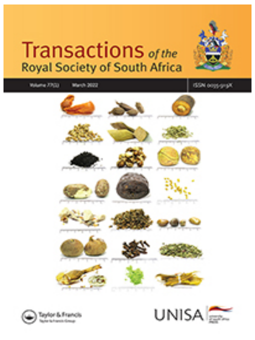

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Acyclic halogenated monoterpenes from marine macroalgae: Estimated atmospheric lifetimes, potential degradation products, and their atmospheric impacts

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The selected acyclic halogenated monoterpenes derived from red macroalgae are investigated in terms of their isolation, their reactions with oxidants (ozone, OH radical) and the impacts of the first-generation oxidation products on the atmosphere. The yields of these monoterpenes from marine algae are small and highly variable (0.01–6.7%), the fractions can then enter the atmosphere through different meteorologically driven processes. The loss of the monoterpenes is mostly driven by OH radical, however, 1,6-dibromo-2,7-dichloro-3,7-dimethyl-oct-3-ene and 4-bromo-8-chloro-3,7-dimethyl-octa-2,6-dienal undergo significant loss via reaction with ozone (>50%). The atmospheric lifetimes of the compounds investigated range from ca. 1.5–10 h. Given their short lifetimes, these compounds can be rapidly oxidised to form a range of stable compounds. The investigation of first-generation products from the OH-initiated oxidation of 5,6-dichloro-2-dichloromethyl-6-methyl-octa-1,3,7-triene, 1,6-dibromo-2,7-dichloro-3,7-dimethyl-oct-3-ene and 4-bromo-8-chloro-3,7-dimethyl-octa-2,6-dienal showed the formation of stable organic hydroperoxides, alcohols and carbonyl compounds which can have significant impact on cloud condensation nuclei as contributors of secondary organic aerosols. Release of free halogen can occur from subsequent product oxidation, notably photolysis of carbonyl type species and these are briefly considered.

Keywords: **marine environment; red macroalgae; acyclic halogenated monoterpenes; atmospheric lifetime; secondary organic aerosol**

INTRODUCTION

The chemical structures and bioactivities of over 80 acyclic halogenated monoterpenes, isolated from marine red macroalgae (Rhodophyta), have been reported in a series of comprehensive reviews of the marine natural product chemical literature over the past four decades (Faulkner, 1984; Faulkner, 2001; Kladi *et al.*, 2004; Lever *et al.*, 2020; Carrol *et al.*, 2020). The wide range of bioactivities associated with these compounds have been regularly reviewed (Cabrita *et al.*, 2010; Paul and Pohnert, 2011; Cikoš *et al.*, 2019) and include antibacterial, antifungal, antiviral, anti-inflammatory, antiproliferative, antitumour, anthelmintic, antioxidant, antifouling, antifeedant, cytotoxic, ichthyotoxic and insecticidal bioactivities. These volatile, marine secondary metabolites are produced in significant quantities by red macroalgae (Maliakal *et al.*, 2001; Barahona and Rorrer, 2003; Mann *et al.*, 2007). However, the variable factors that influence the production of marine monoterpenes in macroalgae are poorly understood (Hay, 1996; Wise, 2003; Kladi *et al.*, 2004; Cikoš *et al.*, 2019) and include *inter alia*: changes in season, reproductive phase of the macroalgae, levels of herbivory and/or microbial infection and availability of nutrients.

Of interest to us, is the possible fate of these volatile halogenated monoterpenes when they enter the atmosphere, either directly when intertidal algae are exposed to the atmosphere during low tide, or indirectly when these compounds diffuse into the water column and then into the atmosphere via wind driven processes (Liss and Slater, 1974; Hackenberg *et al.*, 2017). In this paper, we postulate what can be happened to these secondary metabolites if they reach the atmosphere and consequently what impact they can have on local and regional air composition.

Terpenes are known to have short atmospheric lifetimes as they react rapidly with atmospheric oxidants (e.g. OH radical, O_3, Cl radical and NO_3 radical). The measurements (Hallquist *et al.*, 2009; Jimenez *et al.*, 2009; Ehn *et al.*, 2014; Jokinen *et al.*, 2015; Berndt *et al.*, 2016) and modelling studies (Utembe *et al.*, 2011; Khan *et al.*, 2017) suggested that the oxidised species formed from the reactions of terpenes with oxidants present in the atmosphere can yield secondary organic aerosol (SOA) in the atmosphere. Thus, the marine terpenes have the potential to significantly influence local climate via formation of SOA which can act as nuclei for water droplet formation and ultimately generate clouds (Kim *et al.*, 2017), which, in turn, will reflect solar radiation and contribute to climate cooling in the lower troposphere. Although halogenation of terpenes will tend to have a deactivating effect on the reactivity with tropospheric oxidants to some extent (Atkinson, 1987), these atmospheric oxidative reactions of the marine secondary metabolites considered here are still likely to be sufficiently rapid to provide possible routes to SOA formation. In addition, the oxidation mechanisms also result in the release of Cl and Br atoms into the atmosphere. Both halogens participate in cyclical reactive processes that destroy ground level ozone, which is beneficial, as at this altitude ozone is a potent greenhouse gas and a powerful oxidant causing damage to plants (Vainonen and Kangasjärvi, 2015) and animals (Zhang *et al.*, 2019) and for Cl in particular, also contribute to the initiation of VOC oxidation.

Over 40 halogenated monoterpenes have been reported from the common intertidal red algal genus *Plocamium* and in this paper, we have predicted the likely major atmospheric degradation routes of a selection of 19 acyclic halogenated monoterpenes (**1–19,** see Figure 1) isolated from four *Plocamium* species (*P. cornutum, P. brasiliense, P. cartilagineum* and *P. corallorhiza*) collected from different regions of the world (Mynderse and Faulkner, 1975; Abreu and Galindro, 1996; Mann *et al.*, 2007; Afolayan *et al.*, 2009; Vasconcelos *et al.*, 2010); these compounds possess a range of halogenation extent and hence reactivity. We have used established methods discussed in detail in a later section to estimate their rate coefficients for reaction with the OH radical and ozone, which can consequently afford an approximation of the lifetime of the parent compound. The first-generation oxidised products and the very low volatility highly oxidised multifunctional (HOM) products formed from RO_2 isomerisation/auto-oxidation including H-shift reactions of RO_2 have been investigated concerning their contributions to SOA formation. We have estimated the fraction of the stable possible first-generation oxidation and HOM products from selected oxidation pathways and their vapour pressure. From these hypothetical data we assess the role which these compounds and their products play on aerosol formation and halogen release. The assessment methods used to estimate kinetic and mechanistic information do not distinguish between diastereoisomers and the compounds selected here are a single example of, in some cases, multiple diastereoisomers present in *Plocamium* and other red macroalgal species.

METHODS

Gas-phase rate coefficient estimation methods

OH radical reactions

The rate coefficients for reactions with OH radicals were estimated using the empirically-based structure–activity relationship (SAR) method of Kwok and Atkinson (1995). The SAR method is based upon a number of experimentally determined rate coefficients for volatile organic compounds. The SAR consists of a set of generic rate coefficients for H-atom abstraction and OH addition at a given carbon atom, which are defined in relation to the extent of substitution by alkyl groups. The rate coefficients are further modified to take account of the influence of neighbouring oxygenated and halogenated substituents. In the present work, the following additional assumptions were made:

- The generic rate coefficient for OH addition to CH(-R) = CH (-R) structures was taken to be the average of that given for cis- and trans- isomers in Kwok and Atkinson (1995).
- The substituent factor given for $-CH_2Cl$ groups, in relation to OH addition, was taken to apply to all $-CH_2X$, $-CHX_2$, -CH(X)- and -C(X)< groups, where X = Cl and Br.

Owing to a lack of kinetic data, the Kwok and Atkinson (1995) method does not cover reactions with conjugated trienes, for which there is one example in the current set of compounds (**12**). In the present work, the following additional assumptions were made:

- On the basis of the limited reported data for 1,3,5-hexatriene and 1,3,5-cycloheptatriene (Atkinson and Arey, 2003), a rate coefficient of 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} was assumed representative of OH addition to trienes with no more than one alkyl (R) substitution at each terminal carbon, i.e. CH(-R) = CHCH = CHCH = CH_2 and CH(-R) = CHCH = CHCH = CH(-R).
- Based on the SARs defined for conjugated dienes (Kwok and Atkinson, 1995), additional substitution of each R group was assumed to increase the rate coefficient by a factor of 1.35, up to a maximum rate coefficient of 3×10^{-10} cm^3 molecule^{-1} s^{-1}. For the reference structure CH (-R) = C(-R)C(-R) = CHCH = $C(-R)_2$, containing three additional R substituents (being relevant to Compound N), a rate coefficient of 2.46×10^{-10} cm^3 molecule^{-1} s^{-1} was therefore used.

O_3 reactions

The estimation method used for the reactions with O_3 was also derived from an empirically-based SAR method, developed by Atkinson, as reported in Calvert *et al.* (2000). This is more limited than the OH method, considering only addition of O_3 to monoalkenes and unconjugated polyalkenes. The related generic rate coefficients are very similar to those applied with the Master Chemical Mechanism, MCM (Jenkin *et al.*, 1997). The method was supplemented here to allow rough estimation of addition rate coefficients to conjugated dienes and trienes, and the impact of substituent groups, as summarised in Tables 1 and 2. These supplementary methods are subject to some uncertainty, owing to the highly limited dataset of relevant compounds.

Vapour pressure estimation methods

The vapour pressure of the halogenated monoterpenes and their oxidation products were estimated using the method of Nannoolal *et al.* (2008) in conjunction with species boiling points estimated by the method of Nannoolal *et al.* (2004). This had been previously identified (Booth *et al.*, 2010) as one of the best estimation methods for highly functionalised, low volatility compounds. A brief summary is repeated here: The method is based on group contributions and includes 207

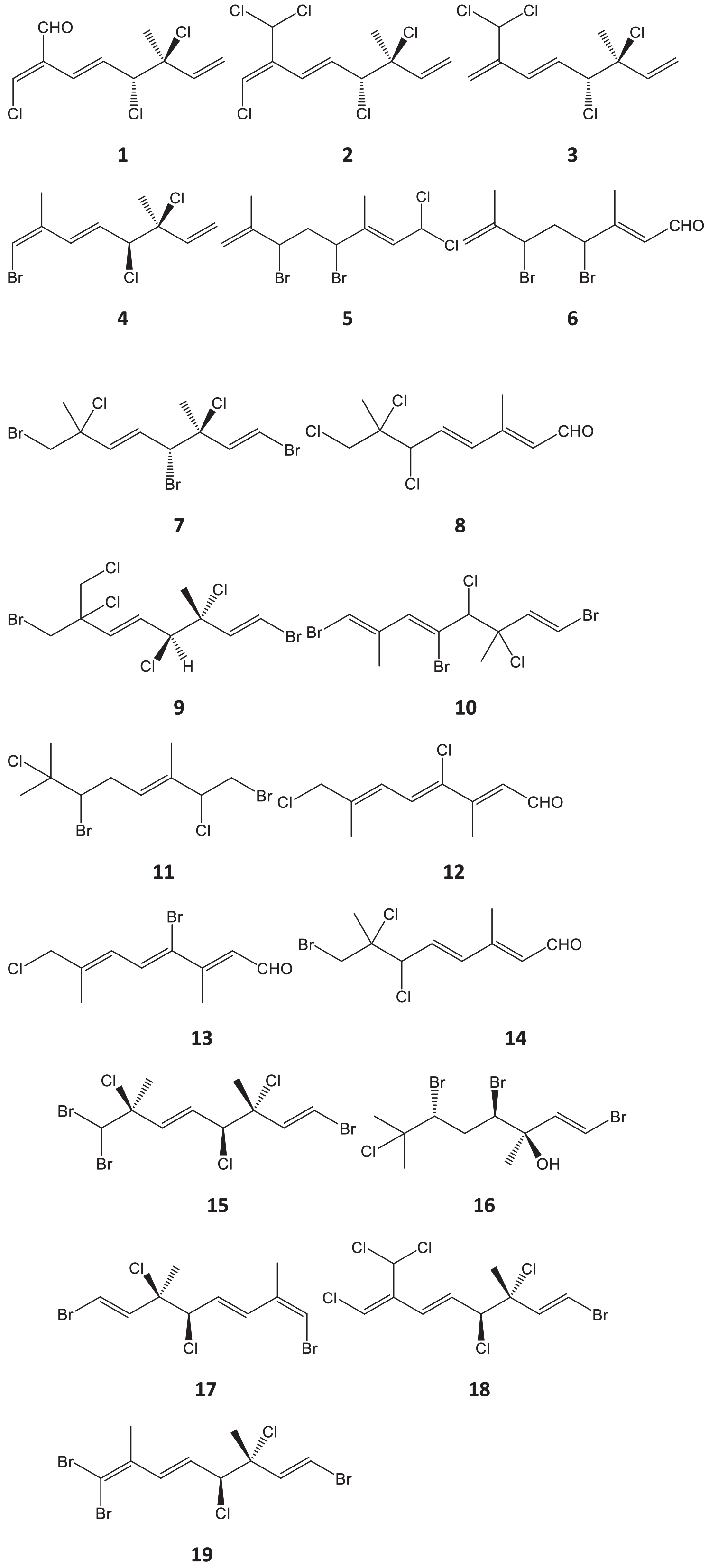


Figure 1. Halogenated acyclic monoterpenes isolated from four *Plocamium* species: **1**–**4** from *P. cornutum* (South Africa; Afolayan *et al.*, 2009); **5–8** from *P. corallorhiza* (South Africa, Mann *et al.*, 2007; Afolayan *et al.*, 2009,) **9**, **10** from *P. brasiliense* (Brazil; Vasconcelos *et al.*, 2010); **11** from *P. cartilagineum* (Portugal, Abreu and Galindro, 1996); **12**–**14** from *P. corallorhiza* (South Africa, Mann *et al.*, 2007) and **15**–**19** from *P. cartilagineum* (California; Mynderse and Faulkner, 1975).

Table 1. Group rate constants used for addition of O_3 to alkenes and conjugated dienes and trienes.

Structure	10^{17} k_{O3}	Comment
Alkenes		
$CH_2=CH(-R)$	1	Taken from Calvert *et al.* (2000).
$CH_2=C(-R)_2$	1.1	Taken from Calvert *et al.* (2000).
cis-CH(-R)=CH(-R)	12	Taken from Calvert *et al.* (2000). Average value of 15.5 used for CH(-R)=CH(-R) structure in the present work.
trans-CH(-R)=CH(-R)	19	
$CH(-R)=C(-R)_2$	40	Taken from Calvert *et al.* (2000).
$C(-R)_2=C(-R)_2$	110	Taken from Calvert *et al.* (2000).
Conjugated dienes		
$CH_2=C(-R)CH=CH_2$	1.3	Based on isoprene (Atkinson and Arey, 2003).
$CH_2=C(-R)C(-R)=CH_2$	2.6	Based on 2,3-dimethyl-1,3-butadiene (Atkinson and Arey, 2003).
$CH_2=CHCH=CH(-R)$	4	Based on 1,3-pentadiene (Atkinson and Arey, 2003).
$CH_2=C(-R)CH=CH(-R)$	8	Based on 2-methyl-1,3-pentadiene (Atkinson and Arey, 2003).
$CH_2=CHC(-R)=CH(-R)$	8	Addition of -R increases k by factor of 2 (relative to 1,3-pentadiene).[a]
$CH_2=C(-R)C(-R)=CH(-R)$	16	Addition of -R increases k by factor of 2 (relative to 2-methyl-1,3-pentadiene).[a]
CH(-R)=CHCH=CH(-R)	34	Based on 2,4-hexadiene (Atkinson and Arey, 2003).
CH(-R)=CHC(-R)=CH(-R)	68	Addition of -R increases k by factor of 2 (relative to 2,4-hexadiene).[a]
CH(-R)=C(-R)C(-R)=CH(-R) $CH(-R)=C(-R)CH=C(-R)_2$	136	Addition of -R increases k by factor of 2 (relative to CH(-R)=CHC(-R)=CH(-R)).[a]
Conjugated trienes		
$CH_2=CHCH=CHCH=CH_2$	2.6	1,3,5-hexatriene (Atkinson and Arey, 2003).
CH(-R)=CHCH=CHCH=CH(-R)	5.4	Based on 1,3,5-cycloheptatriene (Atkinson and Arey, 2003).
Other conjugated trienes		Addition of successive -R groups in conjugated trienes increases k by a factor of 1.44.[b]

Note: Units of *k* is cm^3 $molecule^{-1}$ s^{-1}.

[a] The factor of 2 is derived from the trend observed on going from 1,3-butadiene (0.63), to isoprene (1.3) and 2,3-dimethyl-1,3-butadiene (2.6); and from 1,3-pentadiene (4.3) to 2-methyl-1,3-pentadiene (8.0).

[b] The factor of 1.44 (= $(5.4/2.6)^{1/2}$) is derived from the data for 1,3,5-hexatriene (2.6) and 1,3,5-cycloheptatriene (5.4). For the reference structure $CH(-R)=C(-R)C(-R)=CHCH=C(-R)_2$, containing five -R substituents (being relevant to Compound N), a rate coefficient of $2.6 \times 1.44^5 = 16.1$ (in units of 10^{-17} cm^3 $molecule^{-1}$ s^{-1}) was therefore used.

Table 2. Substituent factors used for addition of O_3 to alkenes and conjugated dienes and trienes.

Substituent group	Factor[a]	Comment
–X (X = Cl, Br)	0.01	Based on a comparison of 2-chloropropene with 2-methylpropene.[b]
$–CH_2X$, $–CHX_2$, –CH(X)–, –C(X)< (X = Cl, Br)	0.24	Based on a comparison of 3-chlorobut-1-ene with 3-methylbut-1-ene.[c]
–CHO	0.11	Based on a comparison of methacrolein with 2-methypropene.[d]
–C(=O)–	0.54	Based on a comparison of methyl vinyl ketone with 3-methylbut-1-ene.[e]
$–CH_2OH$, –CH(OH)–, –C(OH)<	1	Based on a comparison of 2-methyl-3-buten-2-ol with 3-methylbut-1-ene.[f]

[a] The substituent factor relates to substitution of an alkyl group by the given group.

[b] Reference alkene data taken from Atkinson and Arey (2003). Data for chloropropene taken from Leather *et al.* (2011). It should also be noted that data for cis-1,2-dichlororoethene, trans-1,2-dichlororoethene, trichloroethene and tetrachloroethene (Leather *et al.*, 2011) are consistent with respective factors of 0.006, 0.02, 0.01 and 0.006 for each Cl group added (average ≈ 0.01).

[c] Reference alkene data and data for methacrolein taken from Atkinson and Arey (2003).

[d] Reference alkene data and data for methylvinyl ketone taken from Atkinson and Arey (2003).

[e] Reference alkene data taken from Atkinson and Arey (2003).

[f] Approximate data for 2-methyl-3-buten-2-ol (Fantechi *et al.*, 1998) are consistent with little influence from the hydroxyl group.

primary and secondary groups and group interactions. First, this is used to calculate a normal boiling point, T_b for the compound of interest:

$$T_b = \frac{\sum_i N_i C_i}{n^a + b} + c \qquad (1)$$

where N_i is the number of groups of type i, C_i the group contribution of group i, a, b, c are adjustable parameters from a linear regression of the equation to experimental boiling points, and n is the total number of atoms in the molecule (except hydrogen). The boiling point estimate is discussed in further detail in Nannoolal *et al.* (2004). Secondly, using the boiling point as an input, the vapour pressure is calculated by extrapolating this down to the temperature of interest. The vapour pressure is given by:

$$\log_{10} P_L^0 = (4.102 + dB)\left[\frac{T - T_b}{T - 0.125 T_b}\right] \qquad (2)$$

where dB adjusts the slope of the vapour pressure curve and is calculated by a group contribution method:

$$dB = \left(\sum N_i C_i + GI\right) - 0.176055 \qquad (3)$$

where the first term in the brackets is the sum of the primary and secondary group contributions, and the second term is

Table 3. Summary of compounds assessed and their estimated rate coefficients and lifetimes based on an OH radical concentration of 1 × 10^6 molecule cm^{-3} and an ozone concentration of 30 ppbv (~ 7.5 × 10^{11} molecule cm^{-3} at the Earth's surface).

Compound	Name	SMILES	Molecular formula	10^{11}kOH (cm^3 $molecule^{-1}$ s^{-1})	$10^{20}k_{O3}$ (cm^3 $molecule^{-1}$ s^{-1})	k_{O3}/k_{OH}	Gas-phase Lifetime Hours	Vapour Pressure Pa
1	5,6-Dichloro-2-chloromethylene-6-methyl-octa-3,7-dienal	C = CC(C)(Cl)C(Cl)/C = C/C (C = O)=C\Cl	$C_{10}H_{11}Cl_3O$	4.75	258	5.43×10^{-8}	5.6	0.111
2	1,5,6-Trichloro-2-dichloromethyl-6-methyl-octa-1,3,7-triene	C = CC(C)(Cl)C(Cl)/C = C/C (C(Cl)Cl)=C\Cl	$C_{10}H_{11}Cl_5$	5.09	279	5.48×10^{-8}	5.3	0.083
3	5,6-Dichloro-2-dichloromethyl-6-methyl-octa-1,3,7-triene	C = C(C(Cl)Cl)/C = C/C(Cl)C (C)(Cl)C = C	$C_{10}H_{12}Cl_4$	12.9	701	5.45×10^{-8}	2.1	0.346
4	1-Bromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	C = CC(C)(Cl)C(Cl)/C = C/C (C)=C\Br	$C_{10}H_{13}BrCl_2$	5.80	403	6.95×10^{-8}	4.6	0.937
5	3,5-Dibromo-8,8-dichloro-2,6-dimethyl-octa-1,6-diene	C = C(C)C(Br)CC(Br)/C (C)=C/C(Cl)Cl	$C_{10}H_{14}Br_2Cl_2$	9.09	2570	2.83×10^{-7}	2.5	7.13
6	4,6-Dibromo-3,7-dimethyl-octa-2,7-dienal	C = C(C)C(Br)CC(Br)/C (C)=C/C = O	$C_{10}H_{14}Br_2O$	7.97	1320	1.66×10^{-7}	3.1	15.6
7	1,4,8-Tribromo-3,7-dichloro-3,7-dimethyl-octa-1,5-diene	BrC(C(Cl)(C)\C = C/Br)/C = C/ C(Cl)(C)CBr	$C_{10}H_{13}Br_3Cl_2$	4.69	1050	2.23×10^{-7}	5.1	5.39
8	6,7,8-Trichloro-3,7-dimethyl-octa-2,4-dienal	C\C(/C = C/C(Cl)C (C)(Cl)CCl)=C/C = O	$C_{10}H_{13}Cl_3O$	6.66	1800	2.70×10^{-7}	3.5	0.089
9	1,8-Dibromo-3,4,7-trichloro-7-chloromethyl-3-methyl-octa-1,5-diene	ClC(C(Cl)(C)\C = C/Br)/C = C/ C(CCl)(Cl)CBr	$C_{10}H_{12}Br_2Cl_4$	4.70	1050	2.23×10^{-7}	5.1	0.140
10	1,4,8-Tribromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	C/C(/C = C(Br)/C(Cl)C (C)(Cl)\C = C/Br)=C/Br	$C_{10}H_{11}Br_3Cl_2$	2.97	40.5	1.36×10^{-8}	9.3	0.168
11	1,6-Dibromo-2,7-dichloro-3,7-dimethyl-oct-3-ene	CC(C)(Cl)C(Br)C/C = C(C)/C (Cl)CBr	$C_{10}H_{16}Br_2Cl_2$	6.80	9600	1.41×10^{-6}	2.0	2.72
12	4,8-Dichloro-3,7-dimethyl-octa-2,4,6-trienal	C\C(CCl)=C/C = C(Cl)/C (C)=C/C = O	$C_{10}H_{12}Cl_2O$	3.09	4.25[b]	1.38×10^{-9}[a]	9.0	0.022
13	4-Bromo-8-chloro-3,7-dimethyl-octa-2,6-dienal	C\C(CCl)=C/CC(Br)/C(C)=C/ C = O	$C_{10}H_{14}BrClO$	10.6	10700	1.00×10^{-6}	1.5	2.37
14	8-Bromo-6,7-dichloro-3,7-dimethyl-octa-2,4-dienal	BrCC(Cl)(C)C(Cl)/C = C/C (C)=C/C = O	$C_{10}H_{13}BrCl_2O$	6.65	1800	2.70×10^{-7}	3.5	0.371
15	1,8,8-Tribromo-3,4,7-trichloro-3,7-dimethyl-octa-1,5-diene	ClC(C(Cl)(C)\C = C/Br)/C = C/ C(C)(Cl)C(Br)Br	$C_{10}H_{12}Br_3Cl_3$	4.69	1050	2.24×10^{-7}	5.1	0.146
16	1,4,6-Tribromo-7-chloro-3,7-dimethyl-oct-1-en-3-ol	CC(C)(Cl)C(Br)CC(Br)C (C)(O)\C = C/Br	$C_{10}H_{16}Br_3ClO$	2.68	155	5.79×10^{-8}	9.9	1.99
17	1,8-Dibromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	C/C(/C = C/C(Cl)C(C)(Cl)\C = C/Br)=C/Br	$C_{10}H_{12}Br_2Cl_2$	4.99	200	4.02×10^{-8}	5.4	1.83
18	8-Bromo-1,5,6-trichloro-2-chloromethyl-6-methyl-octa-1,3,7-triene	CC(\C = C/Br)(Cl)C(Cl)/C = C/ C(CCl)=C\Cl	$C_{10}H_{11}BrCl_4$	4.11	76.4	1.86×10^{-8}	6.7	0.425
19	1,1,8-Tribromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	C/C(/C = C/C(Cl)C(C)(Cl)\C = C/Br)=C(Br)/Br	$C_{10}H_{11}Br_3Cl_2$	2.99	40.5	1.35×10^{-8}	9.2	0.168

The MCM methodology considers OH-initiated chemistry for all relevant VOCs. O_3-initiated chemistry is also treated when $k_{O3}/k_{OH} > 10^{-8}$, and $k_{O3} > 1.0 \times 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1} (Jenkin *et al.*, 1997). Neither of these criteria is fulfilled for Compound N, based on the estimation methods applied here.

Table 4. The table shows the contributions of OH- and O_3-initiated oxidation, assuming $[O_3]/[.OH] = 7.5 \times 10^5$.

Compound	Name	f_{OH}	f_{O3}	Note
1	5,6-Dichloro-2-chloromethylene-6-methyl-octa-3,7-dienal	94.8%	5.2%	a,b
2	1,5,6-Trichloro-2-dichloromethyl-6-methyl-octa-1,3,7-triene	94.8%	5.2%	A
3	5,6-Dichloro-2-dichloromethyl-6-methyl-octa-1,3,7-triene	94.8%	5.2%	A
4	1-Bromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	93.5%	6.5%	A
5	3,5-Dibromo-8,8-dichloro-2,6-dimethyl-octa-1,6-diene	78.0%	22.0%	A
6	4,6-Dibromo-3,7-dimethyl-octa-2,7-dienal	85.8%	14.2%	a,b
7	1,4,8-Tribromo-3,7-dichloro-3,7-dimethyl-octa-1,5-diene	81.7%	18.3%	a
8	6,7,8-Trichloro-3,7-dimethyl-octa-2,4-dienal	78.8%	21.2%	a,b
9	1,8-Dibromo-3,4,7-trichloro-7-chloromethyl-3-methyl-octa-1,5-diene	81.8%	18.2%	a
10	1,4,8-Tribromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	98.7%	1.3%	a
11	1,6-Dibromo-2,7-dichloro-3,7-dimethyl-oct-3-ene	41.5%	58.5%	a
12	4,8-Dichloro-3,7-dimethyl-octa-2,4,6-trienal	99.9%	0.1%	a,b
13	4-Bromo-8-chloro-3,7-dimethyl-octa-2,6-dienal	50.0%	50.0%	a,b
14	8-Bromo-6,7-dichloro-3,7-dimethyl-octa-2,4-dienal	78.7%	21.3%	a,b
15	1,8,8-Tribromo-3,4,7-trichloro-3,7-dimethyl-octa-1,5-diene	81.7%	18.3%	a
16	1,4,6-Tribromo-7-chloro-3,7-dimethyl-oct-1-en-3-ol	94.5%	5.5%	a
17	1,8-Dibromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	96.1%	3.9%	a
18	8-Bromo-1,5,6-trichloro-2-chloromethyl-6-methyl-octa-1,3,7-triene	98.2%	1.8%	a
19	1,1,8-Tribromo-5,6-dichloro-2,6-dimethyl-octa-1,3,7-triene	98.7%	1.3%	a

[a] Contributions assume removal is only by reaction with OH radical and O_3, with $[O_3]/[.OH] = 7.5 \times 10^5$. In all cases additional removal may occur by photolysis, via C-X bond cleavage, although this is likely to be very slow in comparison.

[b] Removal may also occur by photolysis at the carbonyl group, although this is likely to be slow in comparison.

the group interaction:

$$\mathrm{GI} = \frac{1}{n}\sum_{i=1}^{m}\sum_{j=1}^{m}\frac{C_{i-j}}{m-1} \tag{4}$$

where $C_{i\text{–}j} = C_j - \mathrm{I}$ and m, n are the total number of interacting groups and the number of (non-hydrogen) atoms in the molecule, respectively. The vapour pressure estimate is discussed in further detail in Nannoolal *et al.* (2008). The vapour pressures were calculated from SMILE strings generated for each compound and processed on the University of Manchester multiphase System online Property prediction (UManSysProp) facility (Barley and McFiggans, 2010; O'Meara *et al.*, 2014).

Method for gas-aerosol partitioning of the oxidation products

The representation of SOA formation is based on partitioning between the vapour and condensed phases of the species formed from the considered halogenated monoterpenes over the 1st generations of oxidation. The adsorption coefficient value, $6.2 \times 10^{-3}\ \mathrm{m^3\ \mu g^{-1}\ s^{-1}}$, estimated for collision of the gas molecules with a monodispersed aerosol of 50 nm diameter, is multiplied with condensed organic material concentrations to calculate adsorption rate coefficient of gas molecules. The desorption rate coefficient of aerosol is calculated using the adsorption rate and partitioning coefficients which is calculated using Pankow's expression (Pankow, 1994) and subcooled vapour pressures of the gas molecules. The equilibrium partitioning coefficient is defined as

$$K_p = \frac{7.501 \times 10^{-9} RT}{\mathrm{MW} \mathrm{p}_{\mathrm{L}}^{\mathrm{o}}} \tag{5}$$

where γ is the activity coefficient, $\mathrm{p}_{\mathrm{L}}^{\mathrm{o}}$ is the saturated vapour pressure, MW is the molecular weight of the species, R is the molar gas constant and T is the temperature.

Assuming $\gamma = 1$ as shown in Jenkin (2004) and using the calculated vapour pressure of the 1st generation stable oxidation products as discussed in section 2.3, we calculated K_p which will determine the extent of gas-aerosol partitioning of these stable species as shown in Odum *et al.* (1996).

$$\frac{C_a}{C_g} = K_p C_o \tag{6}$$

where C_a, C_g and C_o are the concentrations of the aerosol phase oxidation product, gas phase oxidation product and the total concentration of condensed organic materials (in $\mu\mathrm{g\ m^{-3}}$), respectively.

RESULTS AND DISCUSSION

Summary of Kinetic results

The estimated gas-phase rate coefficients for the reactions of the selected halogenated terpenes with OH radical and ozone (O_3) is summarised in Table 3, together with the estimated vapour pressure and atmospheric lifetime. The rate coefficients of Cl atoms with terpenes are about one order of magnitude larger than for OH (Timerghazin and Ariya, 2001), but the Cl atom concentration originating from heterogeneous reaction cycles involving sea-salt is believed to generate concentrations ~1% of that of OH in the marine boundary layer. Thus, the contribution of Cl atoms in the oxidation process of halogenated terpenes is assumed to be minor compared with that for OH. However, a few indirect experiments suggest that Cl atom concentrations could be higher in marine locations and so Cl atom removal may be significant in certain locations (e.g. Spicer *et al.*, 1998). Some of the halogenated terpenes in Table 3 (1,6,8,12,13,14) contain an aldehydic group which can undergo photolysis in the presence of solar radiation, but previous studies (O'Connor *et al.*, 2006; Jiménez, *et al.*, 2007; Mellouki *et al.*, 2015) showed

Table 5. Isolated yields of halogenated monoterpenes per dry mass of alga.

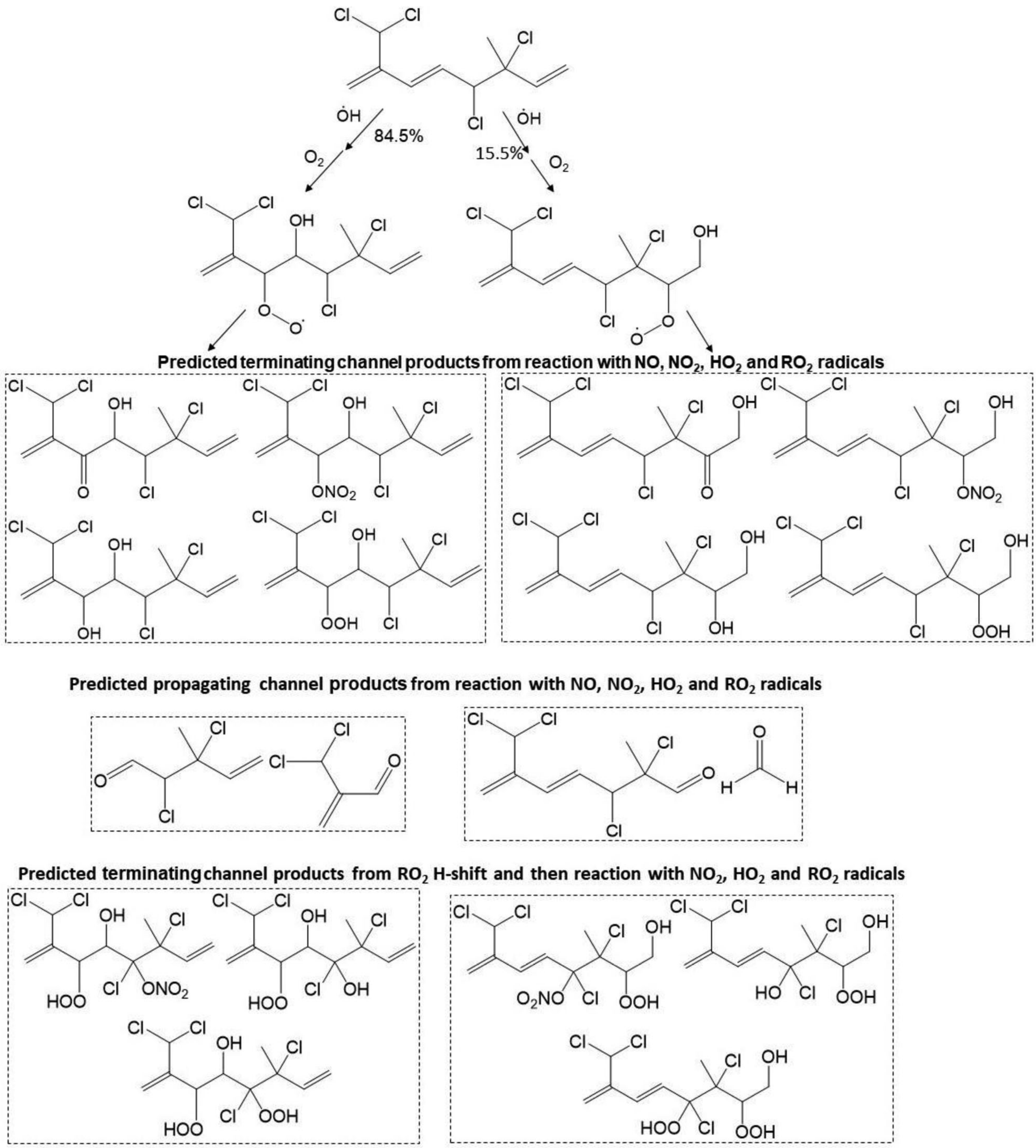
Compound	Sample collection site	Initial dry mass of alga (g) extracted	Mass of isolated monoterpene (g)	% isolated yield based on dry mass of alga	References
1	Kalk bay, Western Cape of South Africa	26.02	0.065	0.25%	Afolayan *et al.* (2009)
2	Noordhoek beach, Port Elizabeth South Africa	16.93	1.14	6.73%	Afolayan *et al.* (2009)
2	Kalk bay, Western Cape of South Africa	26.02	0.186	0.71%	Afolayan *et al.* (2009)
3	Kalk bay, Western Cape of South Africa	26.02	0.004	0.02%	Afolayan *et al.* (2009)
4	Kalk bay, Western Cape of South Africa	26.02	0.013	0.05%	Afolayan *et al.* (2009)
5	South east coast of South Africa	31.5	0.01	0.03%	Mann *et al.* (2007)
6	South east coast of South Africa	31.5	0.061	0.19%	Mann *et al.* (2007)
7	South east coast of South Africa	31.5	0.009	0.03%	Mann *et al.* (2007)
7	Kalk bay, Western Cape of South Africa	14.3	0.0011	0.008%	Knott *et al.* (2005)
11	Sesimba, west coast of Portugal	12.00	0.028	0.23%	Abreu and Galindro (1996)
12	South east coast of South Africa	31.5	0.002	0.007%	Mann *et al.* (2007)
13	South east coast of South Africa	31.5	0.001	0.003%	Mann *et al.* (2007)
14	South east coast of South Africa	31.5	0.002	0.007%	Mann *et al.* (2007)
17	Sea hare Aplysia California	18.8	0.0104	0.055%	Mynderse and Faulkner (1975)
18	Sea hare Aplysia California	18.8	0.0254	0.135%	Mynderse and Faulkner (1975)
19	Sea hare Aplysia California	18.8	0.0261	0.139%	Mynderse and Faulkner (1975)

Note: No data available for compounds (8), (9), (10), (15) and (16).

that photolysis loss for unsaturated aldehydes (even for conjugated aldehydes) is minor compared with the loss process by OH radical. Thus, the reaction of halogenated monoterpenes with Cl and the photolysis loss has not been considered in our kinetic analysis. Rate coefficients for reaction with OH radical vary between $\sim 2 \times 10^{-11}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$ (around 1 in 5 successful collisions) to $\sim 1 \times 10^{-11}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$ (around 1 in 10 successful collisions). Most compounds (90%) in the selected cohort of 19 halogenated marine monoterpenes presented here have predicted atmospheric lifetimes > 2 and < 10 h (Table 3). The vapour pressures of the compounds are found to be in the range of 0.08–15.6 Pa. The fractional contribution from reaction with OH radical and O_3 (Table 4) suggests that O_3-initiated oxidation can be considered a minor atmospheric oxidation process for this majority of halogenated marine monoterpenes and therefore be omitted as a simplification in atmospheric models. The short lifetimes of the compounds suggest that they can affect local and regional atmospheric composition depending on their emission rates and the products formed, the extent of which will have a dependence on meteorology (e.g. wind speed and wind direction). Although OH radical dominates loss of the halogenated monoterpenes, compound **11**(1,6-dibromo-2,7-dichloro-3,7-dimethyl-oct-3-ene) and compound **13**(4-bromo-8-chloro-3,7-dimethyl-octa-2,6-dienal) behave differently, where their losses via reaction with O_3 are around 60 and 50%, respectively.

Possible influence of halogenated, marine monoterpenes on aerosol production

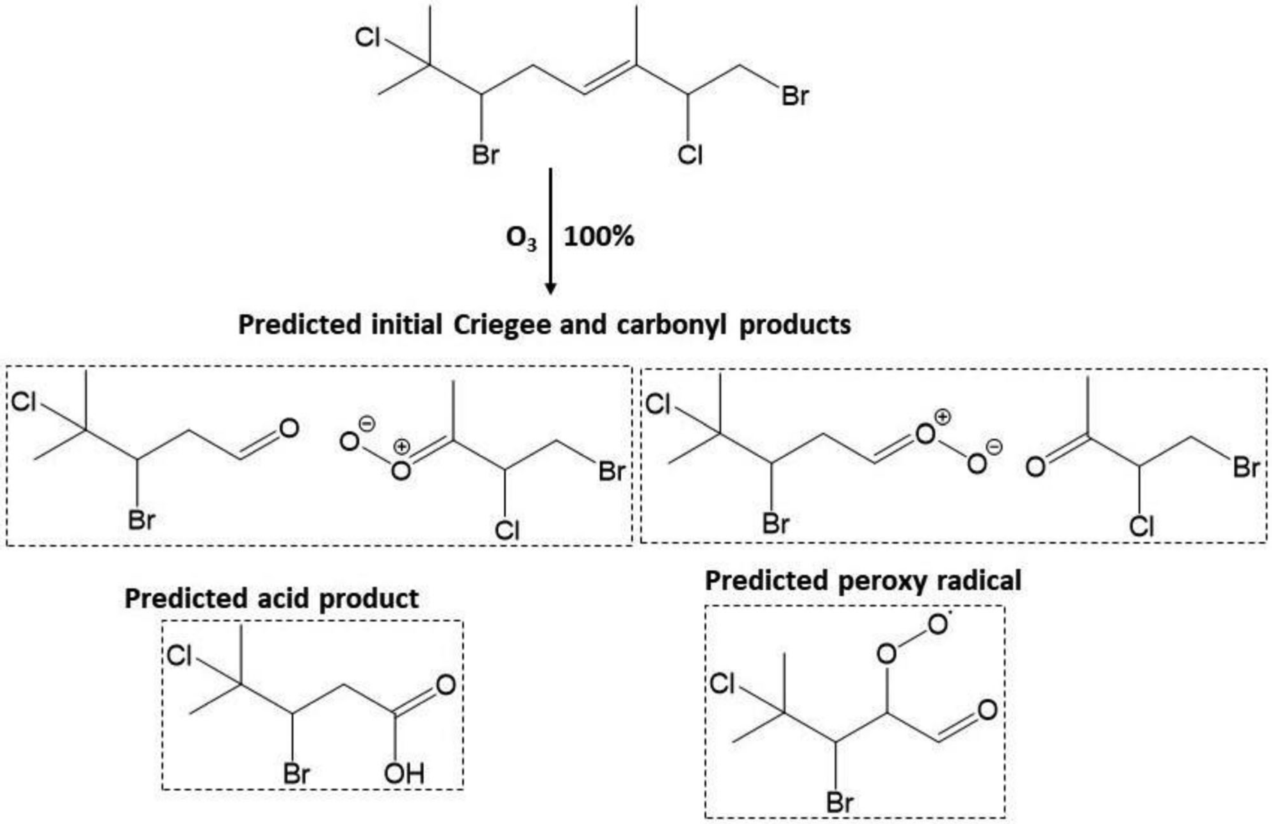
The understanding of marine monoterpene emissions and the characterisation of their degradation products are important to constrain global predictions of cloud condensation nuclei (CCN) sources, properties and abundances in the marine environment. Myriokefalitakis *et al.* (2010) showed that the annual global marine SOA from monoterpene oxidation is minor compared with that from the oxidation of DMS and marine amines. However, Kim *et al.* (2017) found a mean monoterpene sea-to-air emission fluxes of 2.6×10^7 molecules $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, translated to ~5 ppt monoterpenes which could be responsible for the nucleation rates of particles 1.7 nm in diameter ($J_{1.7}$) of $<10^{-3}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. Hu *et al.* (2013) also showed that the monoterpene-derived SOA concentrations were as large as $11\,\mathrm{ng\,m}^{-3}$ during phytoplankton blooms. We investigated the possible influence of halogenated marine monoterpenes on aerosol formation to determine their importance in marine atmospheric chemistry.



Scheme 1. Predicted major peroxy radicals, and terminating and propagating channel products from the reaction of atmospheric OH radical with the Δ^3 and Δ^7 olefins in **3**. Both cohorts of channel products are proposed from reaction of RO_2, with NO, NO_2, HO_2 and RO_2 radicals.

In order to estimate the impact of the atmospheric oxygenation products of halogenated monoterpenes on aerosol production in the intertidal zone during, for example, low tide, a number of factors need to be considered.

First, an estimate of the biomass of monoterpene producing species of alga occurring in the intertidal zone. In an extensive comparative and quantitative study of the trophic structure of rocky intertidal communities of the Cape Peninsular, South Africa, McQuaid and Branch (1985) postulated a mean weighted biomass of primary producers (macroalgae) with a dried mass range of 197–710 gm^{-2} on exposed beaches around the Cape Peninsular and a diversity of 9–31 species of macroalgae in each m^2 quadrat. *P. cornutum*, the source of **1–4,** was collected from the exposed beaches near Kalk Bay on the Cape Peninsular (Afolayan *et al.*, 2009) in a study area, for which McQuaid and Branch had earlier established an average macroalgal biomass of 304 gm^{-2} and recorded 31 different macroalgal species. The contribution of *P. cornutum* to the macroalgal diversity in this study area was not quantified by McQuaid and Branch (1985).



Scheme 2. Predicted major Criegee and carbonyl products, acid product and peroxy radical formed from reaction of atmospheric O_3 at the Δ^5 olefin in **11**.

Second, estimating the amount of monoterpene present in a marine alga. The volatility of marine monoterpenes hampers an accurate measurement of the yield of these compounds *per* dry mass of their algal source (macroalgae can contain as much as 85% seawater, John Bolton, Personal Communication) as significant amounts of these compounds can be lost during the drying and isolation process. Therefore, isolated yields of marine algal monoterpenes following the contemporary lyophilisation, extraction and chromatography protocols reported in the marine natural products literature, is considered an underestimate of the *in vivo* concentrations of these compounds.

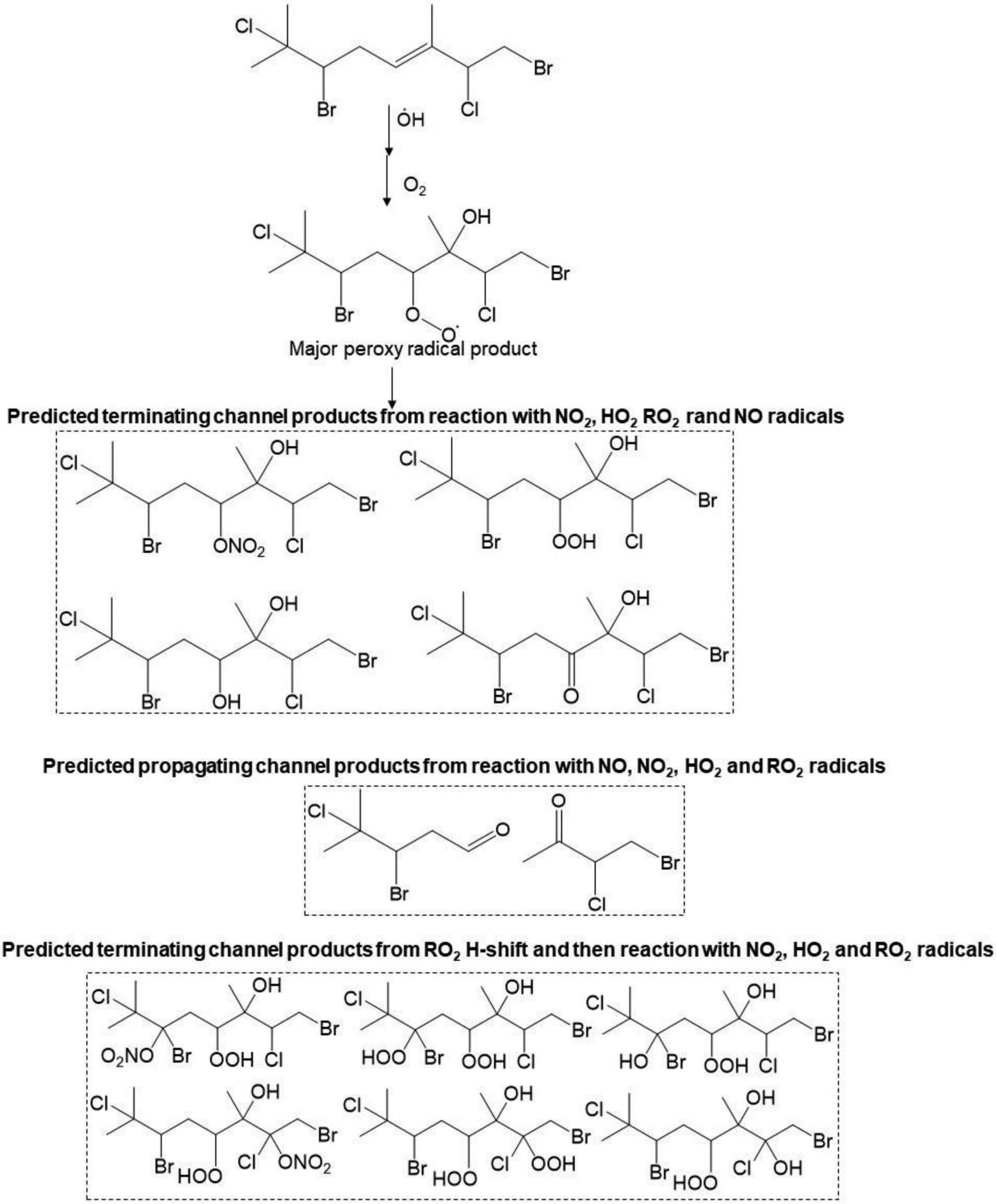
The isolated yields of compounds **1–19** per dry mass of alga (Table 5) showed a range of yields (0.01–6.73%) of monoterpenes is produced from the sample collected from different marine environments. Interestingly, the specimens of *P. cornutum* collected at Noordhoek, Port Elizabeth (750 kms due east of Kalk Bay), afforded predominantly **2** in a significantly higher yield of 6.7% per dry mass of macroalgae (1.14 g of compound **2** from 16.93 g dry mass) than that collected from Kalk Bay on the west coast of South Africa (yield of 0.71% from 26.02 g dry mass) due to the geographical variation of halogenated metabolites (Afolayan *et al.*, 2009).

Possible atmospheric oxidation products of compounds 3, 11 and 13

Of the 19 acyclic, halogenated, macroalgal monoterpenes presented in Figure 1, we have focussed our attention on three short-lived compounds (**3**, **11** and **13**). We postulate that these compounds can influence aerosol production on either a localised or even a macro scale when the three algal species that produce these compounds are exposed during low tide.

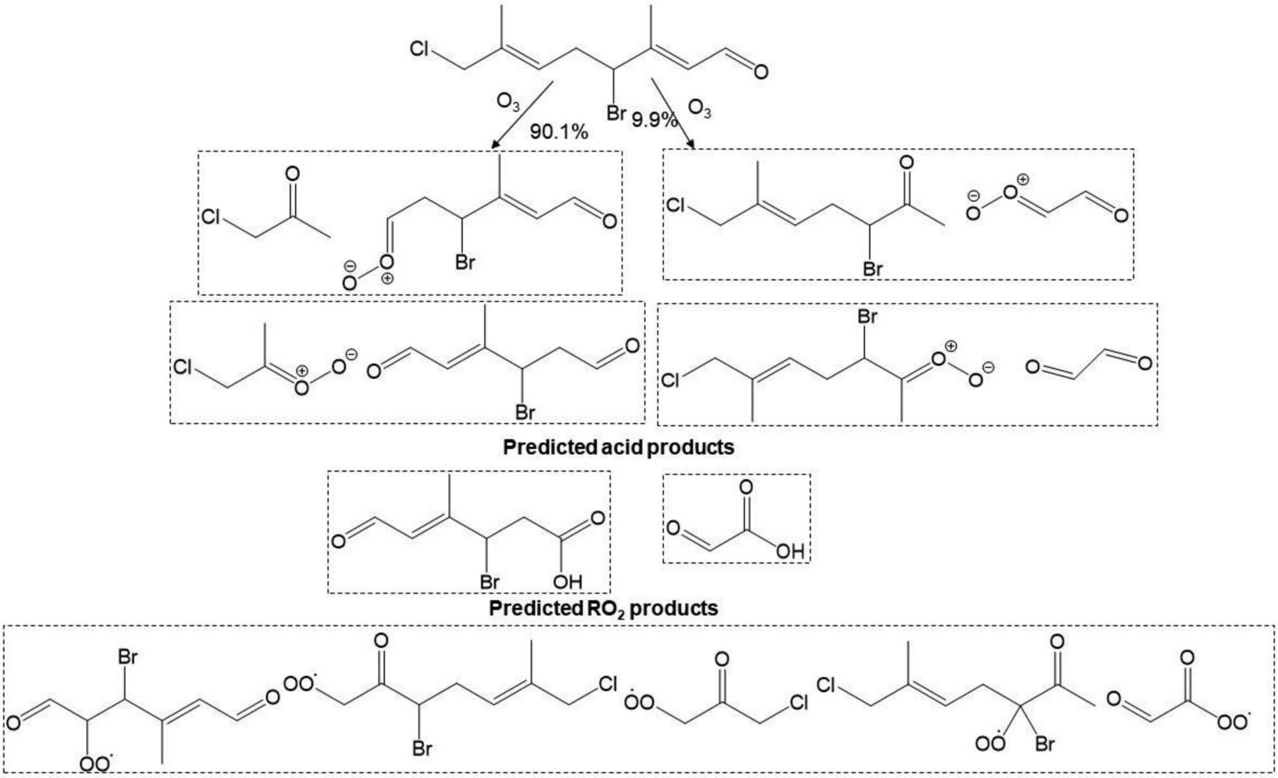
In order to understand the atmospheric implications of three halogenated monoterpenes, one must consider the chemistry and the impacts associated with their degradation products. Major mechanistic features of the OH- and O_3-initiated chemistry of compounds **3**, **11** and **13** with the shortest predicted atmospheric lifetimes of 2.1, 2 and 1.5 h, respectively are summarised schematically in the section that follows. In all cases, the OH initiated chemistry is generally dominated by addition to one or more alkene, diene or triene groups, although a significant H abstraction route also contributes for those species possessing a -CHO group (compound **13**). For each parent compound (or group of parent compounds), the structures of likely first-generation oxidation products are illustrated, following classic atmospheric chemistry reaction sequences after the initiation reactions. For simplicity, in the current assessment, the formation of only one peroxy radical (RO_2) is presented following OH addition to alkene or conjugated diene or triene structures. In each case, the presented RO_2 is judged to be the major contributor to the isomeric set of RO_2 radicals that can potentially be formed (consisting of 2, 6 and 12 isomers in the cases un-symmetric alkenes, conjugated dienes and conjugated trienes, respectively).

For compound **3**, OH radical oxidation almost exclusively dominates with a postulated gas phase lifetime of 2.1 h. The predicted product analysis from the OH radical oxidation of this compound suggests the formation of all first-generation



Scheme 3. Proposed major peroxy radical, and terminating and propagating channel products from the reaction of atmospheric OH radical with the Δ^5 olefin in **11**. Both cohorts of channel products are proposed from reaction of RO_2, with NO, NO_2, HO_2 and RO_2 radicals.

terminating products, e.g. organic hydroperoxides, alcohols, carbonyl compounds, organic nitrates which retain all four chlorine atoms (Scheme 1). Similar types of products are formed from the OH initiated oxidation of compounds **11** and **13** with predicted atmospheric lifetimes of ≤2 h which contain all chlorine/bromine atoms (Schemes 3 and 5). However, the rapid unimolecular RO_2 H-shift (autooxidation) through 6-member ring transition states can form very low volatility highly oxidised multifunctional (HOM) products shown in Schemes 1, 3 and 5. Conversely, O_3 initiated

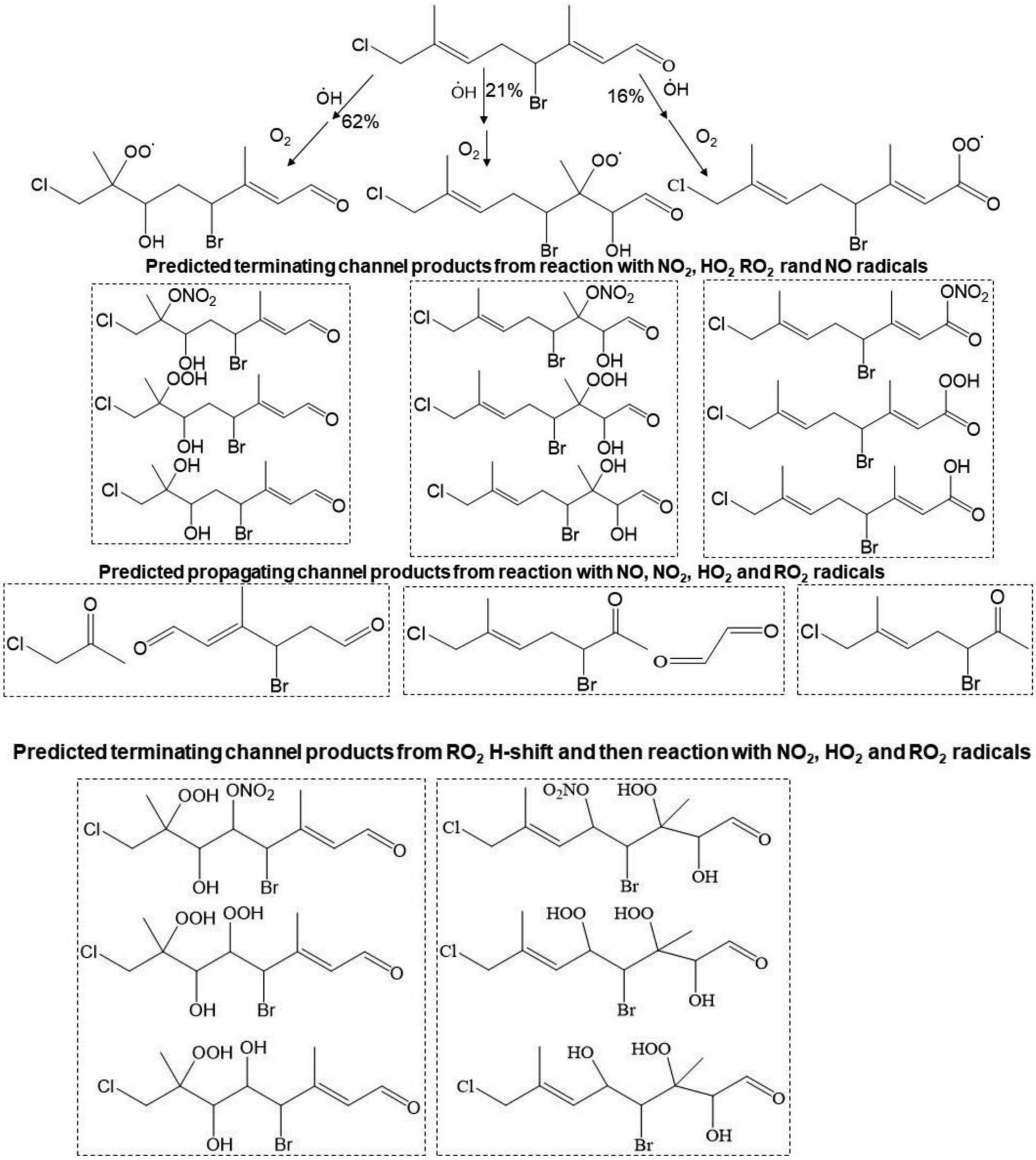


Scheme 4. Predicted major Criegee and carbonyl products, acid product and peroxy radicals formed from reaction of atmospheric O_3 at the Δ^2 and Δ^6 olefins in **13**.

oxidation can play a significant role in the oxidation of compounds **11** and **13**. Both carbonyl and acid products are postulated to form from bimolecular reactions of the stabilised Criegee intermediate (SCI) formed from the ozonolysis of compounds **11** and **13**. In addition, the peroxy radical is hypothesised to form via the hydroperoxide Criegee decomposition mechanism which is available for one Criegee intermediate. The predicted products from O_3 initiated oxidation of **11** and **13** are presented in Schemes 2 and 4.

The NO_x level is low (typically less than <10 ppt) in the marine boundary layer, thus peroxy-peroxy radical self- or/and cross-reactions will dominate leading to the formation of either carbonyl and alcohol or organic hydroperoxide (ROOH). The peroxy radical self-reactions act to slow the production of ozone (Lightfoot *et al.*, 1992), thus impacting the oxidation cycle in the marine environment. Depending on the volatility, organic hydroperoxides, alcohols and carbonyl compounds can be partitioned with the particle phase to form SOA (Paulot *et al.*, 2009; Utembe *et al.*, 2011) which can play an important role by affecting the number and composition of CCN in the marine boundary layer.

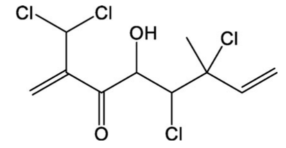
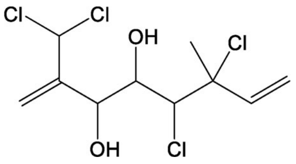
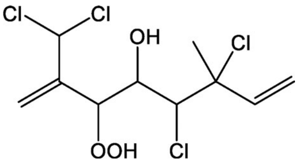
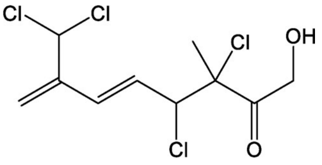
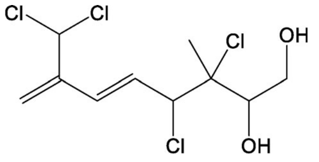
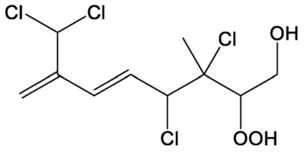
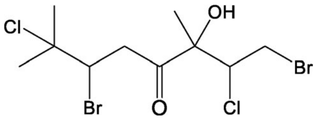
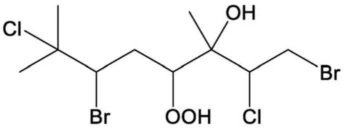
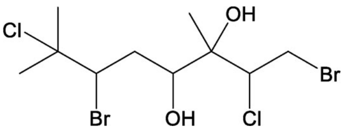
Using the fraction yields of monoterpenes from dry algae (Table 5), OH radical oxidation mechanisms of monoterpenes (Schemes 1, 3 and 5), their first generation OH-oxidation products yields (Table 4 and Schemes 1, 3 and 5), the OH radical oxidation rate coefficients (Table 3), steady-state concentrations of OH, HO_2 and RO_2 radicals taken from STOCHEM model run (Khan *et al.*, 2021) and the rate coefficients for their respective reactions taken from MCM (http://mcm.leeds.ac.uk), we calculated the amount of 1st generation oxidation products of monoterpenes **3**, **11** and **13** produced up to 3 h after release from 1 g dry algae (Table 6). The analysis shows that 1 g dry algae can produce up to 2×10^{20} molecules organic hydroperoxides formed from compound **(11)**. We found 1.6352 g wet mass of *P. cornutum* with a surface area of ~0.0057 m^2 which was used to calculate the wet mass of 688 kg per 2400 m^2 in Kalk Bay. Using this, Kalk Bay can produce 1.2×10^{26} molecules organic hydroperoxides formed from compound **(3)**. We also calculated the equilibrium partition coefficients, K_p from the vapour pressure of these oxidation products which determine the percentage of gas and aerosol phases of the compounds in the partitioning if the total mass of the condensed organic materials is 1.0 μg/m^3 (see Table 6). The data suggests that the OH-initiated 1st generation oxidation leads to produce low volatility, highly oxygenated products (e.g. organic hydroperoxides, alcohols, carbonyl compounds) which can condense thereby enhancing SOA formation. With the inherent heterogeneity of ocean fluxes, the halogenated monoterpenes emissions are high enough along with their high reactivity and SOA yield to contribute an important source of submicron marine SOA (Shaw *et al.*, 2010; Kim *et al.*, 2017; Yu and Li, 2021). A back-of-envelope calculation shows that to generate an increase in SOA concentration of 1 $\mu g/m^3$ from the 1st generation OH-initiated oxidation product, organic hydroperoxides, the halogenated monoterpene **(3)**, **(11)** and **(13)** concentrations need to be at least 14, 191 and 4100 ppt, respectively. Whilst thousands of ppt may be unlikely, 10–100s of ppt can be possible.



Scheme 5. Predicted major peroxy radicals (RO_2), and terminating and propagating channel products from the reaction of atmospheric OH radical with the Δ^2, Δ^6 and Δ^8 olefins in **13**. Both cohorts of channel products are proposed from reaction of RO_2, with NO, O_2, O_2 and $R'O_2$ radicals.

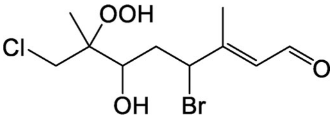
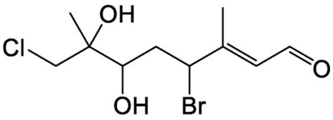
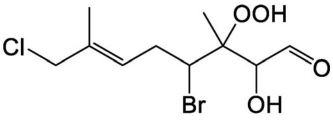
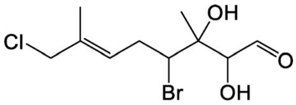
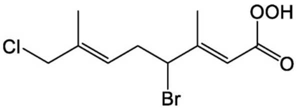
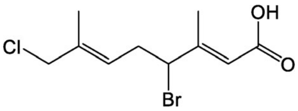
The ozonolysis reactions of the halogenated monoterpenes degrade the compounds into smaller molecules, e.g. carbonyl compounds and peroxy radicals (see Schemes 2 and 4). These peroxy radicals can also form stable organic hydroperoxides, alcohols and carbonyl compounds, but their vapour pressures are not low enough for being a contributor of SOA. However, organic hydroperoxides are a temporary reservoir of HO_x, thus allowing the air to travel away from the marine boundary layer, thus contributing HO_x upon photolysis or undergoes a reaction with OH radical. Further oxidation of the products (e.g. photolysis of carbonyl compounds containingBr or Cl atom) can release Cl and Br radicals into the atmosphere. We showed a simplified example of the photolysis of halogenated carbonyl compound produced from the ozone-initiated oxidation of halogenated monoterpenes, where halogen can be freed by the following reaction sequence (Equtions 7 to 10):

Table 6. The vapour pressure of the 1st generation OH-initiated oxidation products produced from monoterpenes **3**, **11** and **13** and the percentage of gas and particle phase contribution in the formation of the SOA.

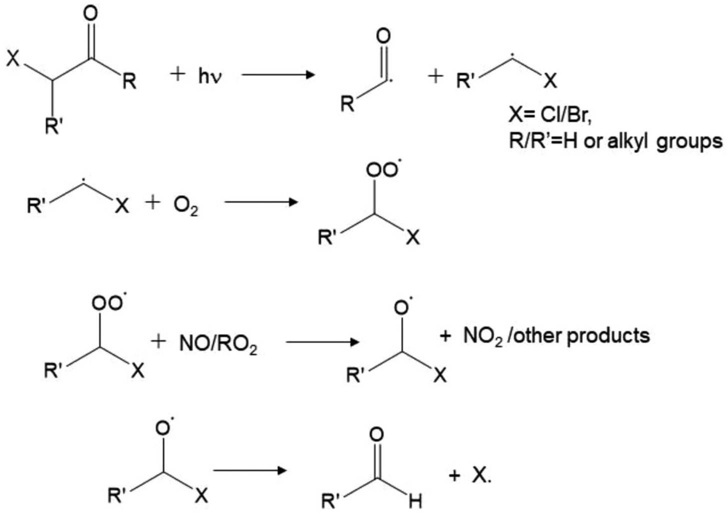
1st generation oxidation product	Product formed (in molecules) per 1 g dry algae	Vapour pressure (atm) of the product	Partitioning of the products	
			% gas	%particle
	8.61×10^{18}	5.37×10^{-9}	96.6	3.4
	3.67×10^{18}	4.27×10^{-10}	30.6	69.4
	7.35×10^{19}	2.57×10^{-11}	12.0	88.0
	1.59×10^{18}	2.40×10^{-9}	92.7	7.3
	6.78×10^{17}	1.25×10^{-10}	40.0	60.0
	1.36×10^{19}	7.24×10^{-12}	3.7	96.3
	2.71×10^{19}	6.72×10^{-8}	99.7	0.3
	1.99×10^{20}	3.41×10^{-10}	64.5	35.5
	1.15×10^{19}	5.35×10^{-9}	96.6	3.4

(*Continued*)

Table 6. Continued.

1st generation oxidation product	Product formed (in molecules) per 1 g dry algae	Vapour pressure (atm) of the product	Partitioning of the products	
			% gas	%particle
	3.65×10^{18}	1.38×10^{-10}	42.3	57.7
	1.82×10^{17}	4.07×10^{-9}	95.6	4.4
	1.24×10^{18}	1.95×10^{-10}	51.0	49.0
	6.19×10^{16}	5.72×10^{-9}	96.8	3.2
	9.31×10^{17}	1.10×10^{-7}	99.8	0.2
	4.65×10^{16}	3.92×10^{-7}	99.9	0.1

Note: The product amount was calculated based on a time lag of 3 h after releasing the halogenated monoterpenes from 1 g dry mass of algae. The calculation of the partition between gas and particle phase is based on the total mass of organic materials in the condensed phase of 1.0 μg/m^3. The products formed from RO$_2$ H-shift have not been included in the calculation.



(7)

(8)

(9)

(10)

Both halogens can participate in cycles that destroy tropospheric level ozone in the marine boundary layer (Simpson *et al.*, 2015). In addition, Cl radical can also react with CH$_4$, another potent greenhouse gas in the atmosphere, reducing the lifetime of this gas. Therefore, when acyclic halogenated marine monoterpenes enter the atmosphere a cursory analysis suggests that they will be potential climate coolers on local and regional scales.

CONCLUSION

A suite of acyclic halogenated monoterpenes produced from marine macroalgae is investigated in terms of their atmospheric lifetimes (due to reactions with OH and ozone), and the atmospheric impacts of the stable products formed from their 1st generation oxidation. The lifetimes of the selected monoterpenes are found to be in the range of 1.5–10 h, thus they have an environmental impact on the marine boundary layer through the formation of stable products such as organic hydroperoxides, alcohols, carbonyl compounds and organic acids. OH-initiated oxidation compounds **(3)**, **(11)** and **(13)** can produce organic hydroperoxides up to 7.35×10^{19}, 1.99×10^{20} and 3.65×10^{18} molecules from 1 g dry algae which can partition with the aerosol phase due to their low vapour pressures resulting in the contribution of SOA formation. The oxidation of compounds **(11)** and **(13)** by ozone is significantly high, contributing up to 60 and 50%, respectively to the total loss process, the oxidation products produced from these channels can free chlorine and bromine radicals by photolysis and further oxidations. The measurements of the emission flux of these halogenated monoterpenes from marine red macroalgae, kinetics and products for the oxidation reactions of these monoterpenes by OH radical and ozone will refine our estimation and constrain the role of oxidation products of halogenated monoterpenes in SOA formation and tropospheric ozone depletion.

DATA AVAILABILITY STATEMENT

The methodological data will be available from the corresponding author on request.

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References

Abreu, P.M. & Galindro, J.M. 1996. Polyhalogenated monoterpenes from *Plocamium cartilagineum* from the Portuguese coast. *Journal of Natural Products* **59**: 1159–1162.

Afolayan, A.F., Mann, M.G.A., Lategan, C.A., Smith, P.J., Bolton, J.J. & Beukes, D.R. 2009. Antiplasmodial halogenated monoterpenes from the marine red alga *Plocamium cornutum*. *Phytochemistry* **70**: 597–600.

Atkinson, R. 1987. A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *International Journal of Chemical Kinetics* **19**: 799–828.

Atkinson, R. & Arey, J. 2003. Atmospheric degradation of volatile organic compounds. *Chemical Reviews* **103**: 4605–4638.

Barahona, L.F. & Rorrer, G.L. 2003. Isolation of halogenated monoterpenes from bioreactor-cultured microplantlets of the macrophytic red algae Ochtodes secundiramea and Portieria hornemannii. *Journal of Natural Products* **66**: 743–751.

Barley, M.H. & McFiggans, G. 2010. The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol. *Atmospheric Chemistry and Physics* **10**: 749–767.

Berndt, T., Richters, S., Jokinen, T., Hyttinen, N., Kurtén, T., Otkjaer, R.V., Kjaergaard, H.G., Stratmann, F., Herrmann, H., Sipilä, M., Kulmala, M. & Ehn, M. 2016. Hydroxyl radical-induced formation of highly oxidized organic compounds. *Nature Communications* **7**: 13677.

Booth, A.M., Barley, M.H., Topping, D.O., McFiggans, G. & Garforth, A. 2010. Solid state and sub-cooled liquid vapour pressures of substituted dicarboxylic acids using Knudsen effusion mass spectrometry (KEMS) and differential scanning calorimetry. *Atmospheric Chemistry and Physics* **10**: 4879–4892.

Cabrita, M.T., Vale, C. & Rauter, A.P. 2010. Halogenated compounds from Marine Algae. *Marine Drugs* **8**: 2301–2317.

Calvert, J.G., Atkinson, R., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J. & Yarwood, G. 2000. *The mechanisms of atmospheric oxidation of alkenes*. New York, Oxford University Press. ISBN 0-19-513177-0.

Carrol, A.R., Copp, B.R., Davis, R.A., Keyzers, R.A. & Prinsep, M.R. 2020. Marine natural products. *Natural Product Reports* **37**: 175–223.

Cikoš, A.-M., Jurin, M., Což-Rakovac, R., Joki⍰, S. & Jerkovi⍰, I. 2019. Update on monoterpenes from red macroalgae: isolation, analysis and bioactivity. *Marine Drugs* **17**: 537–557.

Ehn, M., Thornton, J.A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L.B., Jørgensen, S., Kjaergaard, H.G., Canagaratna, M., Maso, M.D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D.R., Wildt, J. & Mentel, T.F. 2014. A large source of low-volatility secondary organic aerosol. *Nature* **506**: 476–479.

Fantechi, G., Jensen, N.R., Hjorth, J. & Peeters, J. 1998. Mechanistic studies of the atmospheric oxidation of methyl butenol by OH radicals, ozone and NO_3 radicals. *Atmospheric Environment* **32**: 3547–3556.

Faulkner, D.J. 1984. Marine natural products: metabolites of marine algae and herbivorous Marine Molluscs. *Natural Product Reports* **1**: 251–280.

Faulkner, D.J. 2001. Marine natural products (1999). *Natural Product Reports* **18**: 1–49.

Hackenberg, S.C., Andrews, S.J., Airs, R.L., Arnold, S.R., Bouman, H.A., Cummings, D., Lewis, A.C., Minaeian, J.K., Reifel, K.M., Small, A., Tarran, G.A., Tilstone, G.H. & Carpenter, L.J. 2017. Basin-scale observations of monoterpenes in the Arctic and Atlantic Oceans. *Environmental Science and Technology* **51**: 10449–10458.

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Linuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R. & Wildt, J. 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics* **9**: 5155–5236.

Hay, M.E. 1996. Marine chemical ecology: what's known and what's next? *Journal of Experimental Marine Biology and Ecology* **200**: 103–134.

Hu, Q.-H., Xie, Z.-Q., Wang, X.-M., Kang, H., He, Q.-F. & Zhang, P. 2013. Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic. *Scientific Reports* **3**: 2280.

Jenkin, M.E. 2004. Modelling the formation and composition of secondary organic aerosol from α- and β-pinene ozonolysis using MCM v3. *Atmospheric Chemistry and Physics* **4**: 1741–1757.

Jenkin, M.E., Saunders, S.M. & Pilling, M.J. 1997. The tropospheric degradation of volatile organic compounds: a protocol for mechanism development. *Atmospheric Environment* **31**: 81–104.

Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M., Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin, C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., Dunlea, E.J., Huffman, J.A., Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J.Y., Zhang, Y.M., Dzepina, K., Kimmel, J.R., Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R., Wood, E.C., Middlebrook, A.M., Kolb, C.E., Baltensperger, U. & Worsnop, D.R. 2009. Evolution of organic aerosols in the atmosphere. *Science* **326**: 1525–1529.

Jiménez, E., Lanza, B., Martinez, E. & Albaladejo, J. 2007. Daytime tropospheric loss of hexanal and trans-2-hexenal: OH kinetics and UV photolysis. *Atmospheric Chemistry and Physics* **7**: 1565–1574.

Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V.-M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A.B., Worsnop, D.R., Kulmala, M., Ehn, M. & Sipilä, M. 2015. Production of extremely low volatile organic compounds from biogenic emissions: measured yields and atmospheric implications. *Proceedings of the National Academy of Sciences* **112**: 7123–7128.

Khan, M.A.H., Jenkin, M.E., Foulds, A., Derwent, R.G., Percival, C.J. & Shallcross, D.E. 2017. A modeling study of secondary organic aerosol formation from sesquiterpenes using the STOCHEM global chemistry and transport model. *Journal of Geophysical Research Atmospheres* **122**: 4426–4439.

Khan, M.A.H., Schlich, B.-L., Jenkin, M.E., Cooke, M.C., Derwent, R.G., Neu, J.L., Percival, C.J. & Shallcross, D.E. 2021. Changes to simulated global atmospheric composition resulting from recent revisions to isoprene oxidation chemistry. *Atmospheric Environment* **244**: 117914.

Kim, M.J., Novak, G.A., Zoerb, M.C., Yang, M., Blomquist, B.W., Huebert, B.J., Cappa, C.D. & Bertram, T.H. 2017. Air-Sea exchange of biogenic volatile organic compounds and the impact on aerosol particle size distributions: air-sea exchange of biogenic VOCs. *Geophysical Research Letters* **44**: 3887–3896.

Kladi, M., Vagias, C. & Roussis, V. 2004. Volatile halogenated metabolites from marine red algae. *Phytochemistry Reviews* **3**: 337–366.

Knott, M.G., Mkwananzi, H., Arendse, C.E., Hendrickes, D.T., Bolton, J.J. & Beukes, D.R. 2005. Plocoralides A-C, polyhalogenated monoterpenes from the marine alga Plocamium corallorhiza. *Phytochemistry* **66**: 1108–1112.

Kwok, E.S.C. & Atkinson, R. 1995. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update. *Atmospheric Environment* **29**: 1685–1695.

Leather, K.E., McGillen, M.R., Ghalaieny, M., Shallcross, D.E. & Percival, C.J. 2011. Temperature-dependent kinetics for the ozonolysis of selected chlorinated alkenes in the gas phase. *International Journal of Chemical Kinetics* **43**: 120–129.

Lever, J., Brkljača, R., Kraft, G. & Urban, S. 2020. Natural products of marine macroalgae from South Eastern Australia, with emphasis on the Port Phillip bay and heads regions of Victoria. *Marine Drugs* **18**: 142.

Lightfoot, P.D., Cox, R.A., Crowley, J.N., Destriau, M., Hayman, G.D., Jenkin, M.E., Moortgat, G.K. & Zabel, F. 1992. Organic peroxy-radicals-Kinetics, spectroscopy and tropospheric chemistry. *Atmospheric Environment. Part A. General Topics* **26**: 1805–1961.

Liss, P.S. & Slater, P.G. 1974. Flux of gases across the air-sea interface. *Nature* **247**: 181–184.

Maliakal, S., Cheney, D.P. & Rorrer, G.L. 2001. Halogenated monoterpene production in regenerated plantlet cultures of Ochtodes Secundiramea (Rhodophyta, Cryptonemiales). *Journal of Phycology* **37**: 1010–1019.

Mann, M.G.A., Mkwananzi, H.B., Antunes, E.M., Whibley, C.E., Hendricks, D.T., Bolton, J.J. & Beukes, D.R. 2007. Halogenated monoterpene aldehydes from the South African Marine Alga *Plocamium corallorhiza*. *Journal of Natural Products* **70**: 596–599.

Mcquaid, C.D. & Branch, G.M. 1985. Trophic structure of rocky intertidal communities: response to wave action and implications for energy flow. *Marine Ecology Progress Series* **22**: 153–161.

Mellouki, A., Wallington, T.J. & Chen, J. 2015. Atmospheric chemistry of oxygenated volatile organic compounds: Impacts on air quality and climate. *Chemical Reviews* **115**: 3984–4014.

Mynderse, J.S. & Faulkner, D.J. 1975. Polyhalogenated monoterpenes from the Red Alga *Plocamium cartilagineum*. *Tetrahedron* **31**: 1963–1967.

Myriokefalitakis, S., Vignati, E., Tsigaridis, K., Papadimas, C., Sciare, J., Mihalopoulos, N., Facchini, M.C., Rinaldi, M., Dentener, F.J., Ceburnis, D., Hatzianastasiou, N., O'Dowd, C.D., van Weele, M. & Kanakidou, M. 2010. Global modeling of the oceanic source of organic aerosols. *Advance Meteorology* **2010**: 939171.

Nannoolal, Y., Rarey, J. & Ramjugernath, D. 2008. Estimation of pure component properties: Part 3. Estimation of the vapour pressure of non-electrolyte organic compounds via group contributions and group interactions. *Fluid Phase Equilibria* **269**: 117–133.

Nannoolal, Y., Rarey, J., Ramjugernath, D. & Cordes, W. 2004. Estimation of pure component properties: Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via group contributions and group interactions. *Fluid Phase Equilibria* **226**: 45–63.

O'Connor, M.P., Wenger, J.C., Mellouki, A., Wirtz, K. & Muñoz, A. 2006. The atmospheric photolysis of E-2-hexenal, Z-3-hexenal and E, E-2,4-hexadienal. *Physical Chemistry Chemical Physics* **8**: 5236–5246.

Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C. & Seinfeld, J.H. 1996. Gas/particle partitioning and secondary organic aerosol yields. *Environmental Science and Technology* **30**: 2580–2585.

O'Meara, S., Booth, A.M., Barley, M.H., Topping, D. & McFiggans, G. 2014. An assessment of vapour pressure estimation methods. *Physical Chemistry and Chemical Physics* **16**: 19453–19469.

Pankow, J.F. 1994. An absorption model of gas-particle partitioning involved in the formation of secondary organic aerosol. *Atmospheric Environment* **28**: 189–193.

Paul, C. & Pohnert, G. 2011. Production and role of volatile halogenated compounds from marine algae. *Natural Product Reports* **28**: 186–195.

Paulot, F., Crounse, J.D., Kjaergaard, H.G., Kürten, A., St. Clair, J.M., Seinfeld, J.H. & Wennberg, P.O. 2009. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science* **325**: 730–733.

Shaw, S.L., Gantt, B. & Meskhidze, N. 2010. Production and emissions of marine isoprene and monoterpenes: a review. *Advances in Meteorology* **2010**: 408696.

Simpson, W.R., Brown, S.S., Saiz-Lopez, A., Thornton, J.A. & von Glasow, R. 2015. Tropospheric halogen chemistry: sources, cycling and impacts. *Chemical Reviews* **115**: 4035–4062.

Spicer, C.W., Chapman, E.G., Finlayson-Pitts, B.J., Plastridge, R.A., Hubbe, J.M., Fast, J.D. & Berkowitz, C.M. 1998. Unexpectedly high concentrations of molecular chlorine in coastal air. *Nature* **394**: 353–356.

Timerghazin, Q.K. & Ariya, P.A. 2001. Kinetics of the gas-phase reaction of atomic chlorine with selected monoterpenes. *Physical Chemistry Chemical Physics* **3**: 3981–3986.

Utembe, S.R., Cooke, M.C., Archibald, A.T., Shallcross, D.E., Derwent, R.G. & Jenkin, M.E. 2011. Simulating secondary organic aerosol in a 3-D Lagrangian chemistry transport model using the reduced Common Representative Intermediates mechanism (CRI v2-R5). *Atmospheric Environment* **45**: 1604–1614.

Vainonen, J.P. & Kangasjärvi, J. 2015. Plant signalling in acute ozone exposure. *Plant Cell & Environments* **38**: 240–252.

Vasconcelos, M.A., Ferreira, W.J., Pereira, R.C., Cavalcanti, D.N. & Teixera, V.L. 2010. Chemical constituents from the red alga *Plocamium brasiliense* (Greville) M. Howe and W.R. Taylor. *Biochemical Systematics and Ecology* **38**: 119–121.

Wise, M.L. 2003. Monoterpene biosynthesis in marine algae. *Phycologia* **42**: 370–377.

Yu, Z. & Li, Y. 2021. Marine volatile organic compounds and their impacts on marine aerosol—a review. *Science of The Total Environment* **768**: 145054.

Zhang, J., Wei, Y. & Fang, Z. 2019. Ozone pollution: a major health hazard worldwide. *Frontiers in Immunology* **10**: 2518.