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Discussions

# Natural marine bromoform emissions in the fully coupled ocean-atmosphere-model NorESM2

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**Abstract.** Oceanic bromoform ($CHBr_3$) is an important precursor of atmospheric bromine. Although highly relevant for the future halogen burden and ozone layer in the stratosphere, the global $CHBr_3$ production in the ocean and its emissions are still poorly constrained in observations and are mostly neglected in climate models. Here, we newly implement marine $CHBr_3$ in the state-of-the-art Norwegian Earth System Model (NorESM2) with fully coupled ocean-sea-ice-atmosphere biogeochemistry interactions. Our results are validated with oceanic and atmospheric observations from the HalOcAt (Halocarbons in the Ocean and Atmosphere) data base. The simulated mean oceanic concentrations (6.61±3.43 pmol L$^{-1}$) are in good agreement with observations in open ocean regions (5.02±4.50 pmol L$^{-1}$), while the mean atmospheric mixing ratios (0.76±0.39 ppt) are lower than observed but within the range of uncertainty (1.45±1.11 ppt). The NorESM2 ocean emissions of $CHBr_3$ (214 Gg yr$^{-1}$) are in the range of or higher than previously published estimates from bottom-up approaches but lower than estimates from top-down approaches. Annual mean emissions are mostly positive (sea-to-air), driven by oceanic concentrations, sea surface temperature and wind speed, dependent on season and location. During low-productivity winter seasons, model results imply some oceanic regions in high latitudes as sinks of atmospheric $CHBr_3$, because of its elevated atmospheric mixing ratios. We further demonstrate that key drivers for the oceanic and atmospheric $CHBr_3$ variability are spatially heterogeneous. In the tropical West Pacific, which is a hot spot for oceanic bromine delivery to the stratosphere, wind speed is the main driver for $CHBr_3$ emissions on annual basis. In the North Atlantic as well as in the Southern Ocean region the atmospheric and oceanic $CHBr_3$ variabilities are interacting during most of the seasons except for the winter months where sea surface temperature is the main driver. Our study provides improved process understanding of the biogeochemical cycling of $CHBr_3$ and more reliable natural emission estimates especially on seasonal and spatial scales compared to previously published model estimates.

## 1 Introduction

Bromoform ($CHBr_3$) from the ocean is the most important organic compound for atmospheric bromine with an atmospheric lifetime of ~2-4 weeks (Carpenter and Liss, 2000; Quack and Wallace, 2003; Salawitch, 2006; Papanastasiou et al., 2014). As a reactive halogenated compound, it belongs to the very short-lived substances (VSLS) with lifetimes of less than 6 months in the atmosphere (Law et al., 2007). In the tropics, VSLSs are rapidly lifted to the stratosphere by tropical deep convection (Sala et al., 2014; Navarro et al., 2015; Fuhlbrügge et al., 2016), where they contribute up to ~25% to stratospheric bromine (Dorf et al., 2006 and following work). Bromine is ~60 times more efficient in depleting lower stratospheric ozone than chlorine and significantly contributes to ozone depletion in the lower stratosphere (Daniel et al., 1999; Sinnhuber et al., 2009; Montzka et al., 2011; Villamayor et al., 2023) with potential impacts on the radiation budget of the atmosphere from -0.02 W m$^{-2}$ to -0.13 W m$^{-2}$ (Hossaini et al., 2015; Saiz-Lopez et al., 2023).

The oceanic air-sea gas exchange of $CHBr_3$ is parameterized based on the concentration gradient between surface water and air and is related to wind speed and sea surface temperature via the transfer velocity (e.g. Nightingale et al., 2000).

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Due to sparse measurements, marine $CHBr_3$ emission estimates are subject to large uncertainties (Laube et al., 2023). $CHBr_3$ emission inventories from “bottom-up” approaches (e.g. Quack and Wallace, 2003; Butler et al., 2007; Ziska et al., 2013; Lennartz et al., 2015; Stemmler et al., 2015; Fiehn et al., 2018) are based on in-situ oceanic data, whereas “top-down” approaches (e.g. Warwick et al., 2006; Liang et al., 2010; Ordóñez et al., 2012) use in situ atmospheric mixing ratio measurements. Resulting $CHBr_3$ emissions span a large range between 150 and 820 Gg Br $yr^{-1}$ (Laube et al., 2023). The different methods cover e.g., statistical extrapolation of measurement-based data (Ziska et al., 2013; and update in Fiehn et al., 2018), scaling of emissions to chlorophyll-a satellite observations (Ordóñez et al., 2012), modelling atmospheric $CHBr_3$ with a modular flux in a chemistry climate model (Lennartz et al., 2015), and a data-oriented machine-learning algorithm (Wang et al., 2019). These studies use limited spatial and temporal data coverage, underrepresenting seasonal and interannual variations and spatial heterogeneity by averaging concentrations.

Oceanic $CHBr_3$ is mainly linked to primary production through natural processes such as marine organisms like macroalgae and phytoplankton (Gschwend et al., 1985; Carpenter and Liss, 2000; Quack et al., 2004). Elevated surface water concentrations are observed in coastal and shelf waters especially including the eastern boundary upwelling systems (EBUS) (Quack and Wallace, 2003). Laboratory culture studies of phytoplankton production rates by Tokarczyk and Moore (1994) and Moore et al. (1996) reported $CHBr_3$ increase during the exponential growth phase of phytoplankton. Those specific growth rates and the corresponding temporal changes in $CHBr_3$ concentrations were first applied in a physical biogeochemical water column model for the tropical Atlantic (Hense and Quack, 2009), and later implemented in the global biogeochemical HAMburg Ocean Carbon Cycle model (HAMOCC; Stemmler et al., 2015). Stemmler et al. (2015) explicitly implemented sources and sinks of marine $CHBr_3$ in the three-dimensional ocean biogeochemistry model HAMOCC. However, they are not fully coupled with the atmosphere, and resulting emissions rely on fixed, prescribed, extrapolated, observed atmospheric data of Ziska et al. (2013). Since the atmospheric concentrations are regulated by the oceanic emissions, accurate estimates of atmospheric and oceanic $CHBr_3$ variability require such coupling, which can be achieved using an Earth System Model (ESM).

Here, we present the first global model simulation of $CHBr_3$ in the fully coupled Norwegian ESM (NorESM2), where $CHBr_3$ production is prognostically related to the primary production in the ocean taking natural biological processes into account. We present results from a historical experiment focusing on the period 1990 to 2014 and compare them with HalOcAt observations (https://halocat.geomar.de). Furthermore, we evaluate oceanic $CHBr_3$ excess and deficit regions and use multilinear regression analysis to identify drivers of oceanic and atmospheric $CHBr_3$, as wells as $CHBr_3$ emission variations on regional and temporal scales.

## 2 Model and Methods

We use the latest version of NorESM2 (NorESM2-LM; Seland et al., 2020; Tjiputra et al., 2020), which has participated in the Coupled Model Intercomparison Project phase 6 (CMIP6) and contributed to the latest assessment report of the IPCC-AR6 (Masson-Delmotte et al., 2023). The NorESM2 is a fully coupled ESM and is partly based on the Community ESM Version 2 (Danabasoglu et al., 2020), which is developed by the National Center for Atmospheric Research (NCAR) in the United States. NorESM2 is an updated version of its original version NorESM1 (Bentsen et al., 2013; Tjiputra et al., 2013). It consists of a modified version of the Community Atmosphere Model version 6 (CAM6-Nor), the isopycnic coordinate Bergen Layered Ocean Model (BLOM), the ocean biogeochemistry model isopycnic coordinate HAMOCC (iHAMOCC), the sea ice model (Community Ice CodE version 5.1.2; CICE5.1.2), the Community Land Model version 5 (CLM5), and the river runoff model (MOdel for Scale Adaptive River Transport; MOSART). Both BLOM and iHAMOCC apply a tripolar grid with a horizontal resolution of ~1° and 53 vertical isopycnic layers, while CAM6-Nor and CLM5 share a common horizontal resolution of ~2° and 32 hybrid-pressure layers (lowest atmospheric layer thickness: ~120 m) and a model top at 3.6 hPa (~40 km altitude). Here, we briefly highlight key features of iHAMOCC as well as the $CHBr_3$ implementation (Section 2.1). The iHAMOCC ocean biogeochemical module is based on the original work of Maier-Reimer (2012), has gone through several improvements and was later adapted to an isopycnic coordinate ocean model (Assmann et al., 2010; Tjiputra et al., 2010). The model prognostically simulates inorganic carbon chemistry following the standard Ocean Model Intercomparison Project (OMIP) protocol. It includes a Nutrient Phytoplankton Zooplankton Detritus (NPZD) type ecosystem module, where the phytoplankton growth rate is constrained by multi-nutrient limitation as well as ambient light and temperature. Particulate organic matters produced in the euphotic zone is exported to the interior with a sinking velocity that increases linearly with depth before it is remineralized back to inorganic carbon. The NorESM2 is able to simulate the observed large-scale pattern of surface primary productivity as well as the regional seasonal cycle (Tjiputra et al., 2020).

## 2.1 Bromoform module in NorESM2

### 2.1.1 Oceanic bromoform

The marine $CHBr_3$ processes implemented in iHAMOCC comprise of advection (*adv*), production ($\beta$), air-sea gas exchange ($F$), and three sink terms of: photolysis ($UV$), hydrolysis ($H$) and halogen substitution ($S$), as shown in Eq. (1). The production and photolysis occur in the euphotic layer (top 100 m depth) of the model, whereas the air-sea gas exchange is computed in the top-most layer of the ocean (upper 10 m). Advection and other sink terms are calculated throughout the water column. The change over time of the oceanic $CHBr_3$ concentration is modelled as:

$$\frac{[\mathrm{CHBr_3}]}{dt} = adv(\mathrm{CHBr_3}) + \beta - F - UV - H - S. \tag{1}$$

The parameterizations for the different processes are largely based on Stemmler et al. (2015). $CHBr_3$ is produced during biological production as follows:

$$\beta = \beta_0 * \left(\frac{f_1 * Si(OH)_4}{K_{phy}^{Si(OH)_4} + Si(OH)_4} + \frac{f_2 * K_{phy}^{Si(OH)_4}}{K_{phy}^{Si(OH)_4} + Si(OH)_4}\right), \tag{2}$$

where diatom and non-diatom contributing factors, $f_1$ and $f_2$, are set equally to 1. In contrast to Stemmler et al. (2015), the bulk $CHBr_3$ production ratio ($\beta_0$) is modified and set to $2.4 \times 10^{-6}$ nmol $CHBr_3$ (mmol N)$^{-1}$, based on Kurihara et al. (2012) and Roy (2010).

The air-sea gas exchange is calculated as follows:

$$F = k_w * \left(C_w - \frac{C_a}{H_{bromo}}\right), \tag{3}$$

where $C_w$ and $C_a$ are $CHBr_3$ concentrations in the surface ocean and $CHBr_3$ mixing ratios in the atmosphere, respectively. Positive emissions are defined as outgassing to the atmosphere. The temperature-dependent dimensionless Henry's law solubility constant ($H_{bromo}$) is defined in Moore et al. (1995):

$$H_{bromo} = e^{13.16 - \frac{4973}{SST}}, \tag{4}$$

with SST the sea-surface temperature in Kelvin. $k_w$ represents the gas transfer velocity calculated following Nightingale et al. (2000) using the 10 m surface wind speed ($u$):

$$k_w = (0.222u^2 + 0.33u) * \left(\frac{660}{Sc_{bromo}}\right)^{0.5}. \tag{5}$$

The Schmidt number ($Sc_{bromo}$) for $CHBr_3$ is defined in Quack and Wallace (2003) using the sea surface temperature *SST* in °C:

$$Sc_{bromo} = 4662.8 - 319.45 * SST + 9.9012 * SST^2 - 0.1159 * SST^3. \tag{6}$$

The loss term due to photolysis is computed as follows:

$$UV = I_{UV} * \frac{I_0}{I_{ref}} * e^{(-a_w * z)} * [\mathrm{CHBr_3}], \tag{7}$$

where the decay time scale $(I_{UV})^{-1}$ is set to 30 days (Carpenter and Liss, 2000). $I_0$ and $I_{ref}$ are the prognostic incoming UV radiation (i.e., 30% of shortwave radiation) and annual average irradiance at the surface layer, respectively. $z$ is the depth and $a_w$ is the attenuation coefficient of UV radiation, set to 0.33 $m^{-1}$.

The loss term related to hydrolysis is estimated following Stemmler et al. (2015):

$$H = A_1 * e^{\left(-\frac{E_A}{RT}\right)} * [\mathrm{OH^-}] * [\mathrm{CHBr_3}], \tag{8}$$

with $A_1$, $E_A$, and $R$ set to $1.23 \times 10^{17}$ L $mol^{-1}$ $min^{-1}$, 107 300 J $mol^{-1}$, and 8.314 J $K^{-1}$ $mol^{-1}$, respectively (Washington, 1995). $T$ is the seawater temperature in Kelvin.

Degradation due to halogen substitution (Eq. 5-6 of Stemmler et al., 2015):

$$S = L_{ref} * e^{\left(A_2 * (\frac{1}{T_{ref}} - \frac{1}{T})\right)} * [\mathrm{CHBr_3}], \tag{9}$$

with $L_{ref}$ and $A_2$ set to $7.33 \times 10^{-10}$ $s^{-1}$ and 12507.13 K, respectively, and $T_{ref}$ = 298 K.

### 2.1.2 Atmospheric $CHBr_3$

$CHBr_3$ is implemented as a 3-dimensional tracer in the atmospheric model and is transported by the large-scale atmospheric circulation and sub-grid scale processes (shallow and deep convection, and boundary layer turbulence). It is removed in the atmosphere by photolysis:

$$\mathrm{CHBr_3} + hv \rightarrow 3\,Br\,, \tag{10}$$

and by reaction with the OH radical:

$$\mathrm{CHBr_3} + \mathrm{OH} \rightarrow 3\,Br\,. \tag{11}$$

The reaction rate $k$ [$cm^3$ $molecules^{-1}$ $s^{-1}$] for the removal of $CHBr_3$ by OH in

$$\frac{d[\mathrm{CHBr_3}]}{dt} = -k * [\mathrm{CHBr_3}] * [\mathrm{OH}] \tag{12}$$

is defined as follows:

$$k = 9.0 * 10^{-13} \exp\left(-\frac{360}{T}\right), \tag{13}$$

with $T$ the ambient temperature in Kelvin, and $[\mathrm{CHBr_3}]$ and $[\mathrm{OH}]$ in molecules $\mathrm{cm^{-3}}$. The loss rate of $\mathrm{CHBr_3}$ by photolysis can be expressed by

$$\frac{d[\mathrm{CHBr_3}]}{dt} = -I\,[\mathrm{CHBr_3}], \tag{14}$$

where $I$ [$\mathrm{s^{-1}}$] depends on the intensity of solar radiation and photo-physical properties of $\mathrm{CHBr_3}$. The OH concentration is a monthly-varying climatology obtained from a Whole Atmosphere Community Climate Model (WACCM) historical simulation with full tropospheric and stratospheric chemistry (Gettelman et al., 2019).

$\mathrm{CHBr_3}$ in the atmosphere has no other sinks than reaction with OH (annual mean $\mathrm{CHBr_3}$ lifetime: ~46 days) and photolysis ($\mathrm{CHBr_3}$ lifetime: ~23 days) and is not affected by dry or wet deposition.

## 2.2 Model setup

A historical transient model run from 1850-2014, based on the CMIP6 protocol, was performed following a 500-year preindustrial spin-up. The coupling of $\mathrm{CHBr_3}$ between the ocean and the atmosphere is carried out with an hourly time frequency exchanging the air-sea gas transfer. For analysis of the model climatology as well as for analysis of the model validation with observations and further analysis of the driving $\mathrm{CHBr_3}$ factors, daily model output data was averaged over a period of 25 years (1990-2014) resulting in one mean value for each day of the year. The standard deviation of each day reflects the variability within this time period. The 1990 to 2014 interval was chosen as most of the observations for the model validation are within that time period, as compiled in the HalOcAt database (https://halocat.geomar.de, last access: 13.10.2023).

## 2.3 Observations: HalOcAt database

The HalOcAt database, compiled by Ziska et al. (2013), updated by Fiehn et al. (2018) and by this study, is an observation-based database for global oceanic and atmospheric data of short-lived halogenated compounds, such as $\mathrm{CHBr_3}$. To date, there are 9369 oceanic and 65179 atmospheric $\mathrm{CHBr_3}$ measurements listed in 68 oceanic and 156 atmospheric datasets (campaigns), respectively. The following criteria were applied to the observations in order to be used for model validation:

- Sampling locations with an ocean bottom depth less than 200 m or closer than 100 km to land were excluded.
- Sampling depth of oceanic $\mathrm{CHBr_3}$ measurements had to be within the first 10 m of the water column in order to be comparable to the $\mathrm{CHBr_3}$ output of the upper surface ocean model layer (10 m depth).
- Maximum sampling height of atmospheric $\mathrm{CHBr_3}$ measurements was set to 30 m altitude.
- Wherever applicable, individual measurements throughout one day were averaged to result in a daily averaged surface ocean concentration or atmospheric mixing ratio in order to consider the same temporal resolution as the daily model output. The coordinates of the respective averaged data points throughout a day were also equally averaged. These locations were used to compare the observation with the closest grid point of the model output.

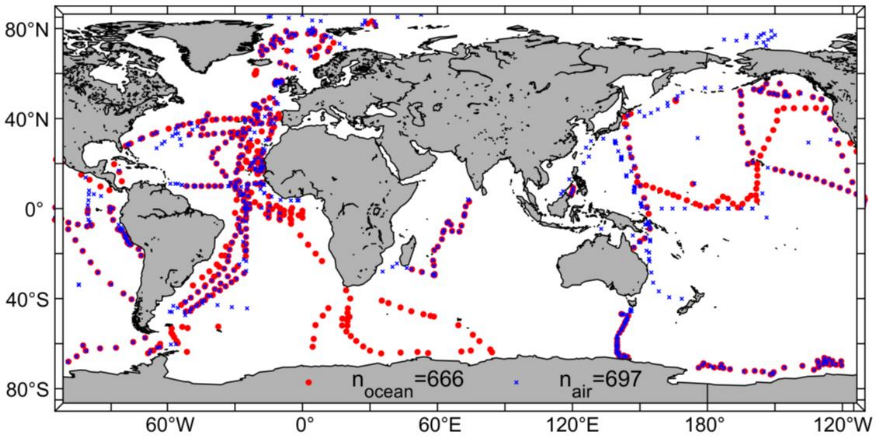

**Figure 1: Locations of oceanic (red, n=666) and atmospheric (blue, n=697) daily mean $CHBr_3$ observations from the HalOcAt database used to compare to daily mean NorESM2 model output.**

After screening the HalOcAt data base with the above-mentioned criteria, the individual oceanic and atmospheric datasets (including the remaining datapoints) were tested for outliers. The mean from each dataset was calculated and the group of all average values was tested for outliers. An outlier was defined as an element with more than three standard deviations from the mean. According to the outlier test for oceanic and atmospheric datasets the corresponding dataset was removed and not used for further validation of the model.

By addressing the mentioned criteria and datasets, we were able to validate the model with 666 daily mean oceanic (5154 individual) and 697 daily mean atmospheric (8411 individual) $CHBr_3$ observations from the HalOcAt database covering both hemispheres (northern hemisphere (NH): 61%, southern hemisphere (SH): 39%), from the tropics (0-20°N/°S; 36%) to the polar regions (60-90°N/S; 18%) with most observations in or above the Atlantic Ocean (44%) (Figure 1).

### 2.4 Bromoform excess/deficit calculation

The $CHBr_3$ excess/deficit (balance) rate ($k_{bal}$, Eq. (15), pmol $m^{-2}$ $h^{-1}$) is the difference between the $CHBr_3$ production rate and the sum of different $CHBr_3$ loss rates, with all rates integrated over the upper 100 m depth):

$$k_{bal} = \sum production\ rate - \sum loss\ rate = k_\beta - (k_{UV} + k_F). \qquad (15)$$

The production term is described as the biological oceanic $CHBr_3$ production rate ($k_\beta$, Eq. (2)) and the loss term includes the two fastest loss processes, i.e., photolysis due to UV radiation ($k_{UV}$, Eq. (7)) and the loss to the atmosphere via air-sea gas exchange ($k_F$, Eq. (3)). We define a positive $k_{bal}$ as $CHBr_3$ excess rate and a negative $k_{bal}$ as $CHBr_3$ deficit rate. The loss terms related to hydrolysis and to halogen substitution are not included as they are several orders of magnitude smaller than $k_{UV}$ and $k_F$, in the surface ocean.

### 2.5 Bromoform driving factor calculation

Different parameters impact the variations of oceanic and atmospheric $CHBr_3$ values and influence the air-sea gas exchange. These impacts can vary in magnitude and frequency dependent on local and seasonal conditions. Daily mean average model output values from 1990-2014 were used to calculate annual and seasonally resolved (DJF, MAM, JJA, SON) driving factors for oceanic $CHBr_3$ concentrations ($Bromo_{oce}$), atmospheric $CHBr_3$ mixing ratios ($Bromo_{air}$) and $CHBr_3$ emissions ($Bromo_{flux}$) in three different specific areas (North Atlantic, tropical West Pacific, Southern Ocean), which are presented in Section 3.4. Driving factors for each area, parameter and season were derived using multilinear regression (MLR) analyses.

In order to compare parameters with different magnitudes, input data of each parameter was standardized prior to MLR analysis by centering to have a mean of 0 and scaled to have a standard deviation of 1. Input data for each parameter consisted of daily mean averages over the specific area, providing 365 values as basis for annually and ~ 90 values for seasonally resolved MLR. Equations for MLR calculations were as follows with coefficients *a, b, c, d, e, f,* $CHBr_3$ production ($Bromo_{prod}$), $Bromo_{oce}$, $Bromo_{air}$ and $Bromo_{flux}$, as well as the 10 m surface wind speed (*wind*) and sea surface temperature (*SST*):

$$Bromo_{oce} = a * SST + b * wind + c * Bromo_{prod} + d * Bromo_{flux} + e * Bromo_{air} + f \tag{16}$$

$$Bromo_{flux} = a * SST + b * wind + c * Bromo_{prod} + d * Bromo_{oce} + e * Bromo_{air} + f \tag{17}$$

$$Bromo_{air} = a * SST + b * wind + c * Bromo_{prod} + d * Bromo_{flux} + e * Bromo_{oce} + f \tag{18}$$

Other oceanic $CHBr_3$ loss processes (e.g. photolysis) were neglected in these calculations as the loss due to gas exchange is ~70 times higher than the loss due to photolysis (data not shown). If the highest resulting coefficient for each season and MLR is significantly higher than all other coefficients, the corresponding parameter is presented as the main driver for either $Bromo_{oce}$, $Bromo_{air}$ or $Bromo_{flux}$. If the highest resulting coefficient is not significantly different from the second or third highest coefficient, more than one coefficient and corresponding parameters are presented as main drivers. Table 1 lists the annual mean coefficients, Table S1 lists the seasonally resolved main drivers.

## 3 Results and Discussion

### 3.1 Model climatology

The annual and seasonal $CHBr_3$ oceanic concentrations, atmospheric mixing ratios and emissions reveal significant spatial variations (Figure 2). The annual global average surface $CHBr_3$ concentrations are 5.04 pmol $L^{-1}$ (DJF: 5.36 pmol $L^{-1}$, JJA: 4.86 pmol $L^{-1}$) with highest annual mean concentrations of 28.37 pmol $L^{-1}$ in the upwelling region off the coast of Peru and lowest annual mean concentrations of 1.37 pmol $L^{-1}$ in the Gulf of Boothia (71°N, 91°W) north of Canada. The areas with the lowest oceanic $CHBr_3$ concentrations are the central parts of the North and the South Pacific Gyres. Concentrations of surface ocean $CHBr_3$ in the entire NH (JJA: 5.9 pmol $L^{-1}$ > DJF: 4.3 pmol $L^{-1}$) and SH (DJF: 6.1 pmol $L^{-1}$ > JJA: 4.1 pmol $L^{-1}$) are generally higher during the respective summer than during the respective winter season. These distinct differences of oceanic $CHBr_3$ concentrations are also due to the higher biological production in summer (NH: 335 pmol $m^{-2}$ $h^{-1}$; SH: 371 pmol $m^{-2}$ $h^{-1}$) than in winter (NH: 235 pmol $m^{-2}$ $h^{-1}$; SH: 173 pmol $m^{-2}$ $h^{-1}$) as shown in Fig. S3. The direct link of $CHBr_3$ to the biological production applies to the low oceanic $CHBr_3$ concentrations in the North and South Pacific Gyres and to the high oceanic concentrations in the areas of the EBUS.

Variations in annual mean atmospheric $CHBr_3$ mixing ratios mainly follow the surface ocean concentrations with highest mixing ratios in the tropics, especially in the EBUS. Global annual average mixing ratios over the ocean are 0.67 ppt (DJF: 0.70 ppt, JJA: 0.69 ppt) with highest annual mean mixing ratios of 2.21 ppt in the south-eastern Pacific upwelling region off the coast of Peru and lowest annual mean mixing ratios of 0.13 ppt over the Persian Gulf. On a global average, the variability of atmospheric mixing ratios is lower than the variability of $CHBr_3$ concentrations in the surface ocean (Figure 2). During austral winter (JJA), mostly dark and cold conditions increase the lifetime of atmospheric $CHBr_3$, which leads to a uniform mixing ratio (0.67±0.05 ppt) over the entire Southern Ocean. Similar to oceanic $CHBr_3$

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concentrations, central parts of the North and South Pacific Gyre have low atmospheric $CHBr_3$ mixing ratios (0.46±0.05 ppt). During austral summer (DJF) atmospheric mixing ratios increase further as strong biological activity increases surface ocean concentrations, which enhance the oceanic emissions.

Generally, supersaturation of $CHBr_3$ in the world's ocean leads to emissions from the ocean to the atmosphere (defined as positive). Global annual mean emissions are 268 pmol $m^{-2}$ $h^{-1}$ (DJF: 294 pmol $m^{-2}$ $h^{-1}$, JJA: 253 pmol $m^{-2}$ $h^{-1}$) with highest annual mean emissions of 953 pmol $m^{-2}$ $h^{-1}$ in the upwelling region off the coast of Peru. In the tropical regions, annual mean emissions of 427 pmol $m^{-2}$ $h^{-1}$ between 10°N and 10°S, add to atmospheric entrainment of oceanic $CHBr_3$ up into the stratosphere (Fiehn et al., 2018; Tegtmeier et al., 2020). Lowest annual mean emissions of -1 pmol $m^{-2}$ $h^{-1}$ are modelled under ice free conditions in the Gulf of Boothia (71°N, 91°W) north of Canada (white regions in Figure 2) with very low oceanic $CHBr_3$ production and low seawater temperatures. However, the atmospheric mixing ratios are comparably high under these conditions. These conditions favour negative emissions, which, according to the results of our fully coupled ESM, can be seen in the Arctic and Antarctic during winter season, confirming the results by Stemmler et al. (2015) and Ziska et al. (2013) although with a lower amount.

Generally, the modelled $CHBr_3$ emissions are high, where the ocean concentration is high and the elevated emissions lead to elevated atmospheric mixing ratios. However, due to oceanic transport processes, locations of high oceanic $CHBr_3$ emissions do not always coincide with locations of high oceanic $CHBr_3$ production (compare Figure 2 and Fig. S3). In the northern part of the Bay of Bengal (>18°N) e.g., ocean concentrations during DJF are very high (average: 21.64 pmol $L^{-1}$), while the emissions are not as high compared to other ocean regions, due to low wind speeds. This leads to a lower atmospheric mixing ratio than expected from the oceanic concentrations and shows that oceanic $CHBr_3$ concentrations and emissions as well as atmospheric mixing ratios show regionally different interdependencies, which is addressed in detail in Section 3.4.

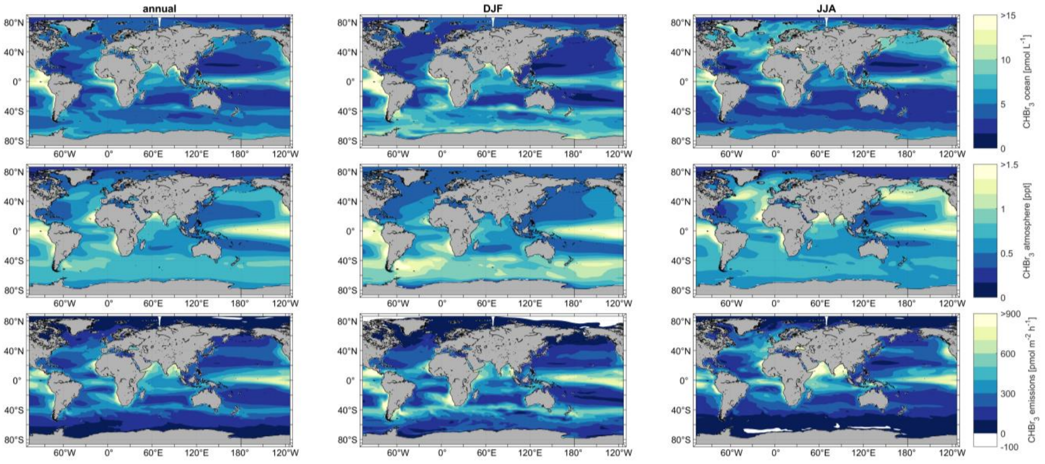

**Figure 2: Simulated annual (left), DJF (middle) and JJA (right) mean oceanic surface $CHBr_3$ concentrations (upper panel), atmospheric mixing ratios (middle panel) and $CHBr_3$ emissions (lower panel) for the period 1990-2014.**

## 3.2 Model validation with observations

The annual median surface oceanic $CHBr_3$ concentration (Figure 3a) from the 666 daily mean observations is 3.65 pmol $L^{-1}$ with a 25th and 75th percentile of 2.19 and 6.16 pmol $L^{-1}$, respectively (min: 0.05 pmol $L^{-1}$, max: 28.21 pmol $L^{-1}$, mean: 5.02 pmol $L^{-1}$). The global annual median surface oceanic $CHBr_3$ concentration from the model using only locations corresponding with an existing observation is 6.00 pmol $L^{-1}$ with a 25th and 75th percentile of 4.23 and 8.10 pmol $L^{-1}$, respectively (min: 1.39 pmol L$^{-1}$, max: 24.25 pmol L$^{-1}$, mean: 6.61 pmol L$^{-1}$). These results indicate that the model values are in the range with observed concentrations of oceanic $CHBr_3$. While the median concentration of the model is higher than the median of the observations, all validated model data points fall within the full range of the observations. The model data cover a grid of ~100 km resolution, which leads to a smoothing of the values, whereas observational data is local daily mean point data.

The median $CHBr_3$ atmospheric mixing ratio (Figure 3b) from the 697 daily mean observations is 1.17 ppt with a 25th and 75th percentile of 0.78 and 1.71 ppt, respectively (min: 0.03 ppt, max: 9.80 ppt). The global median atmospheric mixing ratio of $CHBr_3$ from the model at locations with observations is 0.69 ppt with a 25th and 75th percentile of 0.49 and 0.90 ppt, respectively (min: 0.22 ppt, max: 2.70 ppt). This comparison shows that the observed atmospheric mixing ratios of $CHBr_3$ are in the same magnitude but generally higher than those from the model output. While our model experiment focuses on natural $CHBr_3$ production by phytoplankton, other sources as coastal macroalgae (Carpenter and Liss, 2000) and anthropogenic sources, such as power plant cooling (Maas et al., 2021) or desalination plants (Agus et al., 2009), may explain parts of the higher global annual median observational data of 41%. Jia et al. (2023) calculated an increase of global $CHBr_3$ emissions of 31.5% when including anthropogenic emissions, which partly explains also the lower observed atmospheric mixing ratios in the model compared to the observations.

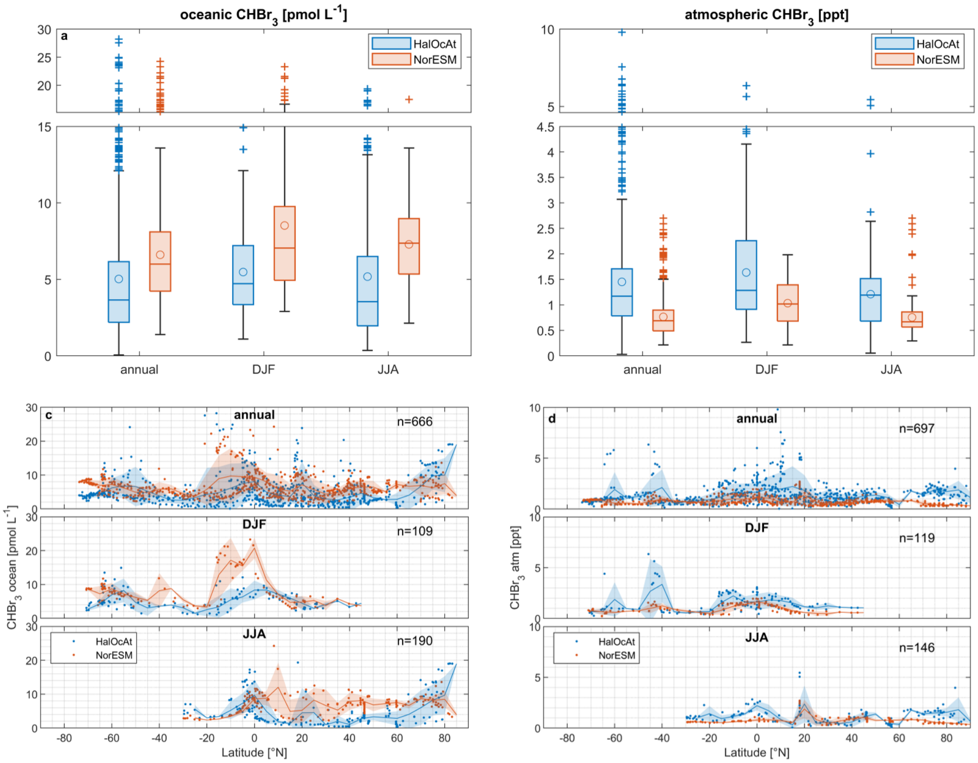

**Figure 3: Boxplot comparison of NorESM2 model results with HalOcAt observations for oceanic (a) and atmospheric $CHBr_3$ (b), c: zonal mean oceanic $CHBr_3$ comparison annually and in DJF and JJA, d: zonal mean atmospheric $CHBr_3$ comparison annually and in DJF and JJA. Shaded areas are standard deviations from 5° zonal bin averages. Boxplots (left) have a break in the y axis to increase readability of the figure. The line inside the box represents the median value, the circle the mean value, the boxes show the first to third quartile, and the whiskers illustrate the highest and lowest values that are not outliers. The plus signs represent outliers.**

Figure 3 also shows a more detailed comparison between observations and model data in 5° meridional binned averages (shaded areas) for oceanic (Figure 3c) and atmospheric (Figure 3d) $CHBr_3$ on annual basis as well as in JJA and DJF. The modelled data compare well with observations of oceanic $CHBr_3$ (Figure 3c) on annual basis over the 5° latitudinal bins. In the HalOcAt database, there are no oceanic and atmospheric observations available north of 50°N and south of 30°S during boreal (DJF) and austral winter (JJA), respectively, which highlights the need of model data to entirely describe spatially and temporally resolved $CHBr_3$ (see also Fiehn et al., 2018). During DJF, the model overestimates the measured concentrations between 20°N and 5°S. During JJA, averaged model concentrations in the NH (10°N – 60°N) are slightly higher than the averaged observations. These discrepancies could indicate a missing process understanding, revealing lower oceanic production or additional loss processes.

With all data available, the 5° latitudinal averaged atmospheric $CHBr_3$ observations have a large spread in the tropics resulting in a high standard deviation (Figure 3d). The model results in this region are uniform with a much lower standard deviation. During boreal winter (DJF) atmospheric $CHBr_3$ observations and model results show a good agreement, with an exception at 40-50°S. In this latitude range, observational atmospheric $CHBr_3$ mixing ratios (>3 ppt, Figure 3d) were recorded between 24° and 60° W in the South Atlantic in 2007 (Gebhardt, 2008). Gebhardt (2008) reports enhanced biological production in the Argentinian shelf-break zone (55°-60° W) with elevated chlorophyll-*a* concentration up to 4.5 µg $L^{-1}$. These values suggest also a high production of $CHBr_3$ and subsequent high emissions to the atmosphere. The prevailing westerly winds, transported the $CHBr_3$ enriched air masses eastward to the remote South Atlantic region in 2007, while in the model lower biological production entails lower atmospheric mixing ratios compared to the observations. During boreal summer (JJA) very good agreement between atmospheric observations and model results is obtained between 10°N and 60°N. North of 60°N, the model underestimates the measured atmospheric mixing ratios in the polar region. Local meteorological and biological conditions (e.g. high wind speed, distinct phytoplankton blooms) are averaged by the model to a resolution of ~100 km. Averaging data over time or space leads to lower values (e.g. gas emissions, Bates and Merlivat, 2001), which explains lower modelled atmospheric mixing ratios compared to the observations. These local and short term temporal variations contribute to the discrepancy in atmospheric values at global scale as well as potential anthropogenic $CHBr_3$ emissions (Jia et al., 2023). Furthermore, discrepancies between model results and observations also point to missing process understanding, which helps to improve our understanding of the biogeochemical cycling of $CHBr_3$.

### 3.3 Excess and deficit regions of oceanic bromoform

In most of the world's surface oceans $CHBr_3$ production and loss rates are balanced on an annual average with a $k_{bal}$ close to zero (e.g. North and South Pacific, top panel of Figure 4). The equator region experiences a strong excess rate (positive $k_{bal}$) on annual average with values up to 300 pmol $m^{-2}$ $h^{-1}$ showing higher $CHBr_3$ production than loss of $CHBr_3$ in the upper ocean, caused by strong primary production (Fig. S3) in the equatorial upwelling. Surface currents transport the $CHBr_3$ enriched surface water masses away from the equator, while experiencing loss of $CHBr_3$ to the atmosphere. Therefore, adjacent marine areas north and south of the equator experience a deficit rate (negative $k_{bal}$) of $CHBr_3$ (blue areas, Figure 4), as no production balances the loss. The seasonality of $k_{bal}$ is pronounced in the extratropics (bottom panels of Figure 4). In these regions, a $CHBr_3$ excess rate is observed mainly during summer and a $CHBr_3$ deficit rate mainly during winter in the respective hemispheres. A high $k_\beta$ (elevated biological production) and a low $k_F$ (weak emissions to the atmosphere) caused by lower winds during summer, lead to a higher $CHBr_3$ surface ocean concentration in summer compared to winter time (Figure 2). During winter in both hemispheres, lower biological activity (low $k_\beta$) and elevated wind speed (high $k_F$) decrease the $CHBr_3$ production and increase the emissions to the atmosphere, which leads to a $CHBr_3$ deficit rate. These results reveal seasonal as well as spatial differences in parameters (driving factors), which influence $CHBr_3$ concentrations in the world's ocean.

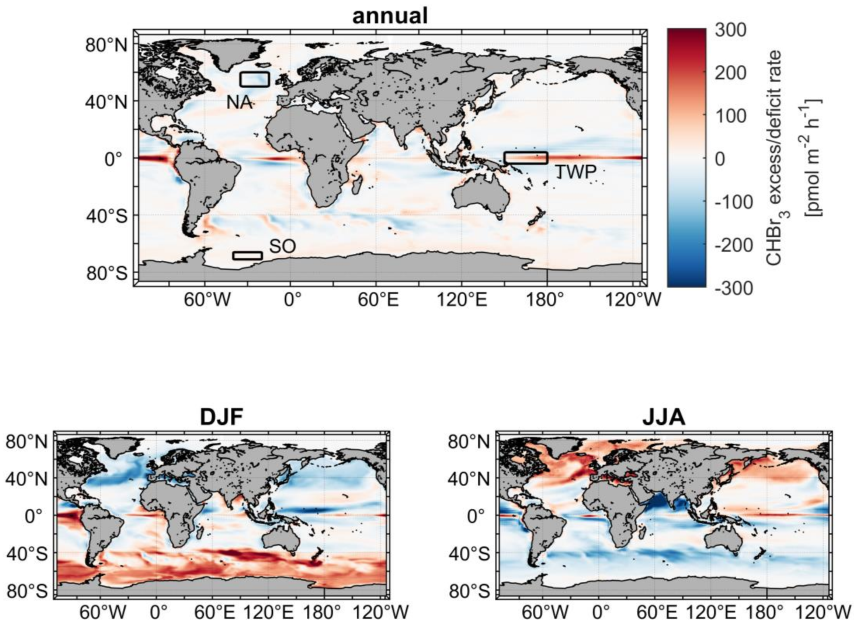

**Figure 4: Mean $CHBr_3$ excess/deficit rates on annual (top) and seasonal (DJF: bottom left; JJA: bottom right) basis. Three rectangles in the top figure illustrate locations of case studies. NA: North Atlantic; TWP: Tropical West Pacific; SO: Southern Ocean.**

In the following subsection, we selected three different case study areas, indicated in Figure 4, in order to contrast the driving factors of the variations of oceanic and atmospheric $CHBr_3$ on regional and temporal scales:

- North Atlantic, with an annual mean $CHBr_3$ deficit rate ($k_{bal}$ = -33 pmol $m^{-2}$ $h^{-1}$)
- Tropical West Pacific, with an annual mean $CHBr_3$ excess rate ($k_{bal}$ = +32 pmol $m^{-2}$ $h^{-1}$)
- Southern Ocean, with negative emissions during the respective winter season ($k_{bal}$ = +15 pmol $m^{-2}$ $h^{-1}$)

### 3.4 Driving factors of bromoform on regional and temporal scales

This section investigates the seasonal changes of oceanic and atmospheric $CHBr_3$ and other parameters in three contrasting regions. Daily means of oceanic $CHBr_3$ concentrations, production, emissions, balance (as defined in Eq. (15)), atmospheric mixing ratios as well as SST and wind speed, in the North Atlantic, tropical West Pacific and Southern Ocean over an entire year reveal large differences between the regions (Figure 5). With MLR analysis, the main driving factors of oceanic and atmospheric $CHBr_3$ variability and its emissions in each region and season are investigated.

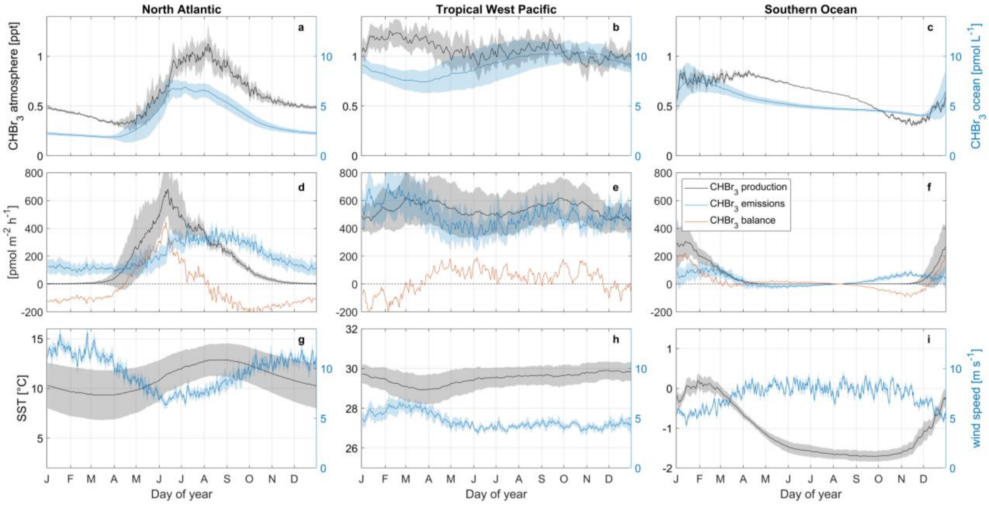

**Figure 5: Seasonal changes of oceanic and atmospheric $\mathrm{CHBr_3}$ (upper panel, a-c), $\mathrm{CHBr_3}$ production, emissions and balance (middle panel, d-f), SST and wind speed (bottom panel, g-i), in the North Atlantic (left), tropical west Pacific (middle) and Southern Ocean (right). Shaded area is one standard deviation of the average value in the corresponding area. Note: y-limits for SST are not similar in between the three regions in order to increase readability of the figure.**

**North Atlantic**

The North Atlantic region (50°N – 60°N, 15°W – 35°W) is characterized by a strong seasonal cycle of both oceanic $\mathrm{CHBr_3}$ concentrations and atmospheric mixing ratios (Figure 5a). The magnitude of the cycle is strongest among the three investigated regions in this study (compare with Figure 5b,c). Oceanic $\mathrm{CHBr_3}$ concentrations are on average 3.64 pmol L$^{-1}$ with a minimum concentration of 1.87 pmol L$^{-1}$ during end of March and a maximum concentration of 6.93 pmol L$^{-1}$ during July. Atmospheric mixing ratios show a similar seasonal cycle, shifted by one month, with average values of 0.60 ppt, a minimum mixing ratio of 0.30 ppt during April and a maximum mixing ratio of 1.12 ppt during August. Figure 5d shows, that the $\mathrm{CHBr_3}$ emissions (199±91 pmol m$^{-2}$ h$^{-1}$) follow the pattern of both oceanic and atmospheric values. The seasonal cycle of $\mathrm{CHBr_3}$ production (171±191 pmol m$^{-2}$ h$^{-1}$) is similar to the cycle of $\mathrm{CHBr_3}$ concentration, while the sharp peak in May/June when the spring phytoplankton bloom evolves in the North Atlantic, is not reflected in the oceanic concentrations. The strong seasonality in $\mathrm{CHBr_3}$ production leads to a $\mathrm{CHBr_3}$ excess rate during summer (JJA: 103 pmol m$^{-2}$ h$^{-1}$) and a $\mathrm{CHBr_3}$ deficit rate in winter time (DJF: -114 pmol m$^{-2}$ h$^{-1}$), respectively (Figure 5d).

The MLR analysis indicates, that on an annual basis, variations in atmospheric mixing ratios are mainly associated with $\mathrm{CHBr_3}$ ocean concentrations (Table 1, $R^2$=0.89, p-value<0.05) and vice versa (Figure 6a,d). A higher surface water $\mathrm{CHBr_3}$ concentration increases the emissions to the atmosphere resulting in increasing atmospheric mixing ratios. According to the MLR analysis on a seasonal basis, oceanic $\mathrm{CHBr_3}$ concentrations are mainly driven by the oceanic production during MAM ($R^2$=0.93, p-value<0.05) and SON ($R^2$=0.99, p-value<0.05) (Table S1), which increases from March to June sharply to 680 pmol m$^{-2}$ h$^{-1}$ before gradually decreasing in SON (Figure 5d). Annually, atmospheric mixing ratios are mainly driven by the oceanic concentration (Figure 6d, Table 1, $R^2$=0.89, p-value<0.05). This is also true on a seasonal basis except for the winter (DJF) season, where SST is the main (indirect) factor influencing the atmospheric mixing ratio variations (Table S1, $R^2$=0.95, p-value<0.05), as lower SSTs increase the solubility of $\mathrm{CHBr_3}$ and hardly any oceanic $\mathrm{CHBr_3}$ production occurs. Thus, the emissions of $\mathrm{CHBr_3}$ decrease, even during comparably high wind speeds, which leads to a decreasing atmospheric mixing ratio. $\mathrm{CHBr_3}$ emissions are mainly driven by oceanic concentrations on an annual basis (Figure 6g, Table 1, $R^2=0.81$, p-value<0.05). The MLR results further indicate that the driving factors are highly variable, when looking on a seasonal basis. During spring (MAM), wind speed, SST, and $CHBr_3$ production are almost equally driving the emissions (Table S1). During this season, $CHBr_3$ emissions are pretty constant at 130±29 pmol $m^{-2}$ $h^{-1}$ (Figure 5d). $CHBr_3$ production and SSTs slightly increase in spring, and an increase of the emissions to the atmosphere is expected. However, emissions stay constant as surface wind speed decreases and lower the emissions. This regional and seasonal pattern explicitly illustrates the interaction of different conditions influencing the $CHBr_3$ emissions. During summer (JJA), low winds and a high oceanic $CHBr_3$ concentration equally influence the increasing emissions (Table S1). In contrast to spring, higher SSTs (lower solubility) are only of minor importance during JJA. In autumn and winter, decreasing emissions are mainly driven by decreasing SSTs and, in DJF, additionally by high atmospheric mixing ratios (in comparison to oceanic concentrations), which additionally dampens the emissions (Table S1).

### Tropical West Pacific

Figure 4 shows that the equatorial regions of the Atlantic and Pacific Oceans generally have positive $k_{bal}$ and therefore are a source of oceanic $CHBr_3$, which is transported to other oceanic regions. $CHBr_3$ ocean concentrations in the tropical West Pacific (4°S – 4°N, 150°E – 180°E) show a reduced seasonal cycle in comparison to the above discussed North Atlantic region (Figure 5b). Oceanic concentrations are on average 9.11 pmol $L^{-1}$ which is significantly higher than average concentrations in the North Atlantic while the seasonal amplitude (min: 7.42 pmol $L^{-1}$ in March; max: 10.58 pmol $L^{-1}$ in October) is less pronounced. $CHBr_3$ production (536±42 pmol $m^{-2}$ $h^{-1}$), $CHBr_3$ emissions (492±84 pmol $m^{-2}$ $h^{-1}$) and atmospheric mixing ratios (1.07±0.08 ppt) show hardly any seasonality (Figure 5b, e). The same is true for SST (29.50±0.28 °C) and wind speed (4.71±0.76 m $s^{-1}$) (Figure 5h). The $CHBr_3$ balance is positive throughout the whole year except for DJF (Figure 5e). During this period high wind speed leads to higher emission than production rates and induces low oceanic concentrations which results in a $CHBr_3$ deficit. However, this deficit does not compensate for the $CHBr_3$ excess during the rest of the year leading to an overall positive $k_{bal}$ of 32 pmol $m^{-2}$ $h^{-1}$.
MLR analysis shows that the wind speed is the main factor influencing the variations of oceanic $CHBr_3$ concentrations ($R^2=0.51$, p-value<0.05), $CHBr_3$ atmospheric mixing ratios ($R^2=0.74$, p-value<0.05), and $CHBr_3$ emissions ($R^2=0.73$, p-value<0.05) on an annual basis (Figure 6b,e,h, Table 1) in the equatorial region. During JJA and SON $CHBr_3$ production drives the $CHBr_3$ concentrations (Table S1, JJA: $R^2=0.43$, p-value<0.05, SON: $R^2=0.51$, p-value<0.05) which increases from 477 pmol $m^{-2}$ $h^{-1}$ in July to 618 pmol $m^{-2}$ $h^{-1}$ by the end of September. This results in an increase of oceanic $CHBr_3$ concentrations as all other parameters stay constant during that period.

### Southern Ocean

The selected Southern Ocean region (71°S – 66°S, 40°W – 20°W) experiences water temperatures, which are negative almost any time around the year (Figure 5i). Average temperature is -1.08°C with minimum temperatures of -1.71°C in September (late winter) and maximum temperatures of +0.19°C in January/February (late summer). Wind speed in this region is nearly constant throughout the year (7.33 m $s^{-1}$) with lower average wind speed of 5.76 m $s^{-1}$ only during austral summer (DJF, Figure 5h). Oceanic $CHBr_3$ concentrations in the Southern Ocean region are on average higher (5.38 pmol $L^{-1}$) than in the North Atlantic region with maximum concentrations (7.74 pmol $L^{-1}$) in January and lowest concentrations (4.04 pmol $L^{-1}$) end of December. This sharp increase of $CHBr_3$ concentrations within two months demonstrates the limited biological activity period, visible in the $CHBr_3$ production rate (Figure 5f). Due to decreasing SSTs as well as a decreased day length, $CHBr_3$ production rates are almost zero from May to October and sharply increase up to 306 pmol $m^{-2}$ $h^{-1}$ in January. Atmospheric mixing ratios are highest (max: 0.85 ppt) from January to beginning of April but decline very slowly (Figure 5c) under low light levels, until they reach their minimum of 0.31 ppt in November.

Constant high atmospheric mixing ratios, due to light limitations in combination with very low SST, and decreasing oceanic $CHBr_3$ concentrations, after the short summer bloom in DJF, influence the switch from positive emissions to negative emissions between April and July (Figure 5f). $CHBr_3$ is in excess during times of $CHBr_3$ production (DJF) and is almost balanced during the autumn and wintertime (April – September, Figure 5f). On annual basis, $CHBr_3$ is almost balanced in this region with a slight excess of 15 pmol $m^{-2}$ $h^{-1}$.

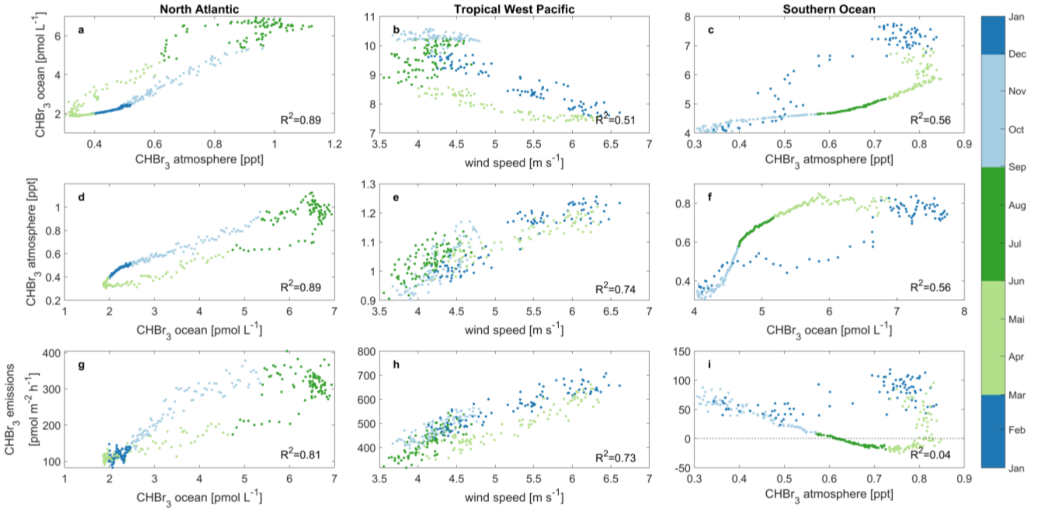

**Figure 6: Main drivers of oceanic $CHBr_3$ concentrations (a, b, c), atmospheric mixing ratios (d, e, f) and $CHBr_3$ emissions (g, h, i) in the North Atlantic (a, d, g), tropical West Pacific (b, e, h) and Southern Ocean (c, f, i). Different colours denote different seasons of the year. Each data point represents a daily mean average over the specific case study area.**

Overall, the MLR analysis confirms that atmospheric mixing ratios are the main factor influencing the variations of oceanic concentrations on annual basis (Figure 6c, Table 1, $R^2=0.56$, p-value<0.05). $CHBr_3$ production is the driving factor for the ocean concentration during autumn (MAM, Table S1). During this time $CHBr_3$ production decreases and so does the ocean concentration Figure 5c,f). The atmospheric mixing ratio is mainly driven by oceanic concentrations at times with high oceanic $CHBr_3$ concentrations (DJF: $R^2=0.88$, p-value<0.05) and by SST during cold winter times (JJA: $R^2=0.95$, p-value<0.05) (Table S1). In winter during low light levels, atmospheric $CHBr_3$ reactions are reduced, which increases the lifetime of atmospheric $CHBr_3$. Additionally, low SSTs increase the solubility of oceanic $CHBr_3$. These two conditions favour the overall dampening of the $CHBr_3$ sea-to-air emissions during winter (JJA). During the summer in DJF $CHBr_3$ emissions are mainly driven by SST (Table S1, $R^2=0.60$, p-value<0.05), as the solubility of $CHBr_3$ in the ocean significantly decreases due to the increasing sea surface temperatures. After this short summer period, temperatures decline in autumn (MAM) and increase the solubility of oceanic $CHBr_3$, which results in decreased emissions (Figure 5f,i). During winter (JJA) and spring (SON), surface temperatures and oceanic $CHBr_3$ concentrations stay low and therefore, increasing emissions are mainly driven by decreasing atmospheric mixing ratios.

These results demonstrate the benefits of simulating $CHBr_3$ in a fully coupled ESM configuration to calculate driving factors for different parameters on temporal and spatial basis. Studying the influence of one or more parameters on the variability of other parameters in the model is not realistic when using prescribed oceanic concentrations or atmospheric mixing ratios. Investigating the $CHBr_3$ cycling in different locations and different time scales helps to understand their interconnection and to better integrate their results in today's as well as in a future climate.

**Table 1: Annual coefficients of predictors for each MLR in the different case studies. Bold coefficients are the highest value within a MLR analysis of one parameter and region and act as indicator for the driving factors of the predicted parameter (Eq. (16)-(18)).**

| | Predictor parameter | North Atlantic | Tropical West Pacific | Southern Ocean |
|---|---|---|---|---|
| Ocean concentration | Wind speed | -0.02 | **-0.96** | -0.10 |
| | SST | <0.01 | <0.01 | <0.01 |
| | Atm. mixing ratio | **0.68** | 0.19 | **0.60** |
| | $CHBr_3$ production | 0.39 | 0.13 | 0.53 |
| | $CHBr_3$ emissions | <0.01 | <0.01 | <0.01 |
| Atmospheric mixing ratio | Wind speed | 0.29 | **0.94** | 0.55 |
| | SST | 0.32 | <0.01 | <0.01 |
| | Ocean concentration | **0.93** | 0.12 | **1.07** |
| | $CHBr_3$ production | <0.01 | 0.02 | <0.01 |
| | $CHBr_3$ emissions | <0.01 | <0.01 | <0.01 |
| $CHBr_3$ emissions | Wind speed | 0.20 | **1.27** | 0.21 |
| | SST | 0.67 | 0.50 | 0.53 |
| | Ocean concentration | **0.83** | 0.16 | 1.00 |
| | $CHBr_3$ production | <0.01 | 0.10 | <0.01 |
| | Atm. mixing ratio | -0.32 | -0.02 | **-1.22** |

### 3.5 Global bromoform emission inventories

A comparison of our modelled versus published global $CHBr_3$ emissions are presented in Figure 7. Global annual $CHBr_3$ emissions from top-down approaches are 449 Gg yr$^{-1}$, 528 Gg yr$^{-1}$ and 592 Gg yr$^{-1}$ based on calculations from Liang et al. (2010), Ordóñez et al. (2012) and Warwick et al. (2006), respectively. These inventories are about two to eight times higher than calculated annual emissions from bottom-up approaches, which are in the range of 76 Gg yr$^{-1}$ (Stemmler et al., 2015) to 238 Gg yr$^{-1}$ (Lennartz et al., 2015). Our results (214 Gg yr$^{-1}$) are similar to emission estimates published by Ziska et al. (2013) of 215 Gg yr$^{-1}$ but significantly higher than the 76 Gg yr$^{-1}$ estimate by Stemmler et al. (2015), which is based on the oceanic $CHBr_3$ observations from HalOcAt.

As we apply a 2.38 higher $CHBr_3$ production rate in the ocean as Stemmler et al. (2015), we simulate a production rate of 0.88 Gmol yr$^{-1}$ compared to 0.37 Gmol yr$^{-1}$ by Stemmler et al. (2015). Our emissions (214 Gg yr$^{-1}$) are 2.82 times higher (Figure 7, global values) compared to the emission estimate (76 Gg yr$^{-1}$) from Stemmler et al. (2015). Our model adaption is based on the higher bulk $CHBr_3$ production ratio ($\beta_0$) according to Kurihara et al. (2012) and Roy (2010) (see Section 2.1.1). This production rate is at the higher end of published values. Therefore, the resulting $CHBr_3$ production can be seen as an upper limit.

Comparing bottom-up and top-down approaches, the annual $CHBr_3$ emissions account for ~47% (105 Gg $yr^{-1}$) and ~66% (351 Gg $yr^{-1}$), respectively, from the tropics (20°S – 20°N, Figure 7), which account for ~37% of global oceanic surface, underlining the tropics as the most important source region of $CHBr_3$ of the earth.

Emissions in the middle latitudes (20 to 50°N/S) of the NH and SH show a similar distinction between top-down and bottom-up approaches. However, the annual $CHBr_3$ emissions are only half that of the tropics. Natural open ocean emission estimates from our study are proportional to the surface area between NH and SH in the middle latitudes. This relationship is reversed for the top-down approach estimates. Top-down emission estimates are higher in the NH compared to the SH although the oceanic surface area is lower in the NH (17%) compared to the SH (26%). This indicates the strong influence of coastal emissions on observational atmospheric mixing ratios used in top-down approaches.

In the high latitudes (50-90°N/S), emissions of bottom-up approaches are in the same range (SH) and even higher (NH) compared to top-down approaches (Figure 7). In the northern polar region (8% of global oceanic surface area), $CHBr_3$ emissions from our study account for 3% (6 Gg $yr^{-1}$) of global emissions and are significantly lower than the other two bottom-up approaches from Lennartz et al. (2015) (11%, 27 Gg $yr^{-1}$) and Ziska et al. (2013) (21%, 45 Gg $yr^{-1}$), which appears mainly due to the resolved seasonality within our study. According to the HalOcAt database, no measurements are recorded from November to February and from May to September north of 50°N in the NH and south of 50°S in the SH, respectively. Therefore, the prescribed atmospheric values in Ziska et al. (2013) but also in Stemmler et al. (2015) are biased to the ice-free summer months, with higher atmospheric mixing ratios, thus artificially dampening the emissions from the ocean to the atmosphere during winter seasons. Due to the influence of the annually fixed prescribed atmospheric mixing ratios in Stemmler et al. (2015), negative emissions are more pronounced between 50°N/S and 70°N/S up to -100 pmol $m^{-2}$ $h^{-1}$ at ~ 60°N/S. Our lesser negative emissions in the coupled ESM approach appear more realistic as they are not based on summer biased prescribed values.

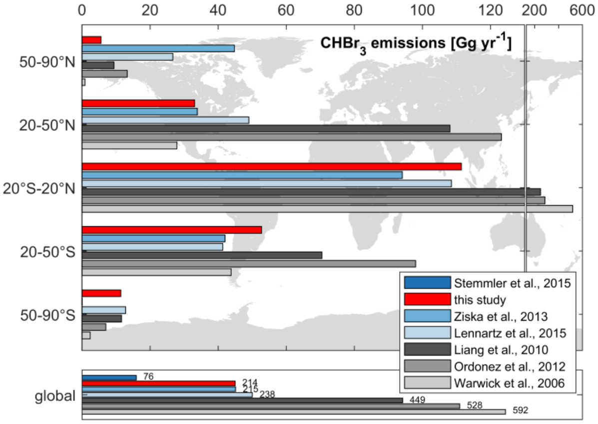

**Figure 7: Comparison of global and latitudinally binned annual $CHBr_3$ emissions from different studies. Grey and blue bars denote top-down and bottom-up approaches, respectively.**

Our global $CHBr_3$ emission inventory indicates distinct differences to the top-down approaches reflecting only 40%-50% of global emissions calculated by Liang et al. (2010), Ordóñez et al. (2012) and Warwick et al. (2006). Atmospheric $CHBr_3$ values in the top-down approaches are higher than the calculated atmospheric mixing ratios from our fully coupled model analysis. They include elevated coastal (Scenario A and C, Liang et al., 2010), including anthropogenic (Ordóñez et al., 2012) sources, which may partly explain the discrepancy.

An additional explanation for the overall higher atmospheric mixing ratios of $CHBr_3$ from observations could be that observations from coastal areas (100 km within the coastline) were excluded from this study and are not represented in the model, as they are difficult to quantify (e.g. tide-dependent $CHBr_3$ emissions of macroalgae) with a horizontal model resolution of 1°. However, coastal emissions lead to higher atmospheric mixing ratios of $CHBr_3$ (Fuhlbrügge et al., 2013; Fuhlbrügge et al., 2016; Hepach et al., 2016), which can be transported to remote open ocean regions, while these higher observational values are not included in the model results (Figure 3).

Another explanation for the underestimation of the modelled atmospheric mixing ratios compared to observations is the use of air-sea gas exchange parameterizations, whose uncertainty is estimated to be 25% (Wanninkhof, 2007) and may be underestimated up to 75% (Yang et al., 2022) at low wind speeds.

## 4 Conclusions and Outlook

Our study is the first one to derive oceanic and atmospheric $CHBr_3$ concentrations, as well as emissions, from a fully coupled ESM simulation. The model prognostically simulates oceanic $CHBr_3$ production by phytoplankton and includes oceanic $CHBr_3$ loss due to air-sea gas exchange, photolysis, hydrolysis and halogen substitution. Atmospheric loss of $CHBr_3$ is described by photolysis and the reaction with OH. We validate the model results with more than 5,100 oceanic and 8,400 atmospheric observations from the HalOcAt database. The simulated global mean $CHBr_3$ emission rate (214 Gg yr$^{-1}$) is in the range of previously published bottom-up approaches (76-238 Gg yr$^{-1}$), but significantly lower than top-down approaches (449-592 Gg yr$^{-1}$). The model allows to realistically resolve seasonal and spatial variations and to identify different drivers of oceanic and atmospheric $CHBr_3$ variability on regional and seasonal scales. Our results indicate that only during high productive seasons a consequently high $CHBr_3$ production drives high oceanic $CHBr_3$ concentrations. During low productive seasons, relatively high atmospheric mixing ratios suppress the gas exchange and consequently influence variations in oceanic $CHBr_3$ concentrations. In tropical regions (e.g. tropical West Pacific) with a small seasonal cycle, but high oceanic concentrations and atmospheric mixing ratios, wind speed is the main factor driving the variability of oceanic and atmospheric $CHBr_3$ and its emissions. The results clearly indicate the benefit of a fully coupled ocean-atmosphere-biogeochemistry ESM. In earlier modelling studies, prescribed, fixed atmospheric or oceanic values were applied, which bias the seasonal impact of different factors on oceanic and atmospheric $CHBr_3$ and subsequently induce additional uncertainties to the magnitude of $CHBr_3$ emissions.

Our fully coupled ocean atmosphere approach resolves natural biogenic oceanic and atmospheric $CHBr_3$ including their emissions at relatively high temporal and spatial model resolution. Validation with observational data shows good agreement for large scale spatial patterns and we attribute the remaining model-data differences to missing coastal sources, which are not implemented in the model. Comparison with other published $CHBr_3$ inventories indicates that approaches without seasonality lack to resolve $CHBr_3$ emissions especially in high latitudes.

Our results demonstrate the potential for applying a fully coupled ESM to elucidate the primary drivers of the observed $CHBr_3$ concentrations and emissions variability across spatial and temporal scales. Moreover, this model set-up allows to implement additional oceanic derived VSLS in order to further investigate their influence on the atmospheric chemistry. The dissociation of open ocean natural derived $CHBr_3$ from coastal area derived $CHBr_3$ in this study reveal that coastal derived $CHBr_3$ influences open ocean atmospheric mixing ratios. Therefore, implementing natural coastal next to anthropogenic sources and concurrent model resolution increase in these areas will help to further close the gap of published $CHBr_3$ emission estimates between bottom-up and top-down approaches. Long-term future changes in $CHBr_3$ dynamics under various scenarios should be investigated with a fully coupled ESM, to study the impact of climate change on $CHBr_3$ dynamics, e.g. in the Arctic, associated with loss of sea-ice and its climate feedback through interaction with ozone chemistry.

**Data availability.** Observational data can be downloaded from https://halocat.geomar.de. Model data will be archived and will be made available upon request.

**Author contributions.**

DB wrote the manuscript and led the discussion with contributions from all authors. DB analysed the model simulations and prepared the graphics. JFT and DJLO implemented the $CHBr_3$ model code changes in NorESM2 in discussion with BQ and all other authors. JFT carried out the model runs. KK led this project and initiated the research idea for this study.

**Competing interests.** The authors declare that they have no conflict of interest.

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