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Relationships between atmospheric organic compounds and air-mass exposure to marine biology

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Environmental context. The exchange of gases between the atmosphere and oceans impacts Earth's climate. Over the remote oceans, marine emissions of organic species may have significant impacts on cloud properties and the atmosphere's oxidative capacity. Quantifying these emissions and their dependence on ocean biology over the global oceans is a major challenge. Here we present a new method which relates atmospheric abundance of several organic chemicals over the South Atlantic Ocean to the exposure of air to ocean biology over several days before its sampling.

Abstract. We have used a Lagrangian transport model and satellite observations of oceanic chlorophyll-*a* concentrations and phytoplankton community structure, to investigate relationships between air mass biological exposure and atmospheric concentrations of organic compounds over the remote South Atlantic Ocean in January and February 2007. Accounting for spatial and temporal exposure of air masses to chlorophyll from biologically active ocean regions upwind of the observation location produces significant correlations with atmospheric organohalogens, despite insignificant or smaller correlations using commonly applied in-situ chlorophyll. Strongest correlations ($r = 0.42–0.53$) are obtained with chlorophyll exposure over a 2-day transport history for $CHBr_3$, CH_2Br_2, CH_3I, and dimethylsulfide, and are strengthened further with exposure to specific phytoplankton types. Incorporating daylight and wind-speed terms into the chlorophyll exposure results in reduced correlations. The method demonstrates that conclusions drawn regarding oceanic trace-gas sources from in-situ chlorophyll or satellite chlorophyll averages over arbitrary areas may prove erroneous without accounting for the transport history of air sampled.

Introduction

Ocean biology impacts the Earth's climate through its effects on atmospheric composition both by taking up atmospheric CO_2 and by releasing various organic compounds back into the atmosphere. The production of dimethylsulfide (DMS) by oceanic phytoplankton, leading to the formation of sulphate aerosol and perturbation to cloud condensation nuclei (CCN) abundance in the marine atmosphere has been studied extensively in this context (e.g. refs [1–4]). More recently, an observed link between oceanic chlorophyll content and cloud droplet number over the remote Southern Ocean[5] and observations of enhanced organic mass in remote marine aerosol during periods of enhanced ocean biology,[6–8] has led to the postulation that a natural source of organic carbon from the oceans may also exert control on marine CCN concentrations. The magnitude of this source,[9,10] and contributions from primary emission and secondary production from ocean-emitted volatile organic compounds (VOCs) such as isoprene[11–13] and monoterpenes[14] remain highly uncertain. Ocean biology also provides a source of halogens to the marine atmosphere through the emission of halogenated organic compounds from phytoplankton and macro algae.[15,16] These natural sources of halogens can impact the oxidising capacity of the remote troposphere.[17,18] The rapid transport of short-lived halogenated organics in deep convection to the tropopause region can also provide a halogen source to the stratosphere, contributing to stratospheric ozone depletion (e.g. Solomon et al.[19]). Our understanding of natural processes in the Earth's climate system underpins our estimates of impacts from anthropogenic changes. An improved quantification of the dependence of atmospheric composition on ocean biological activity is therefore important to our understanding of the Earth's climate system and its response to anthropogenic influence.

The attribution of an ocean-biology dependent source of a trace constituent is commonly based on observed correlation

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between atmospheric concentration and oceanic chlorophyll content, used as a proxy for marine biomass. One problem with such analyses concerns the selection of a suitable chlorophyll concentration to correlate with atmospheric abundance. This may be chlorophyll directly observed in the ocean surface waters at the location of the atmospheric measurements (e.g. Carpenter et al.[20]) or an average value taken from satellite ocean chlorophyll observations over a larger area encompassing the region sampled (e.g. O'Dowd et al.[21]). Both of these choices do not explicitly account for the biological exposure of air masses before their arrival at the observation site.

In the atmosphere, concentration variability in tracers with lifetimes longer than a few hours is primarily driven by changes in air mass origin.[22,23] In a Lagrangian framework, and in the absence of strong influence from sub-grid transport processes such as convection, the spatial and temporal variability in atmospheric tracer structure observed from aircraft and surface sites can be reproduced by simulating the advection of tracer in individual air masses from their origin locations over 3–5 days to the observation point.[23–25] In the marine environment, if the transport history of sampled air masses and upstream exposure to ocean biology is neglected, this may lead to poor or erroneous correlations of atmospheric trace constituents with local oceanic chlorophyll abundance.

Here, we use a Lagrangian transport model, satellite observations of oceanic chlorophyll and ship-board VOC observations from a cruise in the remote Southern Atlantic Ocean during the Organics from the Oceans Modifying Particulates in both Hemispheres (OOMPH) experiment, to investigate how the ocean biology history of air masses control the atmospheric variability of several VOCs. We obtain a quantitative biological exposure history of sampled air over the several days before its interception by the ship, which we relate to observed atmospheric trace gas concentrations. We compare these relationships with those obtained with in-situ chlorophyll-*a* (Chl-*a*) observed at the ship's position. From this we demonstrate the importance of air mass biological history in quantifying oceanic trace gas sources.

Experimental

Ship observations

During Leg 1 of the OOMPH cruise, observations of VOCs were made on board the Research Vessel Marion Dufresne on a route across the South Atlantic Ocean from Cape Town, South Africa to Punta Arenas, Chile, between 19 January and 5 February 2007 (Fig. 1). Air samples were measured in situ for VOCs using gas-chromatography mass-spectrometry (GC-MS). The inlet was located atop a 10-m mast at the foredeck of the ship, 20–25 m above sea level. Air was drawn at 6–8 l min^{-1}, through ~80 m of 1.27-cm shrouded Teflon sampling line, equipped with a Teflon filter to the ship's laboratory, resulting in an air residence time on the order of 1 min. The GC-MS was equipped with a custom-built cooled trap held at −70°C that preconcentrates the chemicals before measurement.[26] This enabled the detection of ambient trace gases at parts per trillion levels. Air was subsampled by the GC-MS from the main sampling line described previously, through a 0.159-cm stainless steel line at 30 mL min^{-1}. The air was dried and the trace gases of interest were then cryogenically trapped. The preconcentrated compounds were released from the

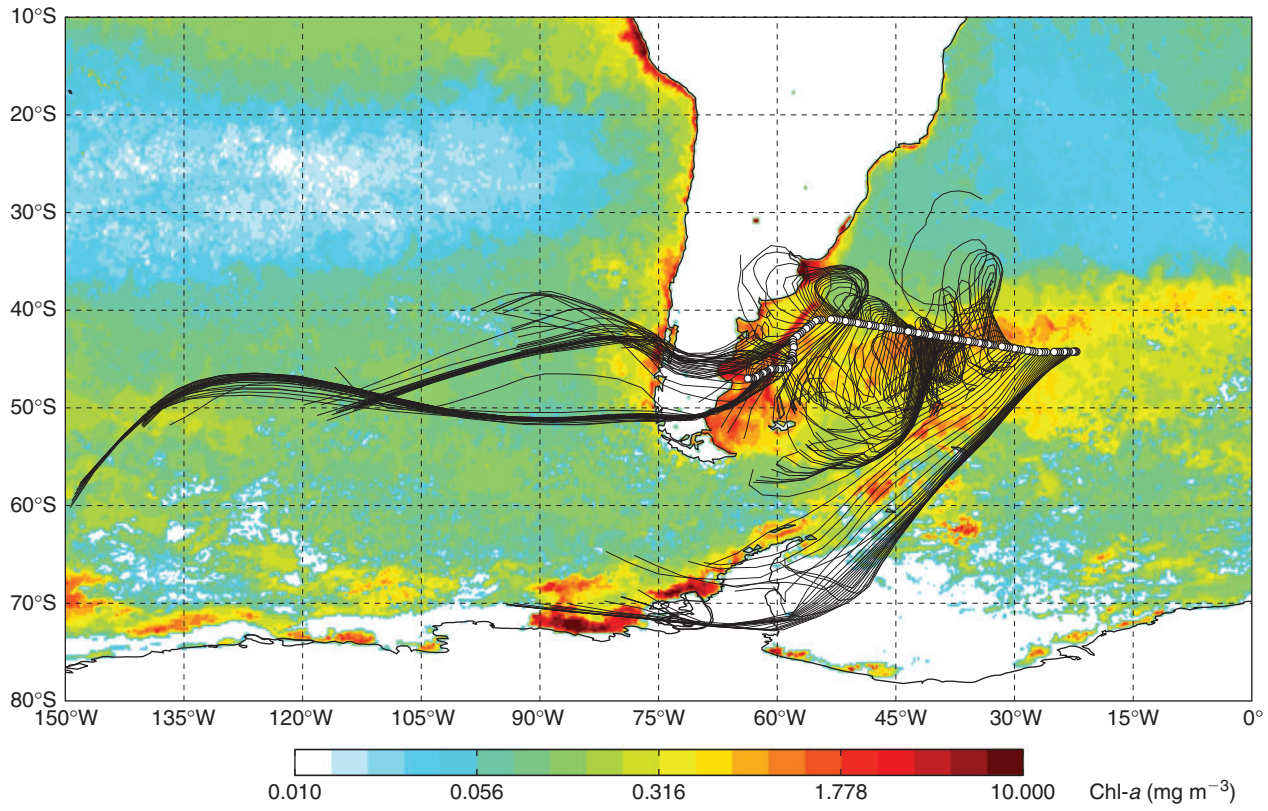

Fig. 1. Locations of VOC samples taken during the final section of the OOMPH cruise (27 Jan–4 Feb 2007) and used in this analysis (white circles). Colours show February 2007 monthly-mean SeaWiFS Chl-*a* concentrations. Five-day back-trajectories are shown arriving at the ship, and are plotted arriving every 10 min for clarity.

trap by rapidly heating it to 200°C and passing it onto a separating column and from there to the mass spectrometer for detection (Agilent GC 6890, MS 5973). The GC-MS was operated in single ion mode to achieve maximum sensitivity. Each sampling sequence for the selection of species sampled took 18–20 min. Between the measurements, the cryotrap was flushed with helium at 200°C to remove any residual trace compounds and blanks revealed no significant levels of the compounds reported. The measurements were conducted continuously once per hour with one calibration gas measurement every 5 h. Calibrations were performed against a whole air working standard, prepared by filling an aluminium cylinder with ambient marine air (German north coast) using a three-stage oil-free piston compressor (RIX Industries, Benicia, CA, USA) modified after.[27] This cylinder was calibrated relative to a NIST primary standard at the Rosenstiel School of Marine and Atmospheric Sciences, University of Miami (courtesy of Prof. Elliot Atlas). DMS was measured using a proton transfer reaction mass spectrometer (PTR-MS). Samples for the PTR-MS were taken from the same inlet line used for GC-MS sampling. Details of the PTR-MS sampling system are given elsewhere.[28] Here we analyse concentrations of CH_3Cl, $CHCl_3$, CH_3Br, $CHBr_3$, CH_2Br_2, CH_3I, toluene and DMS, all of which were observed at concentrations significantly above detection limit.

In-situ phytoplankton Chl-*a* abundance was determined by taking 1–2 L of water from the ship seawater line (7 m below the ship) approximately every 3 h, which was filtered through GF/F filters, and stored at −80°C until they were analysed using high performance liquid chromatography (HPLC). Details are described in reference.[29]

To obtain the large-scale regional ocean biological productivity, 8-day average oceanic Chl-*a* concentrations were obtained from Level-3 binned SeaWiFS satellite instrument global fields at 32-km horizontal resolution, available from the NASA-GSFC (http://oceancolor.gsfc.nasa.gov/SeaWiFS/, accessed 23 June 2009). The fields were re-gridded to 0.25° horizontal resolution, before applying a 1° land–sea mask to retain zero Chl-*a* values over land and flag missing data over the oceans. In our analysis, missing data in the 8-day average satellite fields are replaced by values from monthly-mean SeaWiFS fields where available. Concentrations of Chl-*a* from SeaWiFS fields at the ship location correlate well with Chl-*a* measured in situ from ship water samples ($r = 0.73$) (Fig. 2).

Lagrangian model calculations

The OFFLINE Lagrangian trajectory model[30] was used to calculate kinematic back-trajectories from the ship position every minute by integration of velocity fields taken from operational analyses of the European Centre for Medium-range Weather Forecasts (ECMWF). The fields at the Lagrangian particle positions are obtained from the ~1.0125° horizontal resolution analyses by cubic Lagrange interpolation in the vertical followed by bilinear interpolation in the horizontal and linear interpolation in time. Trajectories were initialised on a hybrid sigma-pressure coordinate of 0.99, just above the surface at the ship location. Seven-day back-trajectories were produced, with position output every 6 h. These trajectories account for large-scale advection by the resolved model winds, and neglect convective and turbulent transport.

Back-trajectory position and satellite Chl-*a* are combined to yield time-series parameters along the cruise ship track based on the sea-surface Chl-*a* 'fetch' of arriving air masses. The first parameter is the average chlorophyll exposure (E), which is the mean of the marine Chl-*a* concentrations taken from the SeaWiFS field at the six-hourly positions along the length of the back-trajectory. SeaWiFS Chl-*a* values only contribute to the mean where the trajectory pressure is greater than 850 hPa, to restrict air mass influence from the sea surface to the approximate height of the marine boundary layer (BL). Where the trajectory pressure is less than 850 hPa, or the trajectory passes over land, a zero Chl-*a* value is included in the average, to account for time spent away from Chl-*a* exposure. Where there is missing SeaWiFS data over the ocean, the trajectory time point is excluded from the averaging. Time periods for which Chl-*a* data are missing for more than 50% of back-trajectory time points over the 5 days before ship arrival are excluded from the analysis. This provides a mean boundary-layer Chl-*a* exposure for each air mass sampled by the ship.

A second parameter, an age-weighted chlorophyll exposure (E_a), is calculated by applying an e-folding lifetime of 5 days to each Chl-*a* value included in the average with time backwards along each back-trajectory:

$$E_a = \frac{\sum_i [\text{Chl-}a]_i \exp(t_i/5)}{n} \quad (1)$$

where $[\text{Chl-}a]_i$ and t_i are respectively the ocean Chl-*a* concentration and the time in days before arrival at the ship position at each point along the back-trajectory, and n is the total number of time points with valid Chl-*a* values included in the calculation. This attempts to account for the decreasing influence of biological exposure further back in time, due to chemical decay of the emitted tracers and diffusive loss due to mixing with free tropospheric air above the marine boundary layer during transport.

Correlations weighted by a wind speed (E_w) and daylight exposure (E_d) term have also been calculated. These terms attempt to account for wind-driven and sunlight-driven sea-air transfer of gases from the biologically active regions. For each 6-hourly back-trajectory time-point average wind speed is derived from the horizontal displacement of the trajectory air parcel over the preceding and following 6 h. This is a crude measure of the average large-scale wind over 12 h, and neglects variability in wind speed on smaller timescales, and spatial variability on scales smaller than the resolution of the ECMWF analyses fields (1.1025°). These wind speeds are cubed before being multiplied by the satellite Chl-*a* value at each back-trajectory point. The mean of these values is calculated along each trajectory to produce a time series of E_w along the ship track. A cubic wind-speed term is applied in line with empirical studies on wind-speed dependence of sea-air transfer of trace gases.[31] Daylight exposure is determined by calculating solar zenith angle from local date, time and location at each back-trajectory point. For each back-trajectory, E_d is the average of Chl-*a* values encountered during daylight only.

Results and discussion

Pearson correlation coefficients (r) of observed atmospheric VOC concentrations with the four different Chl-*a* average parameters over back-trajectory lengths of 1–7 days and with Chl-*a* at the ship are shown in Fig. 2 for each of the VOCs. One-minute resolution E, E_a, E_w and E_d values are averaged over the 20-min experimental air sampling time periods to produce the correlations. The final 48 h of the cruise are excluded from

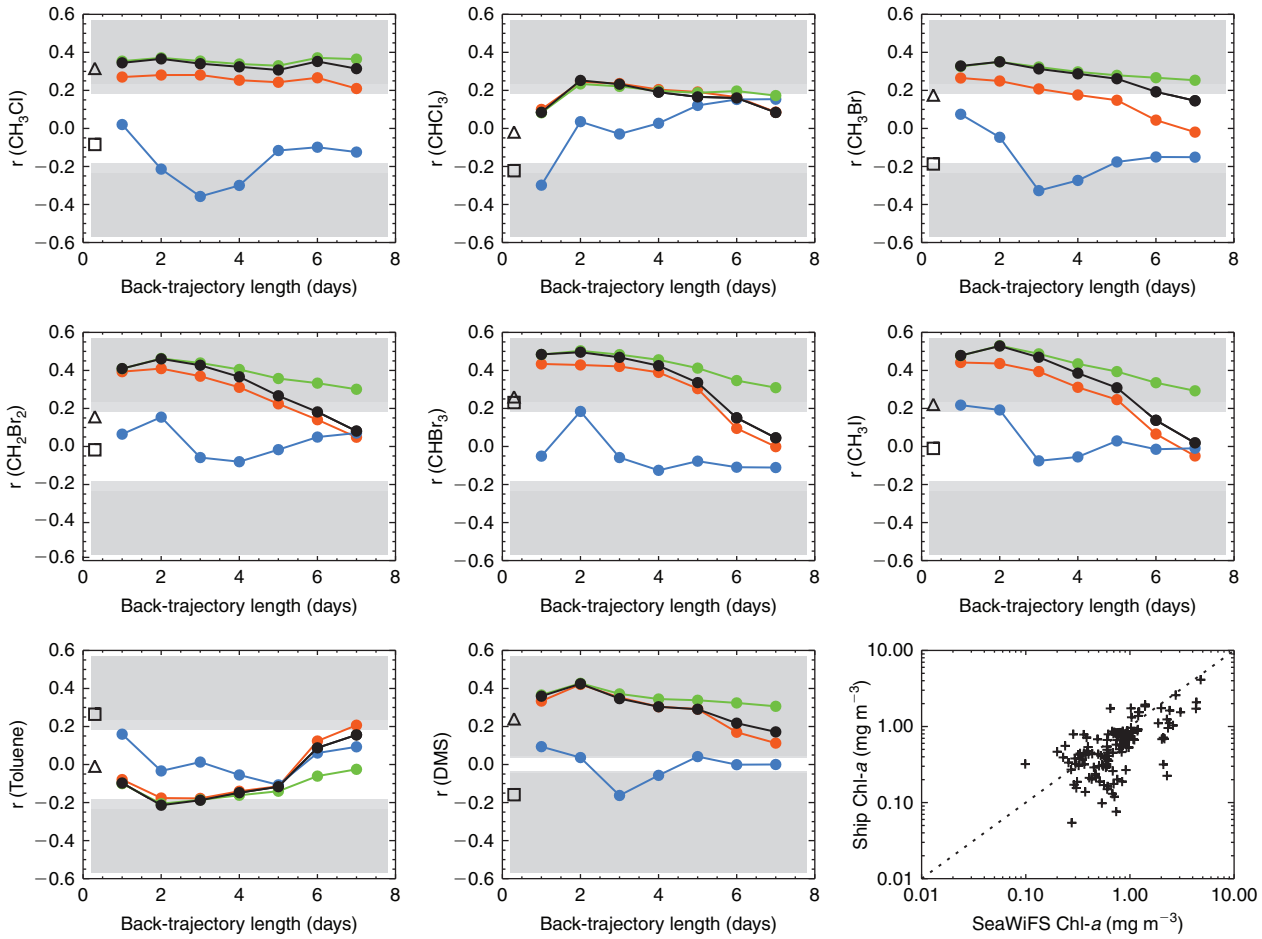

Fig. 2. Pearson correlation coefficient values for relationships between atmospheric VOC concentrations and satellite Chl-*a* concentrations averaged along back-trajectories of increasing length. Black, standard Chl-*a* trajectory average E; green, 5-day aged Chl-*a* trajectory average E_a; red, Chl-*a* average during trajectory daylight only; blue, Chl-*a* average weighted by cubic large-scale wind speed diagnosed from 6-hourly horizontal trajectory displacement. Correlations with in-situ Chl-*a* measured in seawater from the ship and with satellite Chl-*a* at the ship location are shown by squares and triangles respectively. The dark and light grey areas show where correlations are significant at 99 and 95% confidence respectively. Bottom right panel shows correlation between SeaWiFS satellite Chl-*a* at the ship position and in-situ Chl-*a* measured by the ship (r = 0.73). Dotted line denotes 1 : 1 relationship.

the analysis, where the ship travels along the coast of Argentina. This minimises coastal influence of macro algae which may mask the correlations of some of the organohalogens with Chl-*a*.

$CHBr_3$, CH_2Br_2 and CH_3I

Emissions of very short-lived brominated and iodonated organohalogens (lifetimes less than 0.5 years), from terrestrial and anthropogenic sources such as fires, rice paddies and waste water effluent, are believed to be very small compared with their oceanic emissions.[15] Phytoplankton emissions of $CHBr_3$ amount to ~240 Gg Br, and contribute significantly to the global open ocean source of $CHBr_3$.[32] Although in coastal regions macroalgae are likely a significant source of brominated VOCs, in the open ocean evidence suggests that the sources of $CHBr_3$ and CH_2Br_2 are associated with the thermocline Chl-a maximum, at least in the tropical oceans (ref. [15] and references therein). This results in large sources of these gases near the equator and in ocean frontal regions due to ocean upwelling. Consequently, the source of these gases over back-trajectories arriving on the ship may be expected to be correlated with oceanic Chl-*a* content, especially in the nutrient-rich region of the polar oceanic front (Fig. 1). A recent study found that aqueous $CHBr_3$ and CH_2Br_2 concentrations are not always correlated suggesting different production and fate pathways of these compounds.[33] A source of CH_3I from marine phytoplankton has been inferred by some studies,[34,35] which may also be expected to be related to Chl-*a* abundance. Other studies have found a photochemical source,[36,37] which may be active in the presence of dissolved organic matter (DOM).[38] A more recent study suggests that this mechanism is likely more complex than can be accounted for by a simple relationship based on photochemical exposure of DOM, since there is little evidence that all types of DOM would provide substrates for photochemical CH_3I production.[39] Evidence from the tropical North Atlantic Ocean suggests that CH_3I is produced in the open oceans through a photochemical process in the surface waters, not directly dependent on ocean biological activity,[15] and it therefore may not be expected to correlate well with oceanic Chl-*a*. A recent study from a cruise in the Southern Indian Ocean found enhanced marine BL concentrations of these three VOCs in the region of oceanic fronts and Chl-*a* maxima,[40] suggesting a biological source.

Correlations with Chl-*a* at the ship position are insignificant for CH_2Br_2 and CH_3I, and marginally significant for $CHBr_3$ (Fig. 2). Differences between in-situ ship-measured Chl-*a* and satellite Chl-*a* at the ship position (comparison shown in Fig. 2, r = 0.73) result in differences in correlation with the VOCs at the

Table 1. Atmospheric lifetimes, statistics and reported atmospheric abundances of the eight VOCs considered in this study
Italic text indicates correlations are insignificant at 99% confidence

Species	Lifetime[A]	r (in situ)[B]	r (E, 2-day)[C]	Slope[D]	Intercept[D] (pptv)	Atmospheric concentration (pptv)		
						Southern Ocean	Tropical marine BL	Global average
CH_3Cl	1 year	*−0.08*	0.37	14	488	–	–	550[G]
CH_3Br	0.7 year	*−0.19*	0.25	0.41	6.8	–	–	7.9[H]
$CHCl_3$	0.4 year	*−0.22*	0.35	0.63	9.8	–	6.5–9.1[F]	–
CH_2Br_2	0.33 year	*−0.02*	0.46	0.19	1.3	0.33 (0.1–0.88)[E]	0.7–1.5[F]	–
$CHBr_3$	26 days	*0.23*	0.50	1.0	3.6	1.8 (1.0–3.1)[E]	0.5–2.4[F]	–
CH_3I	7 days	*−0.01*	0.53	0.55	1.0	1.7 (1.0–2.7)[E]	0.3–1.9[F]	–
Toluene	2 days	0.26	−0.21	−6.8	51.0	–	–	–
DMS	1 day	−0.16	0.42	110	210	70 ± 30[I]	–	–

[A]Lifetime values taken from *Scientific Assessment of Ozone Depletion: 2006*.[15,16]
[B]Pearson correlation coefficient between atmospheric abundance and in-situ oceanic Chl-*a* concentration measured on board the cruise.
[C]Pearson correlation coefficient between atmospheric abundance and satellite Chl-*a* concentrations averaged along 2-day back-trajectories.
[D]Slope and intercept values from linear regression between E_{2day} and atmospheric abundance.
[E]Clean air sector concentrations observed at the Cape Grim monitoring station (144.7°E, 40.7°S).[44]
[F]Estimated tropical marine BL concentrations.[15]
[G]Estimated global mean tropospheric concentration.[16]
[H]Estimated global mean tropospheric concentration in 2004.[16]
[I]Average concentration observed north and south of oceanic frontal regions in Southern Indian Ocean.[40]

ship location. Analysis using satellite or in-situ Chl-*a* near the ship for these VOCs may lead to the conclusion that ocean biology associated with regions of high Chl-*a* is not a significant driver of their atmospheric variability. Fig. 2 demonstrates substantial improvement in correlations between these three VOCs and Chl-*a* averaged along back trajectories compared with correlations with Chl-*a* at the ship location. Correlations are significant at the 99% confidence level over back-trajectory lengths of 1–5 days. Correlations between VOC concentrations and oceanic Chl-*a* exposure are maximum ($r = 0.45$–0.55) for back-trajectory lengths of 2 days, and become insignificant over trajectories longer than 5 days. This demonstrates the role of air mass biological and transport history in controlling variabilty of these VOCs. Over 6- and 7-day back-trajectories for all three VOCs, the 5-day aged Chl-*a* average (E_a) retains significant r values, as the weight of Chl-*a* encountered further back along trajectories is reduced. A maximum in r for 2-day trajectories is consistent between the three species despite their varied atmospheric lifetimes (Table 1). This may be due to a dynamic control on the longevity of biological influence on the trace gas signature of the air masses, acting in addition to chemical loss. Entrainment of air from above the marine BL is likely to act to dilute any fresh trace gas signatures from ocean emission. A time scale of 2 days corresponds well with that expected for marine BL dilution.[41] Similarly strong correlations are seen for all three VOCs, with no evidence of a weakened correlation for CH_3I due to a non-biological source.

The inclusion of a daylight-weighted Chl-*a* exposure term degrades the strength of correlations along back-trajectories (Fig. 2). The crude application of a daylight-only term neglects more complex processes such as wavelength-dependence of incident radiation, cloud cover, and attenuation of radiation through the ocean mixed-layer depth. Including the basic effect of daytime and night time exposure of air masses to Chl-*a* does nothing to improve correlations with the trace gases, suggesting a photochemically driven source of these gases from Chl-*a* rich regions may not be a significant driver of their atmospheric variability. Chl-*a* exposure weighted by cubic wind speed diagnosed from displacement of the back-trajectories produces insignificant correlations with CH_2Br_2, $CHBr_3$ and CH_3I, despite previous studies supporting such a dependence for ocean-air gas transfer. Poor correlations may result from the crude calculation of wind speed that is permitted from large-scale trajectory advection. Using the large-scale horizontal trajectory displacement to diagnose mean wind speed neglects variability on sub 12-h timescales and spatial scales smaller than the resolution of the wind fields used (1.1025°). Such fine-scale variability in wind speed has been shown to be important in correctly simulating oceanic emission functions for trace-gases.[42,43]

Slope and intercept values are given in Table 1 for linear best fit relationships between VOC concentrations and 2-day E values. Intercept values correspond to background mixing ratios of the species in marine boundary layer air which has not had biological influence over the past two days. Table 1 also shows concentrations of the VOCs in the remote marine atmosphere from previous studies. For the shorter-lived CH_3I, the intercept value is within the range of previous background concentrations sampled in the Southern Ocean at the Cape Grim monitoring station[44] and estimated tropical marine BL concentrations.[15] $CHBr_3$ and CH_2Br_2 intercept values are close to but larger than the range of concentrations seen in background air at Cape Grim during the same months.[44] This may result from the longer lifetimes of $CHBr_3$ and CH_2Br_2 (~1 and 4 months respectively), meaning that Chl-*a* exposure before 2 days back in time likely has more impact on their abundance than may be the case for shorter-lived species.

Scatter plots of species concentrations against in-situ Chl-*a* and 2-day E values are shown in Fig. 3. The linear relationships show a degree of scatter, although this is reduced compared to relationships with ship-measured in-situ Chl-*a*. Factors contributing to scatter in the trajectory-average Chl-*a v.* VOC relationships may be the lack of small-scale wind speed dependence in the biological emission signature as discussed above, or a dependence of biological impact on the VOCs being driven by non-Chl-*a* related exposure such as the presence of DOM. In addition, factors in the model calculations may introduce errors, such the replacement of missing Chl-*a* data in higher time

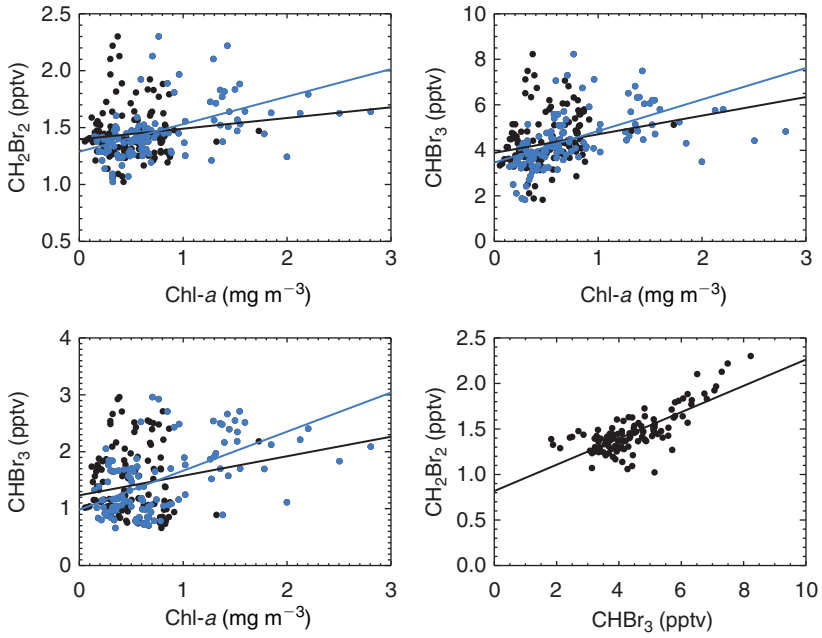

Fig. 3. Atmospheric concentrations of $CHBr_3$, CH_2Br_2 and CH_3I as a function of in-situ ship-measured oceanic Chl-*a* abundance (black) and 2-day back-trajectory averaged Chl-*a* (E) values (blue). Lines show respective linear regressions with the two Chl-*a* parameters. Bottom right: relationship between $CHBr_3$ and CH_2Br_2 atmospheric concentrations ($[CH_2Br_2] = 0.14\ [CHBr_3] + 0.82$; $r = 0.75$).

Table 2. Pearson correlation coefficients for relationships between average Chl-*a* exposure in specific phytoplankton functional types along 2-day back-trajectories and atmospheric VOC concentrations

Data in italic format indicates correlation is not significant at 95% confidence

	Haptophytes	*Prochlorococcus*	*Synechoccocus*	Diatoms
r (CH_3Cl)	*0.17*	0.44	0.31	0.27
r ($CHCl_3$)	0.26	*0.30*	*0.17*	0.29
r (CH_3Br)	0.30	*0.25*	0.33	0.57
r (CH_2Br_2)	0.26	0.54	0.55	0.40
r ($CHBr_3$)	0.40	0.49	0.52	0.37
r (CH_3I)	0.40	0.46	0.56	0.51
n observed	83	30	52	67
r (DMS)	0.09	0.55	0.29	0.50
n observed	3316	1460	1679	2102

resolution (8-day) satellite fields with monthly-mean data, as well as trajectory displacement errors introduced by the finite resolution of the ECMWF wind fields, which could both introduce uncertainty in the calculated Chl-*a* footprint encountered by air masses. Nevertheless, our results demonstrate the importance of air mass biological history in driving variability of the VOCs compared with in-situ Chl-*a*.

Recently, it has become possible to detect major dominant phytoplankton functional types (PFTs) from specific water-leaving radiance signatures in the signal measured by SeaWiFS. The PHYSAT model,[45] compares SeaWiFS measurements and in situ measurements of pigment inventories performed in the framework of the 'Geochemistry, Phytoplankton, and Colour of the Ocean' (GeP&CO) program,[46] to produce distributions of the global regions dominated by diatoms, haptophytes, *Synechoccocus* and *Prochlorococcus* PFTs. Dominant means that a given PFT contributes more than 60% of the total pigment composition in the given area of surface ocean. A large effort has been made to evaluate the PHYSAT method using in-situ observations of phytoplankton communities,[47] giving some confidence in its estimates of phytoplankton community distributions. Many trace gases with biological sources in the oceans show a dependence of emission strength on the phytoplankton community structure.[48,14] Table 2 shows correlations between atmospheric concentrations of VOCs in this study with exposure to Chl-*a* in the four different PFTs as determined by PHYSAT data along 2-day back-trajectories. Correlations of CH_2Br_2, $CHBr_3$ and CH_3I with trajectory Chl-*a* from each of the four PFTs are significant. Largest correlation coefficients are with *Synechoccocus* and *Prochlorococcus* for CH_2Br_2 and $CHBr_3$ and with *Synechoccocus* and diatoms for CH_3I. Previous studies have noted a strong correlation between CH_2Br_2 and $CHBr_3$ in seawater and in the marine atmosphere.[20,44,49,50] Fig. 3 shows a significant correlated relationship between observed $CHBr_3$ and CH_2Br_2 concentrations during the cruise ($[CH_2Br_2] = 0.14\ [CHBr_3] + 0.82$; $r = 0.75$). This slope compares well with that observed between $CHBr_3$ and CH_2Br_2 atmospheric abundance at Mace Head in September.[44] At low $CHBr_3$ concentrations, there is evidence for a shallower slope with some enhancement to CH_2Br_2. The relationship and

the dominant PFT correlations are consistent with a common source for these trace gases in the open ocean, possibly dominated by *Synechoccocus* and *Prochlorococcus* phytoplankton.

CH_3Cl, CH_3Br and $CHCl_3$

The three longest lived VOCs in the analysis (CH_3Cl, $CHCl_3$ and CH_3Br), have lifetimes of several months (Table 1) and have significant emissions from terrestrial and anthropogenic sources in addition to their oceanic emissions. CH_3Cl has a large tropical source from leaf ageing and decay, in addition to a large direct source from tropical and subtropical plants.[16] Biomass burning and the oceans contribute the next most significant sources, with more minor contributions from wetlands, salt marshes, fungi, rice cultivation, fossil fuel burning and industrial processes.[16] The oceans are estimated to contribute between 3 and 28% of the global CH_3Cl source.[16] Emissions of CH_3Br are dominated by the oceans, with smaller contributions from biomass burning, salt marshes, wetland and agriculture.[51] The abundance of CH_3Br in temperate ocean waters appears to show a dependence on sea surface temperature.[52–54] Evidence from high-latitude and coastal waters suggests that at least seasonal variations in CH_3Br fluxes from and to the ocean are modulated by ocean biology. Anthropogenic emissions are dominated by fumigation, and evidence suggests that these may be larger than current best estimates.[16] Emission of $CHCl_3$ from the open oceans constitutes its largest atmospheric source, with about half as much emitted from soil processes and much smaller sources from volcanic activity, anaerobic fermentation and anthropogenic activities.[55]

Recently, a biological source for these compounds has been suggested by the detection of $CHCl_3$, CH_3Br and CH_3Cl production in five different phytoplankton species.[40]

Correlations between each of these three VOCs and ship-measured in-situ Chl-*a* (Fig. 2) are insignificant. A significant positive correlation ($r = \sim 0.3$) is obtained between satellite Chl-*a* at the ship location and CH_3Cl. Correlations with back-trajectory E and E_a values show a small improvement for CH_3Cl, and are relatively invariant over the 1–7 day trajectory lengths. This is consistent with CH_3Cl being the longest lived of the species considered (lifetime ~1 year), meaning that its atmospheric variability would be less sensitive to the temporal pattern of a biological Chl-*a* related source during air mass transport. Despite the postulated dominant open ocean source for $CHCl_3$, correlations with E, E_a and E_d are only marginally significant over 2–3 day back-trajectories. This may suggest a non-Chl-*a* related source. Alternatively it may indicate a dominant source from a specific PFT, resulting in small correlations with overall ocean Chl-*a* content. Table 2 indicates significant correlations of $CHCl_3$ with exposure to Chl-*a* from diatoms and haptophytes and insignificant correlations with *Synechoccocus* and *Prochlorococcus* PFT regions. Correlations of CH_3Br with E and E_a values are significant over 1–5 day back-trajectories. Over longer trajectories, only correlations with E_a values remain significant, indicating that Chl-*a* exposure further back in time is not significantly driving atmospheric CH_3Br variability at the ship, as also seen for shorter lived species. The relationship between CH_3Br and exposure to diatom Chl-*a* shows a strong significant correlation, which agrees with a recent study which measured large CH_3Br in a diatom dominated region of the sub-tropical front of the Southern Indian Ocean.[40]

Correlations with the daylight-weighted Chl-*a* average values E_d are smaller than with E and E_a, as for shorter-lived species. This again suggests a non-dominant role for sunlight-driven variation in the biological source of these gases. The cubic wind speed-dependent Chl-*a* exposure (E_w) produces mostly insignificant correlations, with significant negative correlations for CH_3Cl and CH_3Br over 2–3 day back-trajectories and for $CHCl_3$ over 1-day back-trajectories. However, these relationships should likely be treated with caution since the large-scale wind used is not representative of the true variability in wind speeds experienced along the back-trajectories, as noted above.

Dimethyl-sulfide and toluene

The ocean is considered to be the main source of DMS,[56] with a strong phytoplankton origin.[57,58] However, it has been recognised in several studies that emission of DMS does not correlate well with oceanic chlorophyll content, and a lag exists between local Chl-*a* maximum and DMS maximum.[59] Several microbial production and consumption pathways of DMSP (a precursor for DMS) and DMS are responsible for the surface concentration of DMS and thus its flux to the atmosphere.[60] Another important process of DMS production is grazing by zooplankton, by which DMSP is released from phytoplankton, usually following a phytoplankton bloom.[61,62] Microbial conversion of DMSP to DMS and subsequent DMS emission to the atmosphere then occurs following this grazing, by which time bloom chlorophyll content will have diminished. Recent observations from the Southern Indian Ocean however, show enhanced atmospheric DMS concentrations coincident with regions of enhanced oceanic Chl-*a* associated with oceanic fronts.[40]

A significant positive correlation is obtained between DMS and satellite Chl-*a* at the ship location ($r = 0.24$), whereas a negative correlation is given with in-situ Chl-*a* measured on board the ship (Fig. 2). Largest correlation coefficients are obtained with E, E_a and E_d back-trajectory Chl-*a* averages. As with the short-lived organohalogens, relationships with E_a retain stronger correlations at longer back-trajectories compared with E and E_d. This is consistent with the short DMS atmospheric lifetime (~1 day) and a non daylight dominated source. These results suggest that the ocean DMS source can be related to Chl-*a* exposure of air if transport history over a few days is accounted for. Strong correlations are obtained between DMS and Chl-*a* from *Prochlorococcus* and diatom PFTs along 2-day back-trajectories. *Prochlorococcus* is usually not associated with high DMS emissions[63]; however this species is associated with a regenerative ecosystem with a high dominance of micro-zooplankton and previous studies have shown, that microzooplankton grazing in natural phytoplankton communities is a significant DMS production pathway.[64] The high correlation with diatoms is in good agreement with observations of elevated DMS concentrations in diatom dominated oceanic frontal regions,[40] and has been associated with diatom bloom conditions in the Mauritanian and Peruvian upwelling areas.[65,66]

Toluene (C_7H_8) is an aromatic VOC, which occurs in crude oil. It is primarily emitted from anthropogenic combustion, with smaller additional contributions from industrial processes.[67] There are no known oceanic sources of toluene, however terrestrial vegetation may contribute a natural source.[68,69] As expected, r values for the correlations between toluene and all back-trajectory Chl-*a* products are insignificant (Fig. 2). This confirms the absence of an ocean biology dependent toluene source, and lends further confidence to the significance of larger r values in identifying a dependence on biological air mass history for other species. Toluene is also the only VOC in the

study for which its relationship with 2-day back-trajectory E values displays a negative slope.

Summary and conclusions

We have investigated relationships between the variability in several atmospheric VOCs measured from a ship cruise in the remote marine boundary layer of the South Atlantic Ocean and air mass exposure to oceanic Chl-*a* content, a proxy for ocean biological activity. Significant correlations are found between atmospheric abundance and satellite-derived Chl-*a* exposure averaged along air mass back-trajectories arriving at the ship location for a range of organohalogen compounds and DMS, despite weak or insignificant correlations with Chl-*a* at the ship location measured by satellite or in situ by the ship. Strongest correlations are obtained for DMS, CH_2Br_2, $CHBr_3$ and CH_3I with Chl-*a* averaged over 2-day back-trajectories ($r = 0.42–0.53$), suggesting a significant role for ocean biology in controlling their atmospheric variability, which is not indicated by correlations with Chl-*a* at the ship location. This highlights the importance of air mass origin in driving observed variability in atmospheric tracers. For the longer-lived organohalogens, CH_3Cl, CH_3Br and $CHCl_3$, weaker but significant correlations are obtained with back-trajectory averaged Chl-*a*. This is consistent with the presence of significant non-ocean sources for these species, but indicates that air mass biological history may account for some of their atmospheric variability. Applying a 5-day exponential decay timescale to the weighting of Chl-*a* along back-trajectories, results in stronger correlations at longer trajectory lengths. This is consistent with the impact of biological activity encountered by air masses further back in time being diminished by mixing and chemical processing during transport. Accounting for a daylight weighting in the trajectory Chl-*a* average results in reduced correlations across all species, and averaging weighted by cubic wind-speed along the back-trajectory results in reduced or insignificant correlations. However, the large-scale trajectory wind-speed derived from horizontal displacement of the trajectories does not capture wind variability on small spatial scales or sub-12 h timescales, and is therefore likely not a reliable measure of the true wind speed-dependence of trace gas ocean-air transfer along the back-trajectories. Correlations with toluene are insignificant with Chl-*a* averages over all back-trajectory lengths and with satellite Chl-*a* at the ship location. This lends confidence to the methodology, since its sources are uniquely terrestrial, and it would therefore not be expected to correlate with air mass Chl-*a* exposure.

Using the PHYSAT model we have also investigated relationships between the atmospheric VOC concentrations and 2-day back-trajectory exposure to Chl-*a* in four different phytoplankton functional types. Strong correlations are obtained between Chl-*a* in *Synechoccocus* and *Prochlorococcus* and CH_2Br_2 and $CHBr_3$ abundance, and between Chl-*a* in *Synechoccocus* and diatoms and CH_3I abundance. $CHCl_3$ correlates with exposure to Chl-*a* from diatoms and haptophytes, and DMS correlates most strongly with exposure to Chl-*a* from diatoms and *Prochlorococcus*.

By constructing linear regressions between VOC concentrations and 2-day average back-trajectory Chl-*a*, we estimate 'background' concentrations of these species in South Atlantic marine air which has not been influenced by Chl-*a* exposure in the previous 2 days. These match well with concentrations observed in background air at the Cape Grim monitoring station, Tasmania. However, there is evidence that our estimated background concentrations are larger than previously observed for the longer-lived species, which is likely due to the fact that biological exposure before the 2-day history may impact more on the abundance of the longer-lived species. A degree of scatter remains in these linear relationships, most likely due to parameters missing from our analysis that drive variability in their ocean emissions. These may include small-scale wind variability, temperature dependencies, and non-chlorophyll related biological or ocean surface organic content dependencies. Nevertheless, our method provides an improvement on attempts at correlating ocean biology influence with marine tracer observations based on in situ ocean observations of Chl-*a* or ad hoc regional Chl-*a* averages from satellite, and provides an important caveat to previous studies in which such methods have been used. It is hoped that this methodology can be applied to further ship-borne datasets to derive better insights into the marine contribution to the global budgets of these important trace gases. The methodology used here could be improved in future by improving the treatment of additional processes along back-trajectories which may drive oceanic emission of a given tracer. However, a limitation to the inclusion of such processes is the requirement that they be quantifiable over the large air-mass 'fetch' area impacting sampled air. Future development of satellite retrievals for parameters related to ocean biology in addition to chlorophyll may facilitate such improvements. Newly-emerging satellite retrievals which allow extraction of quantitative PFT information (e.g. Bracher et al.[70]) will allow better quantification of co-occurring trace gas producers in addition to chlorophyll and dominant PFTs and may facilitate such improvements.

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