

Iodine in the Marine Boundary Layer

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1. Introduction

Measurements of gaseous organic iodine¹ and inorganic and particulate iodine^{2,3} made several decades ago indicated that volatilization of organic iodides from the ocean provides the main source of atmospheric iodine. Photooxidation of organoiodines in air to soluble inorganic forms allows a significant fraction of the iodine to partition to the aerosol phase, providing a route for wet or dry deposition to the land or ocean. Thus, the cycle provides a vital route for terrestrial uptake of iodine, an essential component of mammalian health.

Chameides and Davies⁴ first highlighted the potential atmospheric significance of iodine photochemistry, in particular as a catalyst for destruction of tropospheric ozone via reaction with iodine atoms released by organoiodine photodissociation. Other roles for iodine in the atmosphere were suggested, including as an oxidant for DMS,⁵ as a contributor to lower stratospheric ozone depletion,⁶ and as a removal pathway for nitrogen oxides.⁷

Over the past few years, there has been increasing evidence that iodine does have an important influence on atmospheric chemistry in a number of regions. In the Arctic, there have been numerous studies on the role of bromine in ozone depletion



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events following observations of a strongly negative correlation between filterable bromine and ozone concentrations in spring.⁸ The role of iodine is less well established, although strong maxima in both I and Br aerosol concentrations are observed just after polar sunrise.^{9,10} Iodine is at least partially associated with particulate Br during this period but nonlinearly, and shows an additional maximum in autumn that is not exhibited by bromine.¹⁰ The reasons for the seasonal trends in particulate iodine are still not clear,¹¹ though it seems likely that iodine also contributes at least partially to the polar sunrise ozone depletion events. The presence of significant amounts of reactive iodine in the mid-latitude troposphere has been demonstrated by direct spectroscopic observations of IO and OIO^{12–15} and in situ measurements of their organic precursors.¹⁶ Indirect evidence for halogen-related perturbations to the oxidative capacity of the troposphere comes from observations of anomalous ozone^{17,18} and peroxy radical¹⁹ concentrations. Finally, the atmospheric impact of iodine has been recently suggested to include a possible radiative effect, arising from its role in new particle production in coastal regions.^{20,21}

In addition to the contributions from field measurements, knowledge of the effect of iodine-catalyzed chemistry has been improved substantially due to laboratory kinetic studies and advanced knowledge regarding the mechanisms driving atmospheric mod-

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els. Experimental work is continuing to shed light on key photochemical and thermochemical processes.^{22–25} A key modeling study by Vogt et al.²⁶ proposed that the interaction of iodine in sea salt aerosol with bromide and chloride accelerates gaseous halogen release, and subsequent theoretical work has provided further insight into the condensed-phase chemistry of halogens.^{27–30} It is now well established that the efficiency of iodine to perturb atmospheric chemistry depends critically upon its rate of uptake and release from particles in various forms.

Despite the progress made, predictions of the exact impact of iodine photochemistry in the marine boundary layer are still semiquantitative due to a number of uncertainties in the sources, sinks, and recycling of iodine. In this review, current issues and recent research in this wide-ranging and exciting area are described.

2. Sources of Organic Iodine

Anthropogenic releases of atmospheric iodine (such as fossil fuel combustion) are believed to be negligible on a global scale compared to natural sources. The latter are mainly of marine origin, with a lesser contribution from land sources.

2.1. Iodine in the Ocean

Iodine in seawater exists predominantly as iodate, iodide, and nonvolatile dissolved organic iodine, with a total concentration of around 0.45 μM .³¹ Although halides in sea salt represent an important net flux of chlorine and bromine from the ocean to the atmosphere, sea salt particles act mainly to either remove or recycle gaseous iodine. Rather, it is the small fraction of dissolved iodine in insoluble organic form that is believed to be the major carrier of iodine to the atmosphere. Production of molecular iodine in the surface ocean from the reaction of atmospheric ozone with iodide has also been suggested.^{32,33} The rapid reaction of I_2 with organic matter in seawater, however, requires that production must occur in the surface ocean for volatilization of I_2 to occur. There is some evidence for molecular iodine in surface seawater,³⁴ but there are no estimates of the magnitude of such a source.

The main origin of organic iodine in seawater appears to be marine algae. The mechanism for production of monohalogenated compounds involves a halide ion methyl transferase enzyme,³⁵ found in both macroalgae (seaweeds) and microalgae (phytoplankton), whereas di- and tri-halogenated hydrocarbon production involves the haloperoxidase enzyme, present in a wide range of terrestrial and marine organisms.^{36,37} Haloperoxidases catalyze the oxidation of halides by hydrogen peroxide, which is released as part of normal cell metabolism and during defense reactions.³⁸ The resulting reactive electrophilic halogenating species can react with available organic material within the cell apoplast via the iodoform reaction to form volatile organohalogens that are released to the surrounding seawater or air.³⁹ Under conditions of oxidative stress, e.g., at elevated temperatures or when exposed to

grazing, H_2O_2 would otherwise build up to high levels, and thus the mechanism is essential for the health of the organism.

Macroalgae are prolific producers of every volatile organic iodine compound so far detected in the atmosphere,^{40–44} yet their restriction to coastal areas, which occupy only $\sim 0.5\%$ of the ocean surface area,⁴⁵ may limit the global significance of such production. Most studies of volatile iodine production from macroalgae have reported CH_3I only, but those that have monitored CH_2I_2 have found it to be the main form of organic iodine release,^{44,46,47} probably reflecting the mechanism proposed by Theiler et al.³⁹

Primary emission data are limited. Global CH_3I production by macroalgae has been estimated as $\sim 4 \times 10^6 \text{ mol yr}^{-1}$.⁴⁸ The few studies on the more reactive organic iodines report macroalgal emission rates of 0.01–1.5 $\text{pmol h}^{-1} \text{ g}^{-1} \text{ FW}$ for CH_2ICl ,^{44,49} 0–12 $\text{pmol h}^{-1} \text{ g}^{-1} \text{ FW}$ for CH_2I_2 ,^{44,46} and 0.01–4.3 $\text{pmol h}^{-1} \text{ g}^{-1} \text{ FW}$ for CH_2IBr .⁴⁴ Based upon a worldwide algal biomass estimate of 280 million t FW⁵⁰ and production by macroalgae typical of Northern European shores,⁴⁴ crude upper estimates of seaweed release are $4 \times 10^6 \text{ mol yr}^{-1} \text{ CH}_2\text{ICl}$, $3 \times 10^7 \text{ mol yr}^{-1} \text{ CH}_2\text{I}_2$, and $1 \times 10^7 \text{ mol yr}^{-1} \text{ CH}_2\text{IBr}$.

That macroalgae play a dominant role in controlling the atmospheric concentrations of some reactive halocarbons in coastal areas is strongly supported by observations of maxima at low tide,¹⁶ as shown in Figure 1. It is, however, difficult to calculate the relative contributions of macroalgae versus microalgal sources to atmospheric concentrations, given uncertainties in emission rates and algal biomass. Carpenter et al.⁴⁴ found that seaweed production, calculated from measured emission rates in conjunction with biomass estimates, could not support the levels of CH_3I and CH_2ICl measured in surface coastal waters off the coast of Mace Head in west Ireland, and suggested additional marine sources for these compounds. In contrast, measured surface seawater levels of CH_2I_2 and CH_2IBr were lower than those calculated from seaweed production, probably reflecting photodissociation in the water column. In a modeling study aimed at elucidating the location of CH_2I_2 sources in the vicinity of Mace Head, evidence was found⁵¹ that CH_2I_2 was emitted not only from the tidal zone but also from further offshore.

In contrast to seaweeds, microalgae (phytoplankton) inhabit the entire ocean surface. They have been proved to be significant sources of some organic halogens, including CH_3Br .⁵² However, while the utilization of IO_3^- and the concomitant appearance of I^- have been consistently observed in marine phytoplankton cultures,^{53,54} the only organic iodide unequivocally shown to be produced by temperate microalgae in laboratory culture experiments is CH_3I .^{52,55,56} Manley and de la Cuesta⁵⁵ calculated a mean CH_3I production rate from 15 species of marine phytoplankton of $8 \times 10^6 \text{ mol y}^{-1}$, similar to estimates from seaweed release. Neither source is significant compared to the total estimated global CH_3I source strength of $(0.9–2.5) \times 10^9 \text{ mol y}^{-1}$.⁵⁷ Polar microalgae have been shown to be capable of production of $\text{C}_2\text{H}_5\text{I}$, CH_2IBr , CH_2ICl , and CH_2I_2 as well as CH_3I .⁵⁸

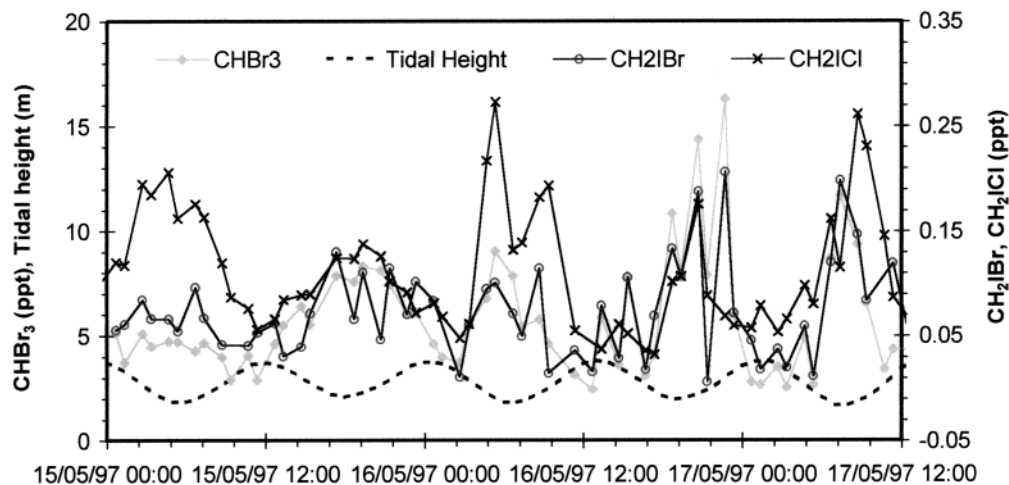


Figure 1. Organohalogen mixing ratios and tidal height at Mace Head, Ireland.

Estimates of total annual production rates are unavailable, although the data indicate rather low rates in comparison to macroalgal production.

Although no direct laboratory evidence has yet been published, there is some field evidence for temperate microalgal production of CH_2I_2 and $\text{CH}_2\text{-ICl}$ from shipboard measurements^{59–61} and from a spring seasonal maximum observed in coastal waters.⁶² Moore and Tokarczyk⁶⁰ found that dissolved CH_2ICl showed highest concentrations away from the coast, and exhibited a depth profile strongly indicative of a planktonic source. They concluded that $\text{CH}_2\text{-ICl}$ is probably formed via nucleophilic substitution of CH_2I_2 produced by phytoplankton. More recently, Yamamoto et al.⁶³ observed depth profiles of chlorophyll-*a*, CH_2I_2 , and CH_2ICl that indicated production by phytoplankton followed by rapid decay in seawater. So far, CH_2I_2 and CH_2ICl have yet to be detected in air over the open ocean. However, the air and seawater findings are not necessarily inconsistent. If CH_2I_2 and CH_2ICl are produced in the pelagic ocean, their absence so far in open ocean atmospheric measurements could be indicative of rapid photolysis in surface waters or fast chemistry in the marine boundary layer, rather than a lack of planktonic production.

Finally, abiological routes for organic iodine production may exist. Moore and Zafiriou⁶⁴ found that irradiation of oxygenated seawater was capable of producing CH_3I at $1\text{--}10\text{ pmol L}^{-1}\text{ h}^{-1}$, notably higher than algal production rates and potentially capable of providing the missing CH_3I source indicated by estimates based upon seawater and air concentrations. A reaction between photochemically produced methyl and iodine radicals was suggested. However, while sufficient concentrations of I^\bullet may be sustained from oxidation of I^- or photolysis of organic iodides, maintaining a high enough steady-state concentration of CH_3^\bullet is problematic because of rapid consumption by oxygen. A possible solution is that photolysis of other organic iodides may form CH_3^\bullet and I^\bullet in close proximity, allowing I^\bullet to compete with oxygen. If this is the case, this form of CH_3I production represents an interconversion of dissolved organic iodine to less photolabile forms, rather than new production of volatile iodine.

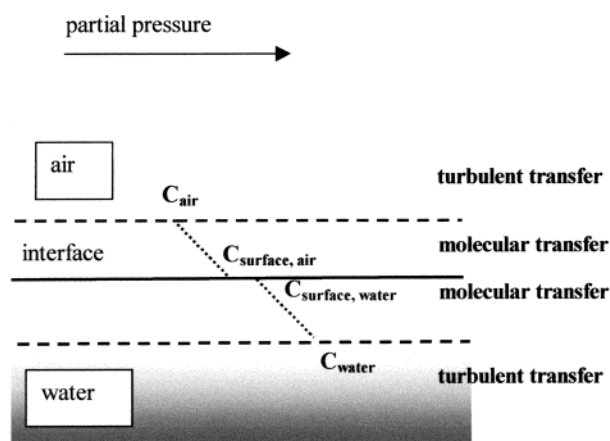


Figure 2. Two-layer model for transfer of a slightly soluble gas across the sea–air interface (after Liss and Slater⁶⁵).

2.1.1. Sea–Air Fluxes

It is clear that primary emission data are not yet sufficiently accurate to gauge the relative contributions of coastal and open ocean sources of organic iodine compounds or their annual release rates. Global estimates of marine trace gas production are often calculated instead using the “two-layer” approach proposed by Liss and Slater,⁶⁵ which assumes an equilibrium between air and seawater concentrations of trace gases. The two-layer model was developed for a gas well mixed in bulk air and seawater, as depicted in Figure 2, such that wind-driven turbulence would increase the transport of the gas from the bulk water (turbulent transfer layer) to the surface, thus increasing the sea–air flux.

The flux is calculated from the partial pressure difference of the gas across the interfacial layer ($\Delta C = C_{\text{water}} - C_{\text{air}}/H$, where H is the Henry’s law coefficient) and a gas transfer velocity k ,^{66,67} such that the flux F of the gas is

$$F = k\Delta C \quad (\text{A1})$$

The transfer velocity k is a function of the interfacial turbulence, which is most often parametrized in terms of wind speed, and the temperature-dependent Schmidt number of the gas (Sc),

$$Sc = \eta_k/D \quad (\text{A2})$$

where η_k is the kinematic viscosity of seawater and D is the diffusivity of the gas in seawater. Experimental and theoretical work has shown that k is proportional to $Sc^{-1/2}$ at intermediate wind speeds. For steady winds, the relationship between gas transfer and wind speed, u , is usually assumed to be quadratic,⁶⁷ although more recent work has suggested a cubic relationship.⁶⁸

$$k = 0.0283u^3(Sc/660)^{-1/2} \quad (\text{A3})$$

Where diffusivity data are unavailable, the Schmidt number may be estimated from an empirical equation.^{67,69}

$$Sc = 335.6M^{1/2}(1 - 0.0065T + 0.002043T^2 - (2.6 \times 10^{-5})T^3) \quad (\text{A4})$$

where T is the sea surface temperature (SST, °C) and M is molecular weight. Yokouchi et al.⁷⁰ found that correlations observed between SST and air CH_3I concentrations were consistent with the temperature dependence of k as defined in (A3) and (A4).

Liss and Merlivat⁶⁶ proposed expressions for the transport of a gas under three different wind regimes: smooth surface ($k = 0.17u$, for $u \leq 3.6$), rough surface ($k = 2.85u - 9.65$, for $3.6 < u \leq 13$), and breaking wave ($k = 5.90u - 49.3$, for $u > 13$). These expressions were derived for transfer of CO_2 in freshwater, for which the Schmidt number is 600. Corrections must be applied for different gases in seawater. Using conservative tracers to measure gas transfer velocities, Nightingale et al.⁷¹ found that a gas exchange relationship with a dependence on wind speed intermediate between those of Liss and Merlivat⁶⁶ and Wanninkhof⁶⁷ showed optimal fit to the data.

It is well recognized that many other factors affect the rate of gas transfer, including wave type, bubbles (where the effect on gas transfer will be a function of the solubility of the gas), temperature gradients, and surface films.^{72–74} While wind speed is linked to many of these parameters, their precise effect on gas transfer is poorly understood but certainly may not scale linearly with u . Yokouchi et al.⁷⁰ also recently pointed out that, for gases such as CH_3I , where production may be focused at the surface, the enhanced transport of the gas from the bulk water by wind may not increase the gas concentration at the interface, resulting in little effect of wind speed on F . Currently, knowledge of the interfacial transfer rate is a fundamental limitation on air–sea flux calculations; it introduces an uncertainty of a factor of about 2 when the transfer rate is parametrized in terms of wind speed alone.⁷¹

Accurate global estimates of production via the approach outlined above rely not only on accurate flux parametrization, but also on air and seawater measurements made in numerous locations, environments, and seasons. Reasonable estimates of marine CH_3I emission are now possible because of the relatively large database of seawater and air measurements. Estimates made over the past decade are in quite good agreement, i.e., $< 3.3 \times 10^9$ (ref 75) and $(0.9–2.5) \times 10^9 \text{ mol yr}^{-1}$ (ref 57), with a large part of

the uncertainty due to the gas transfer parametrization. Estimates of CH_3I release based upon data from restricted and/or biologically productive regions are much higher.⁷⁶ The only global flux estimate for the more reactive organoiodines appears to be from Klick and Abrahamsson,⁵⁹ who suggested a tentative global oceanic CH_2I_2 emission estimate of similar magnitude to CH_3I , based upon data from Swedish coastal waters. Since data on these reactive organoiodines are extremely sparse and variable, gas transfer rates are at present not the major uncertainty in estimating fluxes.

Estimates of primary emissions can be tested against measurements using atmospheric models incorporating the appropriate chemical schemes. Unsurprisingly, given the uncertainties in the sources and sinks of iodine, incorporation of iodine photochemistry into global models has not yet been reported. However, some process-modeling studies have used organic iodine fluxes as inputs. Vogt et al.²⁶ chose oceanic emission rates of CH_3I , $i\text{-C}_3\text{H}_7\text{I}$, $\text{CH}_2\text{-CII}$, and CH_2I_2 of 0.6×10^7 , 1.0×10^7 , 2.0×10^7 , and $3.0 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, respectively, so that the total organic iodine mixing ratio was 3–4 pmol mol^{-1} . Extrapolating these emissions over the entire ocean surface area of $\sim 3.6 \times 10^{18} \text{ cm}^2$, these emission rates become approximately 1.1×10^7 , 1.9×10^7 , 3.8×10^7 , and $5.7 \times 10^7 \text{ mol yr}^{-1}$ for CH_3I , $i\text{-C}_3\text{H}_7\text{I}$, CH_2CII , and CH_2I_2 , respectively. Although it was clearly not the intention of the authors to derive globally representative emissions, it is instructive to compare the values used with other emission estimates. The $\text{CH}_2\text{-CII}$ and CH_2I_2 fluxes used (by far the most important iodine atom sources in the modeling study) are the same order of magnitude as those estimated from macroalgal emissions, as discussed in section 2.1, whereas recent estimates of CH_3I release^{57,75,77} are 2 orders of magnitude higher than those of Vogt et al.

2.1.2. Marine Destruction

Where primary emission data are available, a common approach used to estimate “order-of-magnitude” global fluxes is to ignore destruction and assume that all marine emissions will end up in the atmosphere. For some oceanic gases, such an approach would lead to a reversal in the actual direction of flux. For example, there has been a substantial change in the estimated magnitude of the net ocean “source” of methyl bromide over the past few years, such that the latest data, incorporating biotic and abiotic degradation of CH_3Br , indicate the ocean is a sink.^{78,79} Although deriving fluxes using expression (A1) in principle accounts for destruction, photolabile organoiodines are likely to exhibit a gradient that could lead to an overestimation of F calculated by this method. Valid use of the flux expression requires that dissolved gases should be fairly uniform in concentration throughout the mixed water column, or else a bulk water sample is not representative of the concentration at the surface.

CH_3I in seawater is removed by chloride substitution and volatilization at comparable rates.^{80,81} Photolysis⁸¹ and hydrolysis⁸² are negligible compared to these removal pathways, and as yet any biological

Table 1. Atmospheric Mixing Ratios of Organoiodines Measured in Different Locations

compound	region	concentration (pptv)		reference
		mean	range	
CH ₃ I	W. Ireland (spring)	0.43	0.12–1.47	Carpenter et al. ¹⁶
	W. Ireland (summer)	3.78	1.30–12.03	Carpenter et al. ⁴⁴
	W. Ireland (summer)	3.40	1.9–8.7	Bassford et al. ¹¹⁶
	Spitzbergen	1.04	<0.004–2.12	Schall and Heumann ⁸⁹
	Asian Seas	0.63	0.24–2.0	Yokouchi et al. ^{117,a}
	W. Pacific	0.87	0.05–5.0	Yokouchi et al. ^{117,a}
	Okinawa, Japan	1.20	0.5–2.0	Li et al. ¹¹⁸
C ₂ H ₅ I	W. Ireland (spring)	0.06	<0.02–0.21	Carpenter et al. ¹⁶
	W. Ireland (summer)	0.16	<0.02–0.50	Carpenter et al. ⁴⁴
	Asian Seas	0.09	0.03–0.31	Yokouchi et al. ^{117,a}
	Spitzbergen	0.20	<0.02–2.28	Schall and Heumann ⁸⁹
CH ₂ ICl	Spitzbergen	2.00	<0.02–5.98	Schall and Heumann ⁸⁹
	W. Ireland (spring)	0.11	<0.02–0.21	Carpenter et al. ¹⁶
	W. Ireland (summer)	0.16	<0.02–0.50	Carpenter et al. ⁴⁴
	Spitzbergen	0.07	<0.004–0.18	Schall and Heumann ⁸⁹
CH ₂ IBr	Alert	0.01	<0.01–0.05	Yokouchi et al. ¹¹⁹
	W. Ireland (spring)	0.08	<0.02–0.32	Carpenter et al. ¹⁶
	W. Ireland (summer)	0.06	<0.02–0.30	Carpenter et al. ⁴⁴
CH ₂ I ₂	W. Ireland (spring)	0.05	<0.02–0.36	Carpenter et al. ¹⁶
	W. Ireland (summer)	0.10	<0.02–0.46	Carpenter et al. ⁴⁴
	Spitzbergen	0.46	<0.08–1.02	Schall and Heumann ⁸⁹

^a CH₂I₂ and CH₂ICl below detection limit (<0.1 pptv).

destruction has not been quantified. Volatilization will vary according to interfacial turbulence, and Cl⁻ substitution varies strongly according to temperature,⁸³ so either may dominate depending upon conditions. A recent modeling study incorporating known aqueous destruction rates estimated net marine CH₃I emissions of 1.5×10^9 mol yr⁻¹.⁷⁷

The aqueous destruction pathways following production of the more reactive organoiodines have not yet been established. An indication that rapid organoiodine destruction occurs in seawater was, however, shown by a comparison of calculated and measured surface seawater halocarbon concentrations at Mace Head,⁴⁴ as described in section 2.1. Clearly, both the biological and chemical rates of destruction of these compounds in the oceans require investigation.

2.2. Terrestrial Sources

The natural abundance of iodine in soil is due mainly to direct atmospheric input, decomposition of plant tissue containing iodine sorbed from the atmosphere, and the soil's ability to retain iodine against leaching and volatilization.⁸⁴ Volatilization of organic iodine may occur, however, as a result of both chemical and microbiological processes.

Terrestrial sources for the di and tri-iodated compounds have not been identified. Methyl iodide, however, has several terrestrial sources that together are believed to comprise up to 30% of the total budget.⁷⁷ Estimates of annual terrestrial emissions of CH₃I are between 1.4×10^8 (ref 85) and 4.1×10^8 mol (ref 86) from rice paddies, 5×10^7 mol from natural wetlands,⁸⁷ and 6×10^7 mol from biomass burning.⁷⁷ Keppler et al.⁸⁸ proposed an abiotic route for alkyl halide production in soils and sediments from halide ion alkylation during the oxidation of organic matter by an electron acceptor such as Fe(III). The authors proposed that production of C1–C4 alkyl iodides from soils containing Fe(III) and

iodide could be significant globally, although their data did not allow for an estimate of emission.

3. Atmospheric Observations of Organic Iodine Compounds

Methyl iodide in the oceanic atmosphere was first detected by Lovelock et al.¹ and until the past decade was believed to be the major source of atmospheric iodine. It is now clear that many other organoiodine compounds exist and, although generally present in lower concentrations than CH₃I, almost certainly dominate as iodine atom precursors because of their photochemical instability.^{16,44,89} Note that the CH₂I₂ concentration only has to reach approximately 1/1000 of that of CH₃I (i.e., below the detection limit of current instrumentation) in order to compete as an iodine atom source. Atmospheric mixing ratios of organoiodines measured in different locations are summarized in Table 1.

There is general agreement that CH₃I mixing ratios over the open ocean are between ~0.5 and 2 pptv, with higher amounts near coastal areas. There are too few studies of the more reactive organoiodines to make any general comments about their concentration distributions. Measurements at Mace Head indicate a daytime iodine atom production rate of $\sim 1 \times 10^4$ atom cm⁻³ s⁻¹,^{16,27} dominated by CH₂I₂ photolysis. A recent study has indicated even higher iodocarbon concentrations at a coastal site in Japan.¹⁹

4. Reaction Cycles of Iodine and Their Effect on Tropospheric Photochemistry

4.1. Photoproduction of Iodine Atoms

The current understanding of the main features of gas- and particle-phase iodine photochemistry is shown in Figure 3. The cycle is initiated by photolysis of organoiodines with lifetimes ranging from several

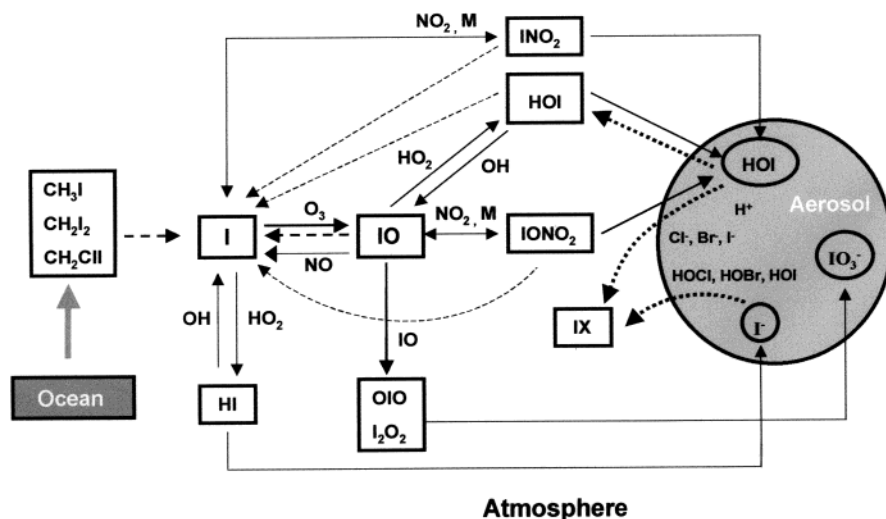
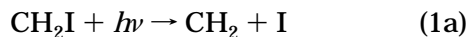


Figure 3. Simplified scheme of tropospheric iodine photooxidation, based upon current knowledge of chemistry. Dashed lines represent photolysis, dotted lines represent volatilization from aerosol, and IX is ICl, IBr, or I₂.

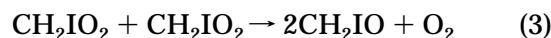
days (CH₃I, C₂H₅I, C₃H₇I^{90,91}), several hours (CH₂-ICl^{90,91}), an hour or less (CH₂IBr⁹²), to about 5 min at midday (CH₂I₂^{91,92}). CHIBr₂ has also been observed in the marine atmosphere,⁴⁴ but as yet its absorption cross section has not been measured. Although the lifetimes of the polyhalomethanes are controlled almost entirely by photodissociation, OH- and Cl-initiated attack could account for 10–20% of the removal of CH₃I and compete with photolysis for removal of the propyl iodides.⁹³ An analysis of the secondary chemistry arising from OH or Cl abstraction of a hydrogen bonded to the same carbon as iodine shows that iodine atom release occurs with greater than 90% yield for CH₃I and slightly lower for the higher alkyl iodides.⁹³

Iodocarbons with two chromophores, e.g., CH₂I₂, CH₂ICl, and CH₂IBr, have been shown to be the most important iodine atom precursors in some environments.¹⁶ Compared to methyl iodide, the absorption bands of these molecules are red shifted and more intense; there are also two possible photofragmentation pathways. Broadband UV photolysis of CH₂-IBr favors C–I cleavage,⁹⁴ while about 14% of the fragmentation leads to formation of bromine atoms and iodomethyl radicals. Release of Br from the CH₂-Br radical should be rapid since its major fate is formation of CH₂BrO, which rapidly undergoes unimolecular decomposition to CH₂O and Br atoms under atmospheric conditions.⁹⁵ Chloriodomethane photolysis appears to leave the C–Cl chromophore unaffected,⁹⁶ producing CH₂Cl and I only. The fate of the CH₂I radical is of importance, however, in the photodissociation of di-iodomethane. Two reaction schemes are possible following the primary production of CH₂I:

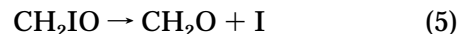


The iodomethyl radical is known to absorb light in the UV–visible,⁹⁷ so instantaneous production of the second iodine atom via (1a) is one outcome. Reaction (1b) produces an iodine-containing peroxy radical

which may react further according to the availability of NO_x (NO and NO₂):



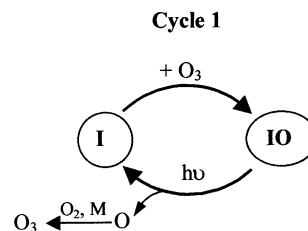
Both (2) and (3) yield CH₂IO, which has two possible fates:



Cotter et al.⁹³ found no evidence for reaction (4) in their experiments on alkyl iodides, so it seems likely that, analogous to CH₂BrO,⁹⁵ the major fate of CH₂-IO is unimolecular decomposition, leading to fairly rapid release of both iodine atoms in the case of CH₂I₂. Note that the halogen-containing peroxy radical arising from OH or Cl attack of alkyl iodides or from photodissociation of dihalomethanes may give rise to production of an ozone molecule via reaction (2).

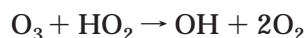
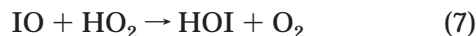
4.2. Gas-Phase Processes

Unlike chlorine and bromine atoms, which react with a range of organic molecules, iodine atoms do not react with either saturated or unsaturated organic compounds. Reaction with O₃, forming the iodine monoxide (IO) radical, is their major fate. Regeneration of I atoms through photolysis of IO is rapid; therefore, a daytime steady state exists between I and IO (collectively termed IO_x). This cycle has no net effect on IO_x or O₃ chemistry, as shown below.



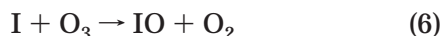
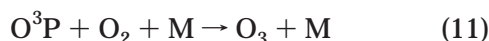
Although reaction cycle 1 is the predominant pathway for I-to-IO interconversion, a number of temporary inorganic reservoir products are formed via IO_x radical termination reactions with HO_2 , NO_x , and IO. Only cycles which regenerate I atoms without concomitant O atom formation can lead to catalytic O_3 loss. The reaction of IO with HO_2 , forming hypoiodous acid, HOI, is an important example:

Cycle 2



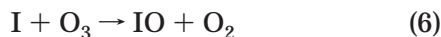
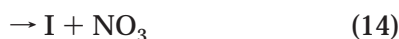
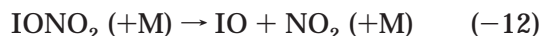
HOI is believed to be the major component of gas-phase inorganic iodine^{7,98} and an important route to the aerosol phase. Cycle 2 has also been suggested as the dominant O_3 loss cycle at NO_x levels below about 500 pptv.⁹⁹ For typical conditions at Mace Head, Ireland, Stutz et al.⁹⁹ calculated 0.3 ppb h^{-1} O_3 loss at 100 pptv of NO_x from the HOI cycle. At higher levels of NO_x , I atoms are regenerated not only through IO photolysis but also via reaction with NO and NO_2 :

Cycle 3



Similarly to cycle 1, cycle 3 regenerates O_3 and has

Cycle 4



a null effect. Cycle 4 is only effective at depleting ozone if reaction (13a) is the dominant pathway for photolysis of iodine nitrate, allowing the subsequent reaction of I atoms with ozone in reaction (1). The branching ratio between channels (13a) and (13b) has not yet been reported. Even if (13a) is dominant, the NO_3 fragment produced photolyzes to form $\text{NO}_2 + \text{O}$ with a branching ratio of 0.8, leading to further ozone formation. The effectiveness of cycle 4 also requires that iodine nitrate photolysis is fast compared to thermal dissociation. Reported rates of k_{-12} , however, differ by nearly an order of magnitude,^{5,100,101} and

photodissociation rates of IONO_2 have not been published. Allan and Plane²⁴ recently assessed these rates on the basis of preliminary data of the absorption cross section of IONO_2 (D. Rowley, U. College London), which gave a midday photolysis rate of IONO_2 of $3.2 \times 10^{-3} \text{ s}^{-1}$ and an estimate of k_{-6} of $1.14 \times 10^{15} \exp(-11890/T) \text{ s}^{-1}$ from RRKM calculations in conjunction with measurements of the $\text{IO} + \text{NO}_2$ recombination reaction at 474 K. These calculations suggested that at around 300 K, photolysis and thermal decomposition rates are comparable, but below 290 K, photolysis should dominate, allowing cycle 4 to contribute to boundary layer ozone depletion.

Finally, the relative rates of the branching channels of the self-reaction of IO radicals and the lifetimes of their products are important in determining both the gas and particulate chemistry of iodine. Early modeling studies assumed that the dimer of IO, I_2O_2 , was the main product and also the major carrier of iodine to aerosol.^{7,26,98} Cox et al.²² identified reaction (15), forming iodine dioxide (OIO), as an additional channel, with a yield of $\sim 40\%$.^{22,102}



The photolysis pathway of OIO is critical in determining its ozone destruction potential; only channel (16a) will result in net loss of O_3 :



Quantum calculations by Ashworth et al.²⁵ indicate that channel (16a) dominates in the visible region and that the photolysis lifetime of OIO is about 1 s, which would suggest that detectable OIO concentrations should be present only at night (see section 5). This is contrary to the work of Cox et al.²² and an independent computational study¹⁰³ that indicated a high photochemical stability for OIO.

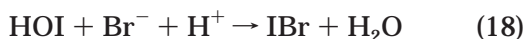
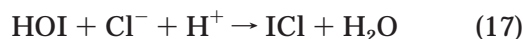
Apart from photolysis, the fate of OIO is uncertain, but von Glasow et al.²⁹ assumed reaction with NO and OH and uptake to aerosol and surfaces.

4.3. Aerosol Recycling

The net transfer of iodine from the gas to the condensed phase is reflected by the factor of 100- to 1000-fold enrichment of I in fine fraction marine aerosol by comparison to the I/Na ratio in seawater.¹⁰⁴⁻¹⁰⁶ Some of the condensed iodine is, however, recycled back to the gas phase; the exact rates and mechanisms involved are key to predicting the atmospheric impact of iodine.

The first mechanisms proposed for release of reactive halogens from aerosol required significant concentrations of nitrogen oxides.^{107,108} Vogt et al.¹⁰⁹ suggested an autocatalytic cycle for bromide and chloride release in low NO_x environments and later²⁶ proposed that the interaction of iodine in sea salt aerosol could accelerate gaseous halogen release, mainly through acid-catalyzed aerosol scavenging of

hypoiodous acid, formed in cycle 2:



Release of ICl and IBr after interaction of HOI on salt surfaces has been verified in laboratory experiments,^{110,111} and is believed to significantly increase the gas-phase halogen reservoir.²⁶

The uptake and hydrolysis of IONO₂ on aerosol is a potentially important removal pathway for NO_x in the remote troposphere,²⁷ leading indirectly to increased rates of ozone destruction.⁹⁹ Removal of atmospheric NO_x by halogens may be as important as catalytic halogen cycling in reducing boundary layer ozone concentrations. However, the effect depends upon the relative rates of IONO₂ uptake and decomposition (reaction (-12)); as discussed in section 4.2, the decomposition rate is currently uncertain.

Following the work of Cox et al.,²² the roles of OIO and I₂O₂ have been re-examined. Note that OIO is a product of both the IO self-reaction and the reaction of IO with BrO; indeed, von Glasow et al.²⁹ found the latter to be the major source. A high photochemical stability of OIO, as found by Cox et al.,²² would reduce the IO concentration and subsequent ozone depletion potential of iodine, with the effect being dependent upon the rates of OIO and I₂O₂ uptake to aerosol. Irreversible accumulation of OIO and I₂O₂ has been assumed as the main cause of iodate enrichment of aerosol (see Figure 3). As discussed earlier, however, more recent work²⁵ suggests a short photolysis lifetime for OIO, increasing the ozone depletion potential but decreasing the potential for aerosol iodate formation.

5. Atmospheric Observations and Modeling of Reactive Iodine Species

As apparent from the discussions above, modeling studies attempting to quantify the effect of iodine chemistry on atmospheric photooxidation chemistry must explicitly include interactions with sea salt bromide and chloride, and coupling of reactive iodine with trace gases including NO_x. Various assumptions concerning kinetic parameters, uptake coefficients, and deposition rates have to be made where data is unavailable. Despite the number of different assumptions made, recent modeling studies have made similar estimates for the contribution of iodine chemistry to the total chemical net destruction of O₃, i.e., of 15–40%²⁹ and up to 50%,^{27,99} corresponding to iodine-catalyzed O₃ destruction of up to ~0.45 ppb h⁻¹. McFiggans et al.²⁷ tuned various unknown parameters to achieve good agreement between observed and modeled IO concentrations. However, the model of von Glasow et al.,²⁹ which was not constrained with IO, did not reproduce the general features of OIO measurements made at Cape Grim, Tasmania.¹⁴ The predicted morning peak of OIO was greater than the afternoon/night peak, whereas Allan et al.¹⁴ found that the marine boundary layer concentration of OIO increased after sunset to 3 pptv

and remained below the detection limit of around 0.5 pptv during the day, consistent with the fast photolysis rate of OIO predicted by Ashworth et al.²⁵

There is some indirect evidence for halogen-mediated tropospheric chemistry outside of the poles. During a cruise over the tropical Indian Ocean, Dickerson et al.¹⁸ measured diurnal variations in ozone concentrations of about 32% of the mean. Model simulations of the observations indicated that homogeneous HO_x chemistry could account for only a 12% diurnal variation in O₃, whereas the addition of aerosol-derived Br reactions to the model increased the predicted diurnal variation to 22%, accounting for most, but not all, of the photochemical loss observed. Similarly, Galbally et al.¹⁷ observed an asymmetric feature at sunrise in the averaged diurnal O₃ cycle at Cape Grim, Tasmania, which was statistically different from the pattern of homogeneous HO_x destruction but comparable in magnitude. Bromine and iodine chemistry was suggested as a cause. It is not surprising that ozone measurements showing evidence for halogen chemistry are rare, given that the effects of transport often dominate chemical features of ozone. Dickerson et al.¹⁸ analyzed air which had spent long periods over the open ocean, and the measurements of Galbally et al.¹⁷ were an average of data collected over 13 years in clean marine sector air, both of which substantially reduce the stochastic effects of transport.

A recent comparison of modeled and measured HO₂ radicals at Rishiri Island (45°N, 141°E) invoked reaction with IO to explain the overprediction of HO₂ of up to 70%.¹⁹ The discrepancies were higher at low NO_x concentrations, which may have been indicative of loss of reactive iodine to IONO₂ and competition between NO and IO for HO₂. Although inorganic iodine was not measured during this study, levels of organoiodines were even higher than those at Mace Head,¹⁶ where several ppt of IO were concurrently observed.^{12,13}

Finally, ultrafine particle production events linked to low tide and solar radiation have been observed at the coastal site of Mace Head, Ireland,^{21,112} driving intense speculation as to the mechanisms involved. It was already established that most particulate iodine in marine environments is in the fine mode¹¹³ and that biogenic organoiodine coastal emissions maximized at low tide.¹⁶ Laboratory investigations revealed that in the presence of ozone, photodissociation of CH₂I₂, which was proposed as the major origin of iodine atoms at Mace Head,¹⁶ leads to rapid new particle formation composed mainly of oxides of iodine.²⁰ Analysis of new ultrafine particles at Mace Head has confirmed that iodine is an important component.¹¹⁴ It is not clear, however, whether the nucleation events observed are a result of homomolecular homogeneous nucleation of iodine compounds or if low-volatility iodine oxides lead to rapid growth of existing, thermodynamically stable sulfate clusters.¹¹⁵ Uptake of HOI, the dominant condensable iodine vapor at low organic iodine concentrations,²¹ to existing particles presumably contributes but cannot alone explain the rapid growth of new particles observed. Hoffmann et al.²⁰ proposed that self-

reaction of OIO to form low-volatility iodine oxides, such as I_2O_4 (or $[IO]^+[IO_3]^-$), leads to stable chainlike structures from further collisions with OIO. O'Dowd et al.²¹ included this mechanism in a simulation of the production of new particles from condensation of low-volatility iodine species on thermodynamically stable sulfate clusters, and concluded that at high iodine concentrations such particles may overcome the coagulation loss barrier, resulting in a higher probability of the new particles surviving and increasing the number and lifetime of condensation sites for production of cloud condensation nuclei (CCN). Note, however, that the recent work by Ashworth et al.²⁵ suggests that self-reactions of OIO are unlikely to be an important mechanism for particle formation, given its short photolysis lifetime.

6. Summary and Conclusions

There is now evidence that iodine in the marine boundary layer has an influence on ozone destruction, the oxidizing capacity of the troposphere, denoxification, and particle formation. Recent spectroscopic measurements of IO and OIO have made a major contribution to understanding these impacts. Where measurements are available, the main precursor to reactive inorganic iodine has been suggested as diiodomethane. Known sources of CH_2I_2 include macroalgae and polar microalgae, with some evidence of an additional open ocean source. Other reactive organic species, including $i-C_3H_7I$, CH_2ICl , and CH_2IBr , may also play a significant role, but it is clear that methyl iodide alone does not lead to significant atmospheric perturbation. Recent modeling studies are reasonably consistent in predicting that iodine-catalyzed ozone destruction may contribute up to half of marine boundary layer chemical net destruction. It is also clear that iodine is involved in the production of ultrafine particles in coastal regions. However, uncertainties in source characteristics and kinetic parameters mean that models are not capable of reproducing field data of reactive iodine species, and that the mechanisms for iodine-related particle formation are uncertain, so predictions must as yet be treated with caution.

7. References

- Lovelock, J. E.; Maggs, K. J.; Wade, R. J. *Nature* **1973**, *241*, 194.
- Moyers, J. L.; Duce, R. A. *J. Geophys. Res.* **1972**, *77*, 5330.
- Kritz, M. A.; Rancher, J. *J. Geophys. Res.* **1980**, *85*, 1633.
- Chameides, W. L.; Davis, D. D. *J. Geophys. Res.* **1980**, *85*, 7383.
- Chatfield, R. B.; Crutzen, P. J. *J. Geophys. Res.* **1990**, *95*, 22319.
- Solomon, S.; Garcia, R. R.; Ravishankara, A. R. *J. Geophys. Res.* **1994**, *99*, 20491.
- Davis, D.; Crawford, J.; Liu, S.; McKeen, S.; Bandy, A.; Thornton, D.; Rowland, F.; Blake, D. *J. Geophys. Res.* **1996**, *101*, 2135.
- Barrie, L. A.; Bottenheim, J. W.; Schnell, R. C.; Crutzen, P. J.; Rasmussen, R. A. *Nature* **1988**, *334*, 138.
- Bottenheim, J. W.; Barrie, L. A.; Atlas, E.; Heidt, L. E.; Niki, H.; Rasmussen, R. A.; Shepson, P. B. *J. Geophys. Res.* **1990**, *95*, 18555.
- Barrie, L. A.; Staebler, R.; Toom, D.; Georgi, B.; Denhartog, G.; Landsberger, S.; Wu, D. *J. Geophys. Res.* **1994**, *99*, 25439.
- Sirois, A.; Barrie, L. A. *J. Geophys. Res.* **1999**, *104*, 11599.
- Alicke, B.; Hebestreit, K.; Stutz, J.; Platt, U. *Nature* **1999**, *397*, 572.
- Allan, B. J.; McFiggans, G.; Plane, J. M. C.; Coe, H. *J. Geophys. Res.* **2000**, *105*, 14363.
- Allan, B. J.; Plane, J. M. C.; McFiggans, G. *Geophys. Res. Lett.* **2001**, *28*, 1945.
- Hebestreit, K.; Hönninger, G.; Stutz, J.; Alicke, B.; Platt, U. *Geophys. Res. Abstr.* **2000**, *2*, 1061.
- Carpenter, L. J.; Sturges, W. T.; Liss, P. S.; Penkett, S. A.; Alicke, B.; Hebestreit, K.; Platt, U. *J. Geophys. Res.* **1999**, *104*, 1679.
- Galbally, I. E.; Bentley, S. T.; Meyer, C. P. *Geophys. Res. Lett.* **2000**, *27*, 3841.
- Dickerson, R. R.; Rhoads, K. P.; Carsey, T. P.; Oltmans, S. J.; Burrows, J. P.; Crutzen, P. J. *J. Geophys. Res.* **1999**, *104*, 21385.
- Kanaya, Y.; Yokouchi, Y.; Matsumoto, J.; Nakamura, K.; Kato, S.; Tanimoto, H.; Furutani, H.; Toyota, K.; Akimoto, H. *Geophys. Res. Lett.* **2002**, *29*, 10.1029/2001GL014061.
- Hoffmann, T.; O'Dowd, C. D.; Seinfeld, J. H. *Geophys. Res. Lett.* **2001**, *28*, 1949.
- O'Dowd, C. D.; Jimenez, J. L.; Bahreini, R.; Flagan, R. C.; Seinfeld, J. H.; Hameri, K.; Pirjola, L.; Kulmala, M.; Jennings, S. G.; Hoffmann, T. *Nature* **2002**, *417*, 632.
- Cox, R. A.; Bloss, W. J.; Jones, R. L.; Rowley, D. M. *Geophys. Res. Lett.* **1999**, *26*, 1857.
- Ingham, T.; Cameron, M.; Crowley, J. N. *J. Phys. Chem. A* **2000**, *104*, 8001.
- Allan, B. J.; Plane, J. M. C. *J. Phys. Chem. A* **2002**, *106*, 8634.
- Ashworth, S. H.; Allan, B. J.; Plane, J. M. C. *Geophys. Res. Lett.* **2002**, *29*, art. no. 1456.
- Vogt, R.; Sander, R.; von Glasow, R.; Crutzen, P. J. *J. Atmos. Chem.* **1999**, *32*, 375.
- McFiggans, G.; Allan, B.; Coe, H.; Plane, J. M. C.; Carpenter, L. J.; O'Dowd, C. *J. Geophys. Res.* **2000**, *105*, 14, 371.
- McFiggans, G.; Cox, R. A.; Mossinger, J. C.; Allan, B. J.; Plane, J. M. C. *J. Geophys. Res.* **2002**, *107*, 4271.
- von Glasow, R.; Sander, R.; Bott, A.; Crutzen, P. J. *J. Geophys. Res.* **2002**, *107*, 4341.
- von Glasow, R.; Sander, R.; Bott, A.; Crutzen, P. J. *J. Geophys. Res.* **2002**, *107*, 4323.
- Wong, G. T. F. *Rev. Aquat. Sci.* **1991**, *4*, 45.
- Garland, J. A.; Curtis, H. *J. Geophys. Res.* **1981**, *86*, 3183.
- Thompson, A. M.; Zafiriou, O. C. *J. Geophys. Res.* **1983**, *88*, 6696.
- Möller, A.; Lovrić, M.; Scholz, F. *Int. J. Environ. Anal. Chem.* **1996**, *63*, 99.
- Wuossmaa, A. M.; Hager, L. P. *Science* **1990**, *249*, 160.
- Wever, R.; Tromp, M. G. M.; Krenn, B. E.; Marjani, A.; Vantol, M. *Environ. Sci. Technol.* **1991**, *25*, 446.
- Harper, D. B. *Metal Ions Biol. Syst.* **1993**, *29*, 345.
- Küpper, F. C.; Müller, D. G.; Peters, A. F.; Kloareg, B.; Potin, P. *J. Chem. Ecol.* **2002**, *28*, 2057.
- Theiler, R.; Cook, J. C.; Hager, L. P.; Studa, J. F. *Science* **1978**, *202*, 1094.
- Gschwend, P. M.; McFarlane, J. K.; Newman, K. A. *Science* **1985**, *227*, 1023.
- Manley, S. L.; Goodwin, K.; North, W. J. *Limnol. Oceanogr.* **1992**, *37*, 1652.
- Nightingale, P. D.; Malin, G.; Liss, P. S. *Limnol. Oceanogr.* **1995**, *40*, 680.
- Pedersén, M.; Collén, J.; Abrahamsson, K.; Ekdahl, A. *Sci. Mar.* **1996**, *60*, 257.
- Carpenter, L. J.; Malin, G.; Kuepper, F.; Liss, P. S. *Global Biogeochem. Cycles* **2000**, *14*, 1191.
- Whittle, K. J. *Mar. Chem.* **1977**, *5*, 381.
- Collén, J.; Ekdahl, A.; Abrahamsson, K.; Pedersen, M. *Phytochemistry* **1994**, *36*, 1197.
- Mtolera, M. S. P.; Collén, J.; Pedersén, M.; Ekdahl, A.; Abrahamsson, K.; Semes, A. K. *Eur. J. Phycol.* **1996**, *31*, 89.
- Manley, S. L.; Goodwin, K.; North, W. J. *Limnol. Oceanogr.* **1992**, *37*, 1652.
- Klick, S. *Mar. Chem.* **1993**, *42*, 211.
- Carpenter, L. J.; Liss, P. S. *J. Geophys. Res.* **2000**, *105*, 20539.
- Carpenter, L. J.; Hebestreit, K.; Platt, U.; Liss, P. S. *Atmos. Chem. Phys.* **2001**, *1*, 9.
- Itoh, N.; Tsujita, M.; Ando, T.; Hisatomi, G.; Higashi, T. *Phytochemistry* **1997**, *45*, 67.
- Udomkit, A.; Dunstan, W. M. *J. Phycol.* **1991**, *27*, 73.
- Moisan, T. A.; Dunstan, W. M.; Udomkit, A.; Wong, G. T. F. *J. Phycol.* **1994**, *30*, 580.
- Manley, S. L.; de la Cuesta, J. L. *Limnol. Oceanogr.* **1997**, *42*, 142.
- Scarratt, M. G.; Moore, R. M. *Limnol. Oceanogr.* **1999**, *44*, 703.
- Moore, R. M.; Groszko, W. *J. Geophys. Res.* **1999**, *104*, 11163.
- Moore, R. M.; Webb, M.; Tokarczyk, R.; Wever, R. *J. Geophys. Res.* **1996**, *101*, 20899.
- Klick, S.; Abrahamsson, K. *J. Geophys. Res.* **1992**, *97*, 12683.
- Moore, R. M.; Tokarczyk, R. *Global Biogeochem. Cycles* **1993**, *7*, 195.
- Schall, C.; Heumann, K. G.; Kirst, G. O. *Fresenius J. Anal. Chem.* **1997**, *359*, 298.
- Klick, S. *Limnol. Oceanogr.* **1992**, *37*, 1579.
- Yamamoto, H.; Yokouchi, Y.; Otsuki, A.; Itoh, H. *Chemosphere* **2001**, *45*, 371.
- Moore, R. M.; Zafiriou, O. C. *J. Geophys. Res.* **1994**, *99*, 16415.
- Liss, P. S.; Slater, P. G. *Nature* **1974**, *247*, 181.

- (66) Liss, P. S.; Merlivat, L. In *The role of air-sea exchange in geochemical cycling*; Buat-Menard, P., Ed.; Reidel: Dordrecht, The Netherlands, 1986; pp 113–127.
- (67) Wanninkhof, R. *J. Geophys. Res.* **1992**, *97*, 7373.
- (68) Wanninkhof, R.; McGillis, W. R. *Geophys. Res. Lett.* **1999**, *26*, 1889.
- (69) Khalil, M. A. K.; Moore, R. M.; Harper, D. B.; Lobert, J. M.; Erickson, D. J.; Koropalov, V.; Sturges, W. T.; Keene, W. C. *J. Geophys. Res.* **1999**, *104*, 8333.
- (70) Yokouchi, Y.; Nojiri, Y.; Barrie, L. A.; Toom-Sauntry, D.; Fujinuma, Y. *J. Geophys. Res.* **2001**, *106*, 12661.
- (71) Nightingale, P. D.; Malin, G.; Law, C. S.; Watson, A. J.; Liss, P. S.; Liddicoat, M. I.; Boutin, J.; Upstill-Goddard, R. C. *Global Biogeochem. Cycles* **2000**, *14*, 373.
- (72) Broecker, H. C.; Siems, W. *Gas Transfer at Water Surfaces*; Reidel: Dordrecht, The Netherlands, 1984; pp 229–237.
- (73) Phillips, L. F. *Geophys. Res. Lett.* **1991**, *18*, 1221.
- (74) Frew, N. M. *The Sea Surface and Global Change*; Cambridge University Press: New York, 1997; pp 121–172.
- (75) Nightingale, P. D. Low molecular weight halocarbons in seawater. Ph.D. Thesis, University of East Anglia, Norwich, England, 1991.
- (76) Reifenhäuser, W.; Heumann, K. G. *Chemosphere* **1992**, *24*, 1293.
- (77) Bell, N.; Hsu, L.; Jacob, D. J.; Schultz, M. G.; Blake, D. R.; Lobert, J. M.; Maier-Reimer, E. *J. Geophys. Res.* **2002**, *107*, 4340.
- (78) King, D. B.; Saltzman, E. S. *J. Geophys. Res.* **1997**, *102*, 18715.
- (79) Kurylo, M. J.; Rodriguez, J. M. *WMO, Scientific Assessment of Ozone Depletion: 1998*; Global Ozone Research and Monitoring Project Report No. 44; World Meteorological Organization: Geneva, Switzerland, 1999.
- (80) Zafiriou, O. C. *J. Mar. Res.* **1975**, *33*, 75.
- (81) Zika, R. G.; Gidel, L. T.; Davis, D. D. *Geophys. Res. Lett.* **1984**, *11*, 353.
- (82) Moelwyn-Hughes, E. A. *Proc. R. Soc. London* **1938**, *164*, 295.
- (83) Elliott, S.; Rowland, F. S. *Geophys. Res. Lett.* **1993**, *20*, 1043.
- (84) Whitehead, D. C. *Environ. Int.* **1984**, *10*, 321.
- (85) Muramatsu, Y.; Yoshida, S. *Atmos. Environ.* **1995**, *29*, 21.
- (86) Redeker, K. R.; Wang, N. Y.; Low, J. C.; McMillan, A.; Tyler, S. C.; Cicerone, R. J. *Science* **2000**, *290*, 966.
- (87) Dimmer, C. H.; Simmonds, P. G.; Nickless, G.; Bassford, M. R. *Atmos. Environ.* **2001**, *35*, 321.
- (88) Keppler, F.; Eiden, R.; Niedan, V.; Pracht, J.; Scholer, H. F. *Nature* **2000**, *403*, 298.
- (89) Schall, C.; Heumann, K. G. *Fresenius J. Anal. Chem.* **1993**, *346*, 717.
- (90) Rattigan, O. V.; Shallcross, D. E.; Cox, R. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2839.
- (91) Roehl, C. M.; Burkholder, J. B.; Moortgat, G. K.; Ravishankara, A. R.; Crutzen, P. J. *J. Geophys. Res.* **1997**, *102*, 12819.
- (92) Mössinger, J.; Shallcross, D. E.; Cox, R. A. *J. Chem. Soc., Faraday Trans.* **1998**, *10*, 1391.
- (93) Cotter, E. S. N.; Booth, N. J.; Canosa-Mas, C. E.; Wayne, R. P. *Atmos. Environ.* **2001**, *35*, 2169.
- (94) Lee, S. J.; Behrson, R. *J. Phys. Chem.* **1982**, *86*, 728.
- (95) Orlando, J. J.; Tyndall, G. S.; Wallington, T. D. *J. Phys. Chem.* **1996**, *100*, 7026.
- (96) Schmitt, G.; Comes, F. J. *J. Photochem. Photobiol. A* **1987**, *41*, 13.
- (97) Kroger, P. M.; Demou, P. C.; Riley, S. J. *J. Chem. Phys.* **1976**, *65*, 1823.
- (98) Jenkin, M. E. *The photochemistry of iodine-containing compounds in the marine boundary layer*; Environ. and Energy Rep. AEA EE-0405; AEA Harwell Lab.; Oxfordshire, England, 1992.
- (99) Stutz, J.; Hebestreit, K.; Alicke, B.; Platt, U. *J. Atmos. Chem.* **1999**, *34*, 65.
- (100) Jenkin, M. E.; Cox, R. A.; Candeland, D. E. *J. Atmos. Chem.* **1985**, *2*, 359.
- (101) Barnes, I.; Becker, K. H.; Starcke, J. *J. Phys. Chem.* **1991**, *95*, 9736.
- (102) Bloss, W. J.; Rowley, D. M.; Cox, R. A.; Jones, R. L. *J. Phys. Chem. A* **2001**, *105*, 7840.
- (103) Misra, A.; Marshall, P. *J. Phys. Chem. A* **1998**, *102*, 9056.
- (104) Duce, R. A.; Hoffman, E. J. *Annu. Rev. Earth Planet Sci.* **1976**, *4*, 187.
- (105) Sturges, W. T.; Barrie, L. A. *Atmos. Environ.* **1988**, *22*, 1179.
- (106) Baker, A. R.; Thompson, D.; Campos, M. L. A. M.; Parry, S. J.; Jickells, T. D. *Atmos. Environ.* **2000**, *34*, 4331.
- (107) Finlayson-Pitts, B. J. *Nature* **1983**, *306*, 676.
- (108) Zetzsch, C.; Pfahler, G.; Behnke, W. *J. Aerosol Sci.* **1988**, *19*, 1203.
- (109) Vogt, R.; Crutzen, P. J.; Sander, R. *Nature* **1996**, *383*, 327.
- (110) Holmes, N. S.; Adams, J. W.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1679.
- (111) Mössinger, J.; Cox, R. A. *J. Phys. Chem. A* **2001**, *105*, 5165.
- (112) O'Dowd, C. D.; Geever, M.; Hill, M. K.; Jennings, S. G.; Smith, M. H. *Geophys. Res. Lett.* **1998**, *25*, 1661.
- (113) Baker, A. R.; Thompson, D.; Campos, M. L. A. M.; Parry, S. J.; Jickells, T. D. *Atmos. Environ.* **2000**, *34*, 4331.
- (114) Mäkelä, J. M.; Hoffmann, T.; Holzke, C.; Väkevä, M.; Suni, T.; Mattila, T.; Aalto, P. P.; Tapper, U.; Kauppinen, E. I.; O'Dowd, C. D. *J. Geophys. Res.* **2002**, *107*, 8110.
- (115) Kulmala, M.; Pirjola, U.; Makela, J. M. *Nature* **2000**, *404*, 66.
- (116) Bassford, M. R.; Nickless, G.; Simmonds, P. G.; Lewis, A. C.; Pilling, M. J.; Evans, M. J. *Atmos. Environ.* **1999**, *33*, 2373.
- (117) Yokouchi, Y.; Mukai, H.; Yamamoto, H.; Otsuki, A.; Saitoh, C.; Nojiri, Y. *J. Geophys. Res.* **1997**, *102*, 8805.
- (118) Li, H.-J.; Yokouchi, Y.; Akimoto, H. *Atmos. Environ.* **1999**, *33*, 1881.
- (119) Yokouchi, Y.; Barrie, L. A.; Toom, D.; Akimoto, H. *Atmos. Environ.* **1996**, *30*, 1723.

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