October 2019 to January 2020 (<https://agage.mit.edu/>). However, the level reported here was lower than the concentration reported by He et al. (2013c) for the East China Sea (9.1 pptv) from May 2 to 9, 2012. Similarly, it was considerably lower than those reported by Blake et al. (2003) for the Pacific Ocean (132 pptv) from February 24 to April 10, 2001. It was also lower than the observed concentrations in the Pearl River Delta region (53 pptv) from October 25 to December 1, 2007, by Zhang et al. (2010); the Mt. Fuji Research Station in Japan

(4.0 pptv) from August 12 to August 17, 2015, by Ou-Yang et al. (2017); and the Yellow River Delta region, Northern China (2.8 pptv) from June 8 to July 9, 2017, by Zheng et al. (2019). These discrepancies likely reflect temporal variability in emissions and changes in the global burden, as well as differences in the sampling locations. Most samples in this study were collected in regions less influenced by continental outflow, resulting in relatively low concentrations.

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. 1c 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).

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 CCl₄ 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, CCl₄ and CH₃CCl₃ 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 CCl₄ and CH₃CCl₃ levels in China and Japan, respectively. Lunt et al. (2018) identified continued CCl₄ emissions from Eastern Asia. Collectively, these findings suggested that continental air mass transport was likely the dominant factor driving the elevated CCl₄ and CH₃CCl₃ levels observed at station P1-4 during the study period. In contrast, the lowest CCl₄ and CH₃CCl₃ concentrations were observed at station P1-24, where all affecting air mass trajectories came from the Pacific Ocean (Fig. 1c and Fig. S4), indicating the influence of clean marine background air (Fig. 1c).

3.1.2 CHCl₃ and C₂HCl₃

The atmospheric mixing ratios of CHCl₃ and C₂HCl₃ over the Western Pacific ranged from 6.0 to 29.4 pptv (mean: 12.4 ± 5.7 pptv) and from 1.1 to 3.4 pptv (mean: 2.0 ± 0.7 pptv), respectively. The concentration of CHCl₃ measured in the current work was similar to the average background mixing ratio of 11.82 pptv measured in the Northern Hemisphere during the survey period from October 2019

to January 2020, as reported by AGAGE network (<https://agage.mit.edu/>). However, it was lower than values reported from other areas, such as in a Western Pacific marginal sea—the South Yellow Sea—from May 2 to 9, 2012 (27.3 pptv; He et al., 2013c), the Mt. Fuji Research station of Japan from August 12 to August 17, 2015 (39 ± 11 pptv; Ou-Yang et al., 2017), and the Yellow River Delta region, Northern China, from June 8 to July 9, 2017 (283 pptv; Zheng et al., 2019). The measurements of C_2HCl_3 were lower than in areas close to land sources, such as the South Yellow Sea from May 2 to 9, 2012 (27.3 pptv; He et al., 2013c) and the Yellow River Delta region, Northern China, from June 8 to July 9, 2017 (20 pptv; Zheng et al., 2019). This difference could be attributed to the surveyed area being a relatively open sea, where the dilution effect by air from the marine boundary layer (MBL) is more pronounced. Furthermore, the air in the study area is more photochemically aged, leading to lower observed values of C_2HCl_3 .

Spatially, elevated concentrations of atmospheric $CHCl_3$ and C_2HCl_3 were detected in nearshore regions, such as the KEO area and stations EQ12, E130-15, and E130-18 (Fig. 2 and Fig. 3). Both $CHCl_3$ and C_2HCl_3 showed significant correlations with SF_6 ($r = 0.56$, $n = 38$, $p < 0.01$ and $r = 0.54$, $n = 38$, $p < 0.01$, respectively; Fig. S5). The result indicated that the high concentrations of these two gases in the atmosphere mainly originated from anthropogenic input, as SF_6 is an important indicator of terrigenous sources. 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 ($39 \pm 11 \text{ pptv}$) at the Mt. Fuji research station, Japan, in 2015; and in 2017, the highest annual mean CHCl_3 ($43 \pm 18 \text{ pptv}$) 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.

In addition to terrestrial contributions, positive saturation anomalies of CHCl_3 and C_2HCl_3 in surface seawater (Fig. 4) indicated supersaturation, suggesting the oceanic emissions as a potential source of atmospheric CHCl_3 and C_2HCl_3 . Previous studies have reported that substantial amounts of CHCl_3 and C_2HCl_3 are released from marine macroalgae and microalgae (Abrahamsson et al., 1995; Abrahamsson et al., 2004a; Chuck et al., 2005; Ekdahl et al., 1998; Lim et al., 2018) and subsequently transferred to the atmosphere via sea–air diffusion. Consistent with this, atmospheric CHCl_3 and C_2HCl_3 exhibited significant positive correlations with *Chl-a* levels in the study area ($r = 0.83$ and 0.58 , $p < 0.01$, $n = 41$; Fig. S6), supporting a potential biological contribution. Nevertheless, atmospheric levels of CHCl_3 and C_2HCl_3 were not fully consistent with oceanic emissions indicators (saturation anomalies and sea–air fluxes). In the KOE region, where

atmospheric mixing ratios and Chl-*a* were elevated, their saturation anomalies were relatively low compared to other regions (Fig. 4), and estimated sea–air fluxes showed no significant enhancement (Fig. 5). Moreover, strong correlations atmospheric concentrations of CHCl₃ and C₂HCl₃ with terrestrial tracers (CCl₄, CH₃CCl₃, and SF₆; Fig. S6 and Fig. S7) suggested shared terrestrial sources or common atmospheric processes. Collectively, these results indicate that although marine biological production contributes to CHCl₃ and C₂HCl₃ emissions, terrestrial transport was the dominant factor controlling their atmospheric variability in the study region.

3.2 Regional characteristics of seawater VCHCs and their driving factors

The seawater distributions of CHCl₃, C₂HCl₃, CCl₄, and CH₃CCl₃ are shown in Fig. 2. Seawater CHCl₃, C₂HCl₃, CCl₄, and CH₃CCl₃ exhibited significant regional variability in the Western Pacific. Surface concentrations of CHCl₃, C₂HCl₃, CCl₄, and CH₃CCl₃ in the KOE region were notably higher than those in the NPSG and WPWP (Fig. 2).

3.2.1 Kuroshio-Oyashio Extension

The Kuroshio-Oyashio Extension (KOE) area is characterized by a complex hydrography, with sharp meridional gradients in temperature and salinity due to the convergence of the warm, saline Kuroshio Current and the cold, less saline Oyashio Current (Fig. 2). Moreover, the Kuroshio Current transports warm seawater northward, where it cools and blends with the nutrient-rich Oyashio Current (Wan et al., 2023; Xu et al., 2023). The resulting upward flux of nutrients induced by the mesoscale eddies from the Kuroshio and the Kuroshio Extension replenish the upper ocean in the KOE with a substantial nutrient supply (Fig. S2).

This, in turn, enhances primary productivity in the surface seawater, as evidenced by the elevated Chl-*a* concentrations observed here (Fig. 2 and Fig. S2).

The higher surface concentrations of CHCl₃ and C₂HCl₃ found in the KOE region could be due to a combination of phytoplankton abundance, the transport of terrestrial air masses, and surface seawater temperature (SST). Firstly, the elevated concentrations of CHCl₃ and C₂HCl₃, corresponding to high Chl-*a* concentrations in the KOE region (Fig. 2), could be indicative of the influence of emissions from phytoplankton. The study by Roy et al. (2011) indicated that the distribution of CHCl₃ in the ocean was influenced by phytoplankton abundance. Indeed, phytoplankton blooms are known to contribute to the production of CHCl₃ and C₂HCl₃, as suggested by previous studies (Abrahamsson et al., 1995; Abrahamsson et al., 2004b; Chuck et al., 2005; Roy et al., 2011; Lim et al., 2018). Diatoms and prymnesiophytes have been identified as dominant marine microalgae species responsible for releasing CHCl₃ (Roy et al., 2011; Lim et al., 2018). Wang et al. (2022) identified diatoms and dinoflagellates as the predominant microalgae species in the Northwest Pacific Ocean, with diatoms in particular thriving in the eutrophic Oyashio region. Secondly, given the proximity of the KOE region to Japan, atmospheric CHCl₃ and C₂HCl₃ might have been augmented by inputs from long-distance land-based air masses originating from land (as discussed in Section 3.1). Additionally, the lower SST in this region facilitated the dissolution of CHCl₃ and C₂HCl₃, while high atmospheric concentrations of these compounds from long-distance land transport could have helped to replenish the CHCl₃ and C₂HCl₃ in the surface seawater. However, the saturation anomalies of CHCl₃ and C₂HCl₃ were positive during this cruise, suggesting CHCl₃ and C₂HCl₃ in the study area were supersaturated (Fig. 4). Therefore, given the seawater saturation of CHCl₃

and C_2HCl_3 in the region, and their short atmospheric lifetimes (< 6 months; WMO, 2022), it was inferred that emissions from phytoplankton in situ could have a stronger impact on seawater concentrations of $CHCl_3$ and C_2HCl_3 than terrestrial sources of atmospheric inputs.

In contrast to $CHCl_3$ and C_2HCl_3 , CCl_4 and CH_3CCl_3 exhibited negative saturation anomalies in the KOE region, indicating undersaturation. Previous studies have established that CCl_4 and CH_3CCl_3 primarily originate from anthropogenic sources (Wang et al., 1995; Rigby et al., 2014). Therefore, the elevated concentrations of CCl_4 and CH_3CCl_3 in the KOE region (Fig. 2) might have been caused by the long-distance transport of air masses from land (as discussed in Section 3.1). Moreover, the lower SST in the KOE region may facilitate the dissolution of CCl_4 and CH_3CCl_3 , thereby increasing their concentrations in these regions. Additionally, Fig. 4 shows that CCl_4 and CH_3CCl_3 were undersaturated in KOE region, further indicating that atmospheric transport influenced their concentrations in seawater.

3.2.2 North Pacific Subtropical Gyre

Subtropical ocean gyres are often likened to marine deserts because of their persistent nutrient depletion and low organism standing stocks. In the NPSG, the primary mechanism for nutrient replenishment is from below, primarily through vertical eddy diffusion (Gupta et al., 2022). In contrast to the KOE region, the NPSG region lies at the center of the subtropical gyre, predominantly influenced by the deep nutricline and characterized by elevated temperatures, salinity, and diminished nutrient contents (Fig. S2). Xu et al. (2023) reported that the subsurface layer between $10^\circ N$ and $35^\circ N$ in the NPSG experiences nutrient depletion. This is because the environmental conditions of the NPSG limit the

upward flux of nutrients through vertical transport, leaving the surface waters chronically nutrient-depleted. Figure 2 shows that concentrations of CHCl_3 , C_2HCl_3 , CCl_4 , and CH_3CCl_3 in the NPSG were significantly lower than in the KOE, possibly because the NPSG is located far from land and has a high SST (Fig. 2). Additionally, the Chl-*a* levels and nutrients were considerably lower in the NPSG than in the KOE region (Fig. S2). This suggested that the reduced release of CHCl_3 and C_2HCl_3 from phytoplankton could have also contributed to the lower concentrations of these gases observed in the NPSG. The lower nutrient levels in the NPSG lead to reduced phytoplankton biomass, resulting in lower production and release of halocarbons (Smythe-Wright et al., 2010; Liu et al., 2021).

3.2.3 Western Pacific Warm Pool

The concentrations of seawater CHCl_3 and C_2HCl_3 in the WPWP were similar to those in the NPSG (Fig. 2). Xu et al. (2023) proposed that this similarity could be because the WPWP region has a strong barrier layer, i.e., the layer of water between the isothermal layer and the mixed layer. In the WPWP, heavy precipitation enhances density stratification in the surface layers, resulting in a shallow mixed layer and a substantial barrier layer (Qu and Meyers, 2005). Despite the subsurface layer containing an abundance of nutrients, the presence of a robust barrier layer hinders the upward transport of nutrients and organic matter in the WPWP area (Fig. S2). This, combined with the high SST in this region (Fig. S2), might result in low surface concentrations of CHCl_3 and C_2HCl_3 in the WPWP region. However, near the equator of the WPWP, seawater concentrations of CCl_4 and CH_3CCl_3 were relatively high (Fig. 2). This pattern likely resulted from the area's proximity to land (e.g., Papua New Guinea), where terrestrial inputs via riverine runoff and atmospheric transport (Fig. 1c) could have elevated

their concentrations in surface seawater.

3.2.4 Correlations between VCHCs in seawater

CHCl_3 and C_2HCl_3 were found to be supersaturated in seawater, with previous studies suggesting that they primarily originate from biological processes within the ocean rather than relying solely on atmospheric inputs (Section 3.2.1). The strong positive correlation between CHCl_3 and C_2HCl_3 in seawater ($r = 0.71$, $p < 0.01$, $n=65$; Fig. S8) supported the idea that these compounds share a common production mechanism, specifically emissions from biological processes. In contrast, CCl_4 and CH_3CCl_3 were undersaturated in seawater and primarily entered the ocean through atmospheric deposition, meaning that their concentrations in seawater were more influenced by atmospheric inputs (Section 3.2.1). Moreover, despite the supersaturation of CHCl_3 and C_2HCl_3 in seawater and the undersaturation of CCl_4 and CH_3CCl_3 , these four compounds still exhibited significant linear correlations in their concentrations (Fig. S8), suggesting that they were influenced by common oceanic and atmospheric processes. This correlation likely reflected partially overlapping sources, such as riverine input and atmospheric transport (Fogelqvist, 1985; He et al., 2013a, 2013b). Additionally, oceanic physical processes, such as water mass mixing, diffusion, and vertical movement, played a crucial role in the distribution of gases in seawater (Doney et al., 2012). The synchronous influence of these processes on VCHCs might have been the reason for the linear correlation and similar distribution patterns observed for these four VCHCs in seawater. Specifically, in the Western Pacific, the unique hydrodynamic conditions significantly influenced the distribution patterns of CHCl_3 , C_2HCl_3 , CCl_4 , and CH_3CCl_3 . Major ocean currents, such as the Kuroshio and Oyashio, created zones of convergence and divergence that enhanced vertical

and horizontal mixing, transporting gases from deeper waters to the surface and redistributing them across different regions, affecting their concentrations and distribution. Additionally, mesoscale eddies contribute to the diffusion of gases within the water column, resulting in gases from different sources (biogenic and atmospheric deposition) being more uniformly distributed in seawater (McGillicuddy, 2016; Xu et al., 2023).

3.3 Sea–air fluxes and saturation anomalies of VCHCs

The saturation anomalies and sea–air fluxes of CHCl_3 , C_2HCl_3 , CCl_4 , and CH_3CCl_3 were estimated based on their simultaneously measured seawater and atmospheric concentrations, as outlined in Section 2.5 (Fig. 4 and Fig. 5). The saturation anomalies of CHCl_3 and C_2HCl_3 were positive, whereas CCl_4 and CH_3CCl_3 exhibited negative saturation anomalies at most stations of this study (Fig. 4). Moreover, the mean sea–air fluxes (range) for CHCl_3 , C_2HCl_3 , CCl_4 , and CH_3CCl_3 were 23.96 (0.10–121.98), 7.18 (0.02–29.76), -0.73 (-3.44–0.00), and -0.02 (-0.18–0.07) $\text{nmol m}^{-2} \text{ d}^{-1}$. These results indicated that CHCl_3 and C_2HCl_3 were in a state of supersaturation in the surface seawater, leading to their emission into the overlying atmosphere. In contrast, CCl_4 and CH_3CCl_3 were undersaturated within the surface seawater and were assimilated from the overlying atmosphere. Hence, we tentatively concluded that the Western Pacific was a source of CHCl_3 and C_2HCl_3 and a sink for CCl_4 and CH_3CCl_3 during the cruise periods.

Compared to the marginal sea of the Western Pacific, this study’s estimates of CHCl_3 and C_2HCl_3 emission and CCl_4 and CH_3CCl_3 uptake were lower (Yang et al., 2015; He et al., 2017; Wei et al., 2019). For example, the average flux of CHCl_3 and C_2HCl_3 in this study was significantly lower than those reported in the northern Yellow Sea and Bohai Sea by He et al. (2017) (C_2HCl_3 : 162.6 nmol m^{-2}

d⁻¹), Wei et al. (2019) (CHCl₃: 177.5 nmol m⁻² d⁻¹, C₂HCl₃: 99.5 nmol m⁻² d⁻¹), He et al. (2019) (C₂HCl₃: 59.4 nmol m⁻² d⁻¹), and Yang et al. (2015) (CHCl₃: 183.4 nmol m⁻² d⁻¹). Compared with the average fluxes of CCl₄ (-21.3 nmol m⁻² d⁻¹) and CH₃CCl₃ (-6.8 nmol m⁻² d⁻¹) in the South Yellow Sea and East China Sea as reported by Yang et al. (2015), the average fluxes of CCl₄ and CH₃CCl₃ in this study were lower. Although there were significant differences in sea-air fluxes compared with the marginal sea of the Western Pacific, both indicated that the ocean is a source of CHCl₃ and C₂HCl₃ in the atmosphere, but a sink of CCl₄ and CH₃CCl₃.

As shown in Fig. 5 and Fig. 6, the fluxes of CHCl₃ and C₂HCl₃ in the Western Pacific exhibited considerable spatial variability and generally corresponded with wind speeds. For instance, high fluxes of CHCl₃ and C₂HCl₃ at station P1-6 coincided with high wind speeds, while the low CHCl₃ and C₂HCl₃ fluxes at station E130-15 coincided with low wind speeds. However, as shown in Fig. 6, at a given wind speed, the fluxes were low due to low seawater concentrations of CHCl₃ and C₂HCl₃. Thus, seawater concentrations also had a large influence on the spatial variability of the sea-air fluxes of CHCl₃ and C₂HCl₃. The air-sea fluxes of CCl₄ and CH₃CCl₃ were also higher at stations with high wind speeds (Fig. 5 and Fig. 6). Similarly, Butler et al. (2016) found that the air-sea exchange rate was the primary driver of oceanic uptake of CCl₄, mainly driven by wind speed. However, the highest air-sea fluxes of CCl₄ and CH₃CCl₃ were observed at station P1-2, which had the highest equilibrium solubility (ratio of atmospheric concentration to Henry's Law constant) (Fig. 5). Moreover, at a given wind speed, the fluxes of CCl₄ and CH₃CCl₃ were lower where their atmospheric concentrations were lower and where SST was higher (Fig. 6). Therefore, the

spatial variability of air-sea CCl_4 and CH_3CCl_3 fluxes were not only affected by wind speed but were also related to atmospheric CCl_4 and CH_3CCl_3 concentrations and SST. A similar investigation observed a comparable relationship between sea-air fluxes, wind speed, and atmospheric concentration while examining the distribution of SF_6 in seawater (Ni et al., 2023).

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 3.2), 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 (October–December 2019), mean atmospheric CCl_4 concentrations at both GSN sites and the global scale were approximately 1% lower than their respective annual means, while the global CH_3CCl_3 concentration was about 6% lower (Fig. 7). These results suggest that atmospheric CCl_4 levels in the Western Pacific were likely close to the annual mean during this period, whereas CH_3CCl_3 levels were possibly somewhat lower. In addition, SST and *Chl-a* in the study region during the observation period were broadly consistent with their annual means, whereas wind speeds were on average 6% higher (Fig. 7a; Tang et al., 2022). Consequently, the sea–air fluxes of CHCl_3 , C_2HCl_3 , and CCl_4

reported in this study are likely somewhat higher than the annual mean, primarily due to the elevated wind speeds during the cruises.

In the Western Pacific (130°E–180°E, 0°–40°N, area: 2.17×10^7 km²), the estimated annual oceanic uptake of CCl₄ was 0.9 Gg yr⁻¹. The associated uncertainty was quantified by combining the 95% confidence interval, derived from the standard error of fluxes within the study region, with the inherent >20% systematic uncertainty of flux estimates. The resulting uptake range is 0.5–1.3 Gg yr⁻¹, with an overall uncertainty of 0.4 Gg yr⁻¹. Given that fluxes during the observation period were likely higher than annual averages, the annual CCl₄ uptake estimated in this study may be slightly overestimated. Moreover, considering that elevated SST reduces gas solubility, strengthens ocean stratification, and alters wind patterns, future warming of the western Pacific is expected to diminish the oceanic sink capacity for CCl₄.

3.4 The role of the Western Pacific in regulating Eastern Asia CCl₄

Eastern Asia, particularly eastern China, was a major source of global CCl₄ emissions, significantly contributing to the global CCl₄ burden (Lunt et al., 2018). The primary emission sources included the manufacture of general-purpose machinery, the production of CH₃Cl, CH₂Cl₂, CHCl₃, and C₂Cl₄, which generate CCl₄ as a byproduct, as well as the use of CCl₄ as a raw material and processing agent in the chemical manufacturing industry (Park et al., 2018; Li et al., 2024). Although CCl₄ emissions from eastern China declined significantly by nearly 45% between 2016 and 2019, Eastern Asia remained a major source of atmospheric CCl₄ (WMO, 2022). Our study suggested that CCl₄ emissions from Eastern Asia may have been a significant source of atmospheric CCl₄ in the Western Pacific (Section 3.1). The Western Pacific, as a sink for East Asian CCl₄, played a key role

in regulating atmospheric CCl₄ concentrations. Based on our estimates (Section 3.3), the estimated oceanic absorption of CCl₄ in the Western Pacific (0.9 ± 0.4 Gg yr⁻¹) accounted for $14.3 \pm 6.8\%$ of the Eastern China emissions (6.3 ± 1.1 Gg yr⁻¹ in 2019; WMO, 2022), $5.6 \pm 2.5\%$ of the emissions from Eastern Asia (16 (9–24) Gg yr⁻¹ on average between 2009 and 2016; Lunt et al., 2018), and $2.1 \pm 1.1\%$ of the total global emissions (global emissions were 44 ± 14 Gg yr⁻¹; WMO, 2022). Furthermore, the estimated oceanic absorption of CCl₄ in the Western Pacific accounted for $6.3 \pm 2.8\%$ of the global oceanic absorption (14.4 Gg yr⁻¹; Butler et al., 2016). These data indicated that the Western Pacific as a sink of CCl₄ was crucial for regulating atmospheric CCl₄ concentrations and mitigating the accumulation of CCl₄ in the atmosphere of Eastern Asia. This result was consistent with Butler et al. (2016), further confirming the critical role of the Western Pacific in the global CCl₄ cycle and emphasizing the ocean's indispensable role as a sink for atmospheric CCl₄. Notably, despite the estimate originating from a region with relatively little anthropogenic influence, the absorption capacity of the Western Pacific indicates it can significantly contribute to reducing global CCl₄ levels. This finding also aligned with Yvon-Lewis and Butler (2002), who demonstrated that oceans could effectively remove substantial quantities of CCl₄ from the atmosphere.

Additionally, a substantial body of prior data has indicated there is a CCl₄ deficit in deep ocean waters, especially in regions characterized by low oxygen levels (Krysell et al., 1994; Tanhua and Olsson, 2005). Recent studies have observed widespread undersaturation of CCl₄ in the surface waters of the Pacific, Atlantic, and Southern Oceans, suggesting the oceans consume a substantial amount of atmospheric CCl₄ and that biological sinks for CCl₄ may exist in the

surface or near-surface waters of the oceans (Butler et al., 2016; Suntharalingam et al., 2019). These findings further supported the role of oceans as a CCl₄ sink and provided important insights for future oceanic environmental management and pollution control.

4 Conclusions

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. As summarized from Figure 8, the presence or absence of upwelling, whether the upwelling carries nutrients, and the transport of terrestrial inputs govern the biogeochemical characteristics of surface seawater in the Western Pacific, thereby influencing the concentrations and distributions of climatically relevant VCHCs. Specifically, the mesoscale eddies in the KOE region induced upwelling, bringing nutrient-rich subsurface water to the surface. This upwelling supplied ample nutrients to the surface seawater, enhancing phytoplankton growth and organic matter photoreactions. These processes potentially enhanced the production of CHCl₃ and C₂HCl₃, resulting in high seawater concentrations of these compounds in the KOE. In contrast, the lower seawater concentrations of CHCl₃ and C₂HCl₃ in the NPSG and WPWP were attributed to the oligotrophic subsurface seawater in the NPSG and the suppression of upward nutrient and organic matter fluxes due to a robust barrier layer in the WPWP. The elevated seawater concentrations of CCl₄ and CH₃CCl₃ observed in the coastal area were caused by atmospheric inputs, seawater temperatures, and upwelling. Atmospheric mixing ratios of CCl₄ and CH₃CCl₃ over the Western Pacific were predominantly determined by atmospheric inputs from land, as revealed through backward trajectory analysis. However, the atmospheric

concentration of CHCl_3 and C_2HCl_3 in the study area was likely influenced by a combination of atmospheric transport from the continent and ocean emissions, with continental air mass transport potentially contributing more significantly. The preliminary estimation indicated that approximately $2.2 \pm 1.1\%$ of global CCl_4 emissions were absorbed by the Western Pacific. Our study also showed that $14.3 \pm 6.8\%$ of CCl_4 emitted from Eastern China and $5.6 \pm 2.5\%$ of Eastern Asia CCl_4 emissions could be absorbed by the Western Pacific, highlighting its crucial role in regulating atmospheric CCl_4 concentrations and mitigating accumulation in the Eastern Asia atmosphere. In light of these findings, we tentatively propose that the capacity of the ocean to act as a sink for CCl_4 may warrant reevaluation. The global oceanic uptake of CCl_4 and CH_3CCl_3 and emissions of CHCl_3 and C_2HCl_3 could have an influence on their global abundances and impact atmospheric chemistry. Future studies should prioritize expanded temporal and spatial observations to better constrain these processes and improve climate predictions.

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Data availability statement

The datasets are accessible via Figshare at <https://doi.org/10.6084/m9.figshare.25639146>.

Author contributions:

SL and JN designed the study, conducted VCHC measurements in the Western Pacific, analyzed the results, and contributed to manuscript writing. XG assisted with the observations. JS reviewed and revised the manuscript. ZH interpreted the data and contributed to the manuscript. GY interpreted the analyzed results and reviewed and revised the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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FIGURE CAPTIONS

Fig. 1. (a) Locations of sampling stations (orange diamonds represent atmospheric sampling stations; SDZ: Shangdianzi background station; GSN: Gosan station). VCHCs data for the GSN were obtained from AGAGE network (<https://agage.mit.edu/>), and for the SDZ were derived from Yi et al. (2023). (b) A schematic map of the major currents of the Western Pacific. (c) Cluster analysis of 96-h backward trajectories for different stations over the Western Pacific. The ensemble 96-h back-trajectories were within the lower troposphere above 100 m.

Fig. 2. Latitudinal distributions of SST, salinity, and Chl-*a*, and surface seawater and atmospheric concentrations of CHCl₃, CCl₄, C₂HCl₃, and CH₃CCl₃, along with wind speed in the Western Pacific.

Fig. 3. Distributions of CHCl₃, CCl₄, C₂HCl₃, and CH₃CCl₃ in the marine atmospheric boundary layer of the Western Pacific.

Fig. 4. Saturation anomaly of CHCl₃, CCl₄, C₂HCl₃, and CH₃CCl₃ in the Western Pacific.

Fig. 5. Sea–air fluxes of CHCl₃, CCl₄, C₂HCl₃, and CH₃CCl₃, along with wind speeds in the Western Pacific.

Fig. 6. Relationships between sea–air fluxes of VCHCs and wind speed, SST, and VCHCs concentrations in seawater and the atmosphere.

Fig. 7. (a) Interannual variations of wind speed, SST, and Chl-*a* concentration in the study area during 2019. (b) Interannual variability of CCl₄ at the GSN site in 2019 compared with the global mean. (c) Interannual variability of CH₃CCl₃ 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

1137 (2022). Atmospheric CCl_4 and CH_3CCl_3 data were obtained from the AGAGE
1138 network (<https://agage.mit.edu/>). Shaded areas indicate the cruise sampling
1139 periods.

1140 **Fig. 8.** Schematic diagram of key processes and factors controlling the production,
1141 distribution, and sea–air interactions of VCHCs in the Western Pacific.

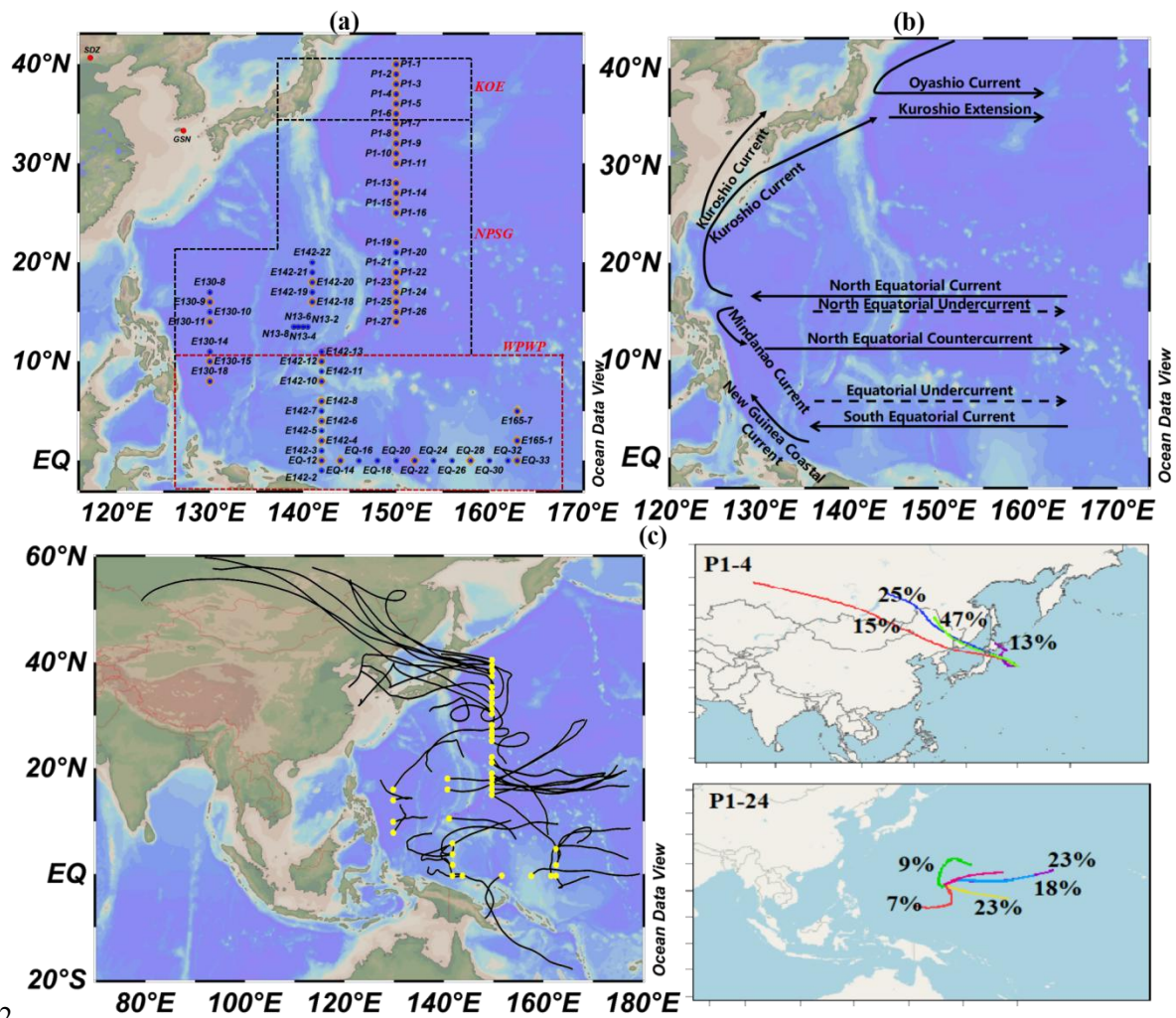


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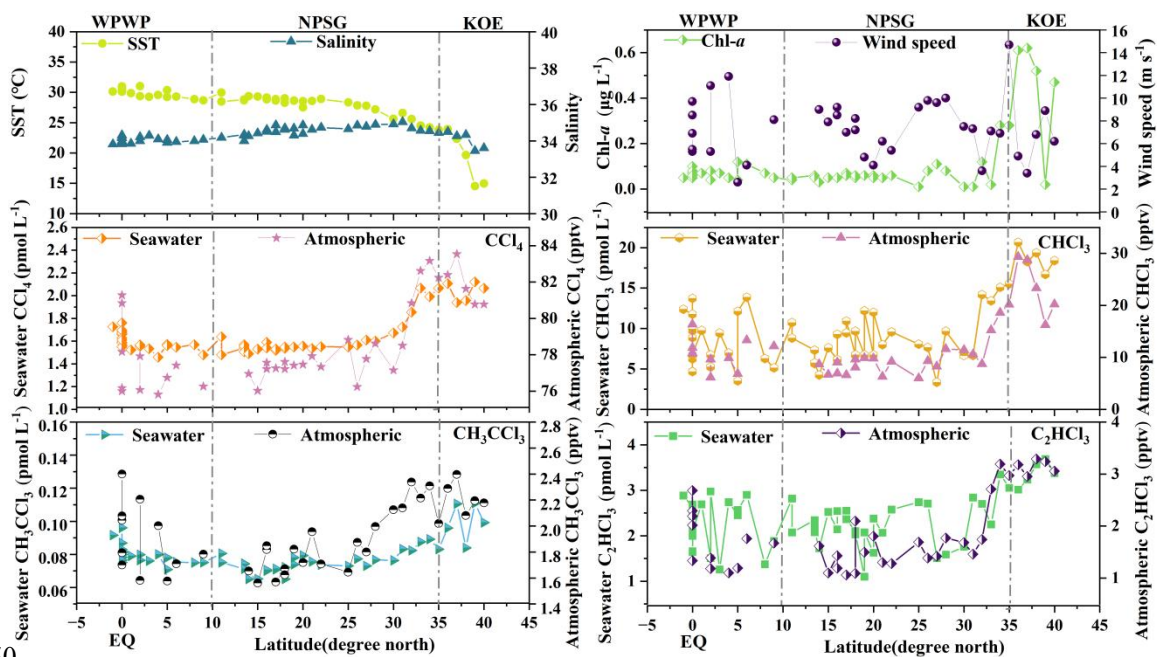


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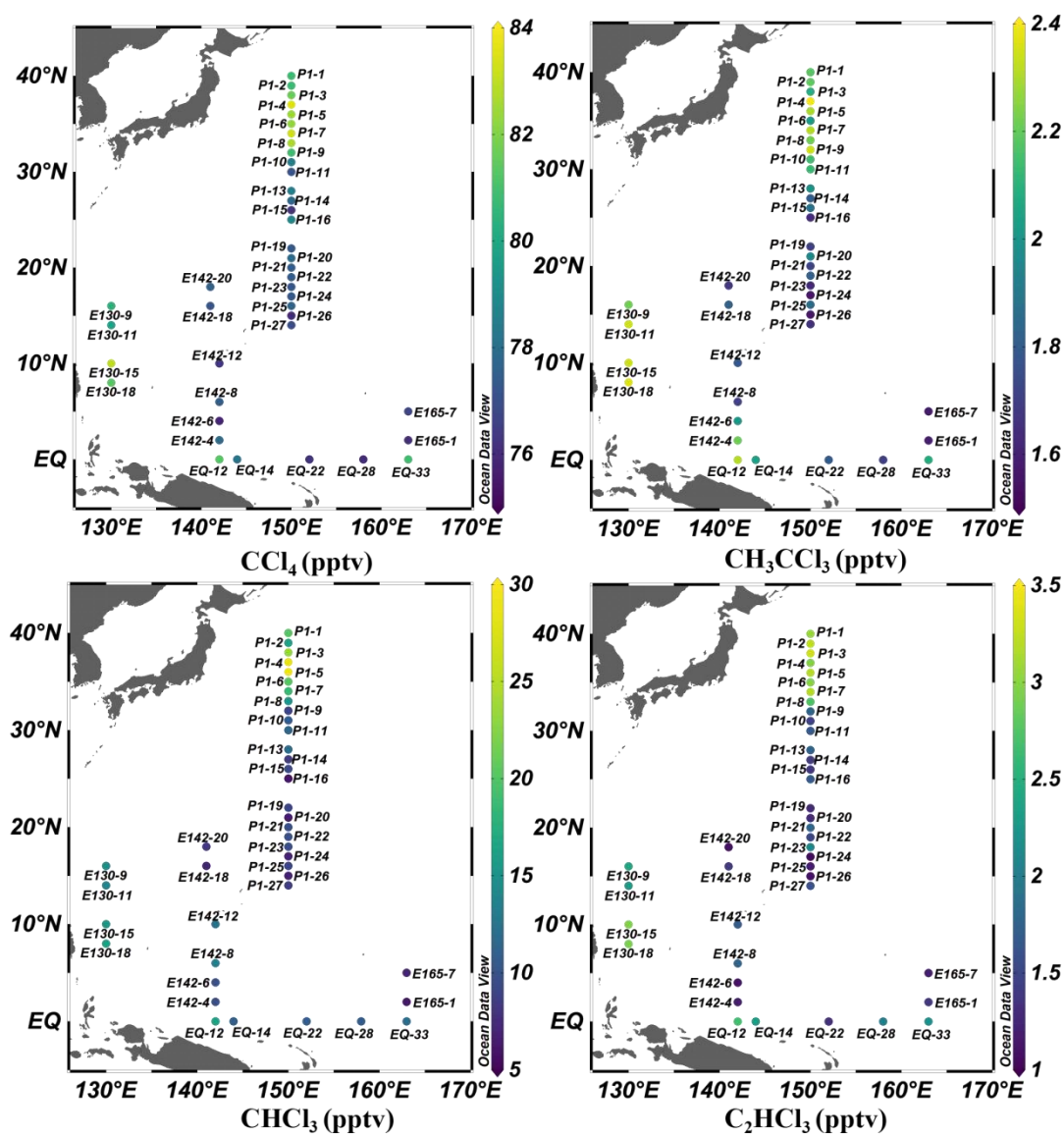


Fig. 3. Distributions of CHCl_3 , CCl_4 , C_2HCl_3 , and CH_3CCl_3 in the marine atmospheric boundary layer of the Western Pacific.

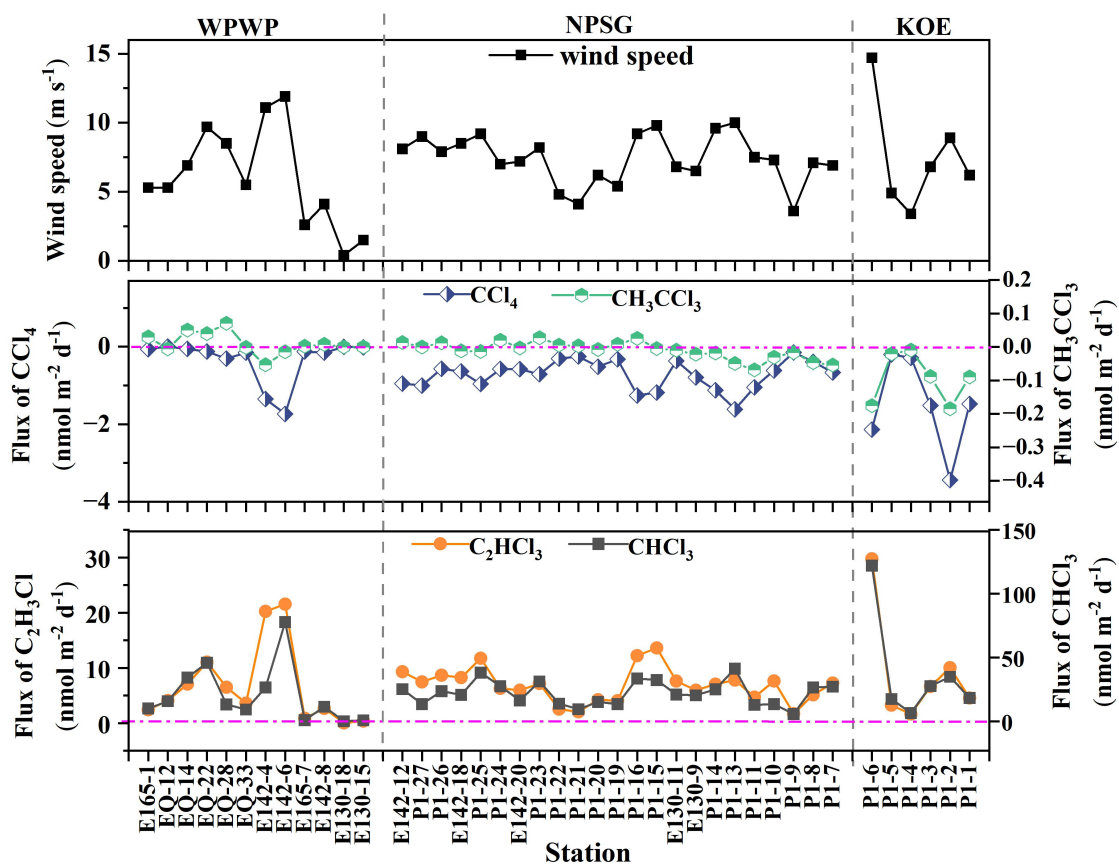


Fig. 5. Sea-air fluxes of CHCl_3 , CCl_4 , C_2HCl_3 , and CH_3CCl_3 , along with wind speeds in the Western Pacific.

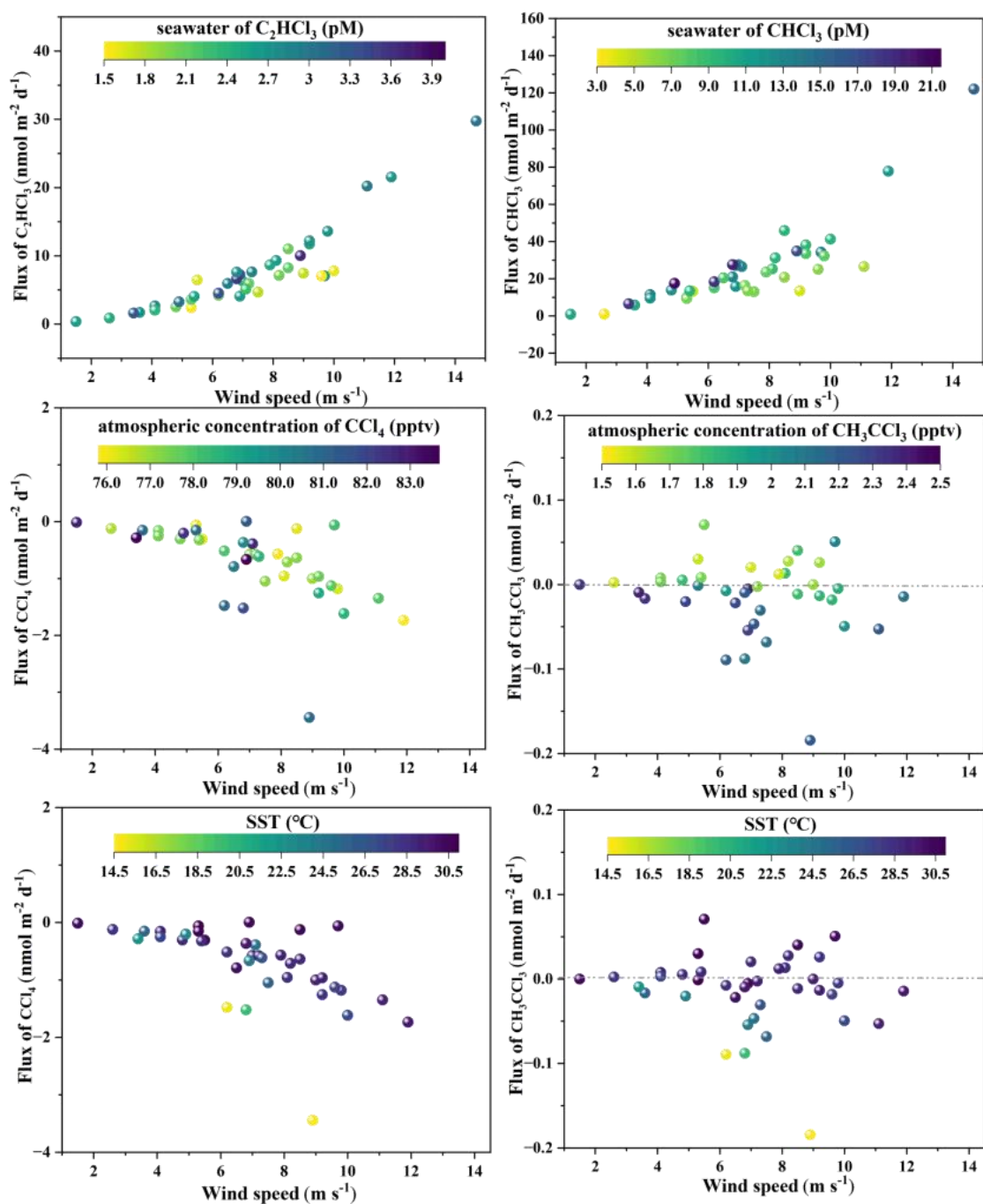


Fig. 6. Relationships between sea–air fluxes of VCHCs and wind speed, SST, and VCHCs concentrations in seawater and the atmosphere.

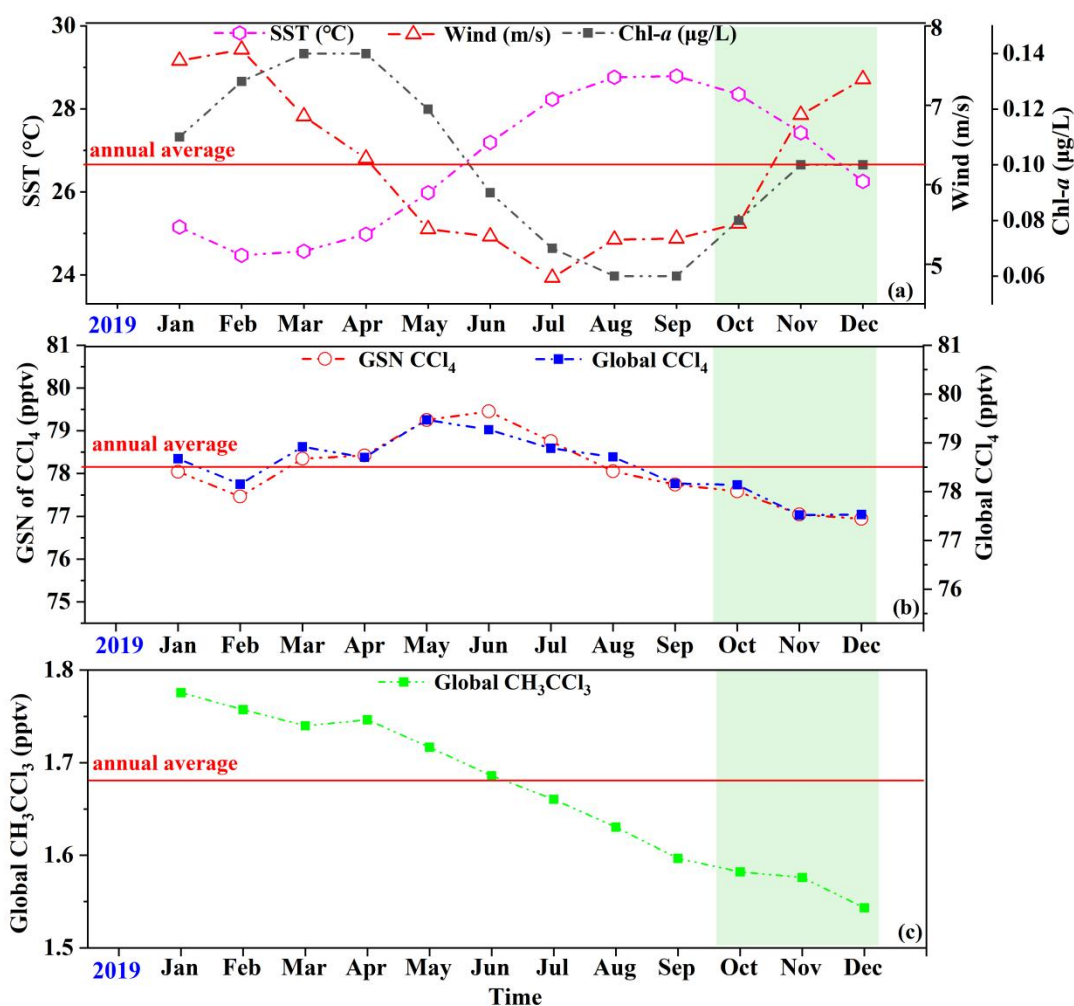


Fig. 7. (a) Interannual variations of wind speed, SST, and Chl-*a* concentration in the study area during 2019. (b) Interannual variability of CCl₄ at the GSN site in 2019 compared with the global mean. (c) Interannual variability of CH₃CCl₃ at the global scale in 2019. Wind speed data were obtained 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). Atmospheric CCl₄ and CH₃CCl₃ data were obtained from the AGAGE network (<https://agage.mit.edu/>). Shaded areas indicate the cruise sampling periods.

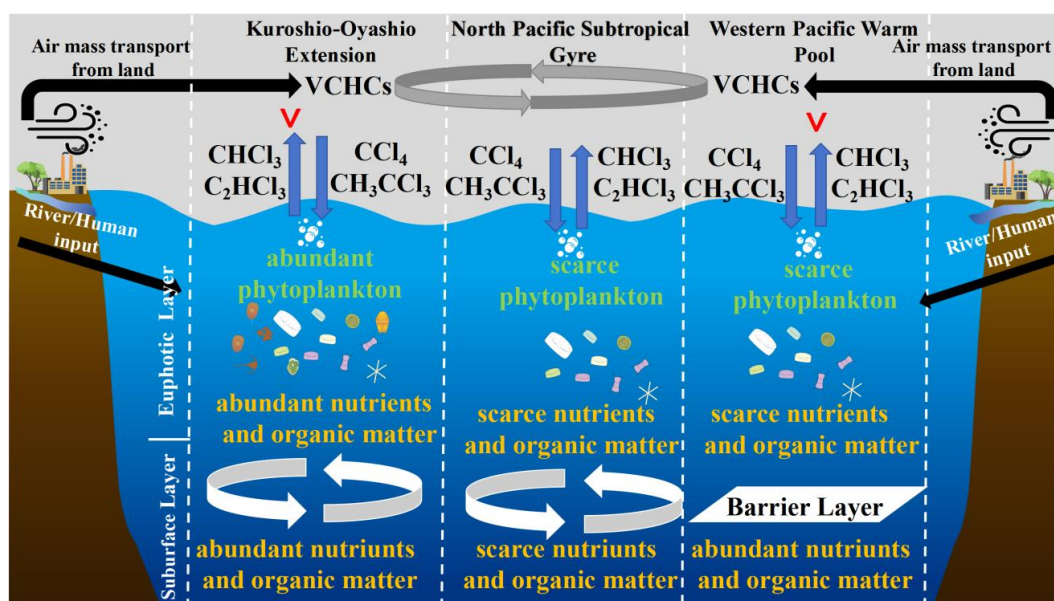


Fig. 8. Schematic diagram of key processes and factors controlling the production, distribution, and sea-air interactions of VCHCs in the Western Pacific.