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The influence of iron fertilization on the fluxes of methyl halides and isoprene from ocean to atmosphere in the SERIES experiment

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Abstract

As a part of an iron-fertilization experiment in the NE Pacific in July 2002 measurements were made of isoprene and methyl halides both within the fertilized patch and outside. Isoprene showed the response that would be expected of a gas having a source in phytoplankton: its concentration within the patch increased relative to outside, and after 10–14 days its calculated net production rate was about 6-fold higher within the patch. In contrast, the methyl halides showed no clear effect of fertilization, though the production rates of methyl iodide were appreciable. Hence there is no evidence that any of the algal groups present, such as diatoms that were stimulated by the fertilization played a significant role in the net production of methyl halides. The results are not inconsistent with a photochemical source of the gases, though light levels were attenuated by persistent cloud cover.

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1. Introduction

1.1. Relevance of the methyl halides

The primary relevance of methyl halides lies in their ability to transfer halogens in the gas phase from the ocean into the atmosphere and, in the case of Cl and Br, to give them a sufficiently long atmospheric lifetime that a portion can mix into the stratosphere. There the released chlorine and bromine play a role in controlling ozone concentrations through their catalytic loss reactions. Before

the introduction of anthropogenic chlorinated gases to the atmosphere, CH₃Cl was the main source of gas phase chlorine, and CH₃Br was (and remains) a major contributor to atmospheric bromine. Methyl iodide, being subject to relatively facile photolysis in the troposphere, has a shorter lifetime and consequently releases most of its iodine at low altitudes; only under special conditions may it be lofted to the tropopause or lower stratosphere (Solomon et al., 1994). Iodine is the most effective halogen catalyst of ozone breakdown, followed by bromine and chlorine. It contributes to ozone destruction in the marine boundary layer and, through deposition on aerosols, enhances release of active Br and Cl (McFiggans et al., 2000). The ocean is relevant to these gases as the predominant source of CH₃I, a

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major source and sink of CH_3Br , and a source of about 15% of the natural flux of CH_3Cl to the atmosphere.

1.2. *What is their origin?*

Though the ocean has long been known as a source of methyl halides (Lovelock et al., 1973), the actual production processes within the ocean have remained poorly understood. Early studies (Lovelock, 1975) provided evidence for a biological source, though details of its exact nature and magnitude have been lacking. In the coastal zone there is evidence for a macroalgal source of CH_3I (Manley and Dastoor, 1988), while in the pelagic zone there is some evidence that phytoplankton are a source. Such evidence is mostly indirect, coming from laboratory studies of phytoplankton cultures (e.g., Scarratt and Moore, 1996, 1998; Manley and de la Cuesta, 1997; Saemundsdottir and Matrai, 1997). Several studies found that the microalgal production rates fall short of those needed to explain observed surface ocean concentrations. Moore and Zafriou (1994) provided evidence from laboratory studies for a photochemical source of methyl iodide, and recently field evidence from the tropical Atlantic has been reported by Richter and Wallace (2004). It has been shown that biological processes also account for some loss of methyl chloride and bromide in seawater (e.g., King and Saltzman, 1997; Tokarczyk et al., 2003). Chemical processes play a role in the production of methyl chloride, for example by the nucleophilic reaction of chloride with CH_3Br and CH_3I , and in the loss of all three compounds by hydrolysis (Elliott and Rowland, 1993).

1.3. *Objectives*

The first objective of this study was to determine the effect of an iron addition on the fluxes of methyl halides to the atmosphere. This is relevant because of possible Fe-stimulated changes in ocean primary productivity in the past which have been speculated to play a role in the major changes in atmospheric carbon dioxide abundance between glacial and interglacial periods (Martin, 1990). Furthermore, it has been proposed that iron fertilization may be used to engineer a reduction in atmospheric CO_2 in the future. Amongst the numerous questions raised by such a proposal is the effect it would have on other atmospherically reactive trace gases, including

halogenated compounds. A second important objective of the study was to use this perturbation to cast light on the production processes, in particular to elucidate biological influence. Potentially, this approach can avoid the serious shortcomings of laboratory experiments that typically cannot use oceanic algae and employ conditions that bear little resemblance to the ocean environment.

The low molecular-weight hydrocarbon, isoprene, that laboratory studies indicate is released by all marine algal species that have been studied (Shaw et al., 2003), was also measured as a model for gases that would be expected to have increased production and flux to the atmosphere within the fertilized patch. Isoprene itself is relevant to atmospheric chemistry over the oceans as a component of the non-methane hydrocarbons (NMHC) that play a role in controlling the oxidant concentrations (Carslaw et al., 1999). The study reported here was conducted in the northeast Pacific as a part of the subarctic ecosystem response to iron enrichment study (SERIES) in July 2002 (Boyd et al., 2004).

2. Methods

Details of the iron fertilization, re-infusion of iron, development of the patch, and biological changes induced by the fertilization are given in Boyd et al. (2004), and only a brief summary will be provided here. The area of 77 km^2 that was initially fertilized spread to 1000 km^2 after about 18 days and was mapped daily (Law et al., 2006) by measurement of SF_6 added with the first iron infusion. Chlorophyll increased 5-fold within the patch over a period of 15 days before declining. Marchetti et al. (2006b) report that particulate organic primary productivity inside the patch started to increase relative to outside within 2 days of the fertilization and, after 15 days, reached a rate 20 times that outside. The depth of euphotic zone varied from ca. 30 to 57 m in the patch, and ca. 40 to 70 m out of the patch during the 13 days following fertilization. Stations were normally occupied daily both within the patch and outside (identified by the absence of excess SF_6 in the mixed layer). The work described here utilized daily depth profiles from 5 to 200 m, with sample spacing increasing with depth. All the samples were collected during daylight hours, but timing varied from day to day. Water samples were collected from Niskin bottles and stored in 100-ml glass syringes held submerged in a container of seawater until analysed, typically

within 4 h. Gases were stripped from 40-ml aliquots of water, held in a double-walled glass purge vessel at 40 °C, by a stream of high-purity He flowing at 40 ml min⁻¹ for 12 min. Water vapour was removed from the gas stream by passage first through a condenser held at 4 °C and then through a trap containing magnesium perchlorate. Analytes were trapped in a length of steel tubing (length 30 cm, od 0.8 mm) held at -150 °C from which they were desorbed by electrical heating to ca. 30 °C. Separation was effected on a pair of DB624 columns in series (30 and 70 m, i.d. 0.53 mm, J&W Scientific) and measurement was made using a quadrupole mass spectrometer (Finnigan TraceMS) operating in single ion mode. Less volatile compounds than those being measured were backflushed from the first column. To correct detector drift, a fixed volume of a mixture of deuterated methyl halides was added to the purge gas downstream from the purge vessel.

Calibration was done by injection upstream from the purge vessel of volumes (50–200 µL) of a gravimetrically-prepared mixture of analytes at ppm levels in nitrogen (Happell and Wallace, 1997) with gas-tight syringes (Hamilton). The reproducibility of measurement of water samples from the same Niskin bottle was measured once using five replicates. The coefficients of variation for CH₃I, CH₃Br, CH₃Cl, isoprene and CFC 11 were 1.0%, 5.2%, 1.5%, 4.2% and 1.7%, respectively. The day-to-day precision is likely to be lower but cannot be measured because there is no way to preserve a reference water sample. One of the reasons for the relatively low precision for CH₃Br was the existence of interference from dimethyl disulphide in one of the masses normally monitored (94); so only mass 96 was used for measuring this compound with a consequent decrease in the signal to noise ratio. The calibration of CH₃Br is subject to an uncertainty that did not affect CH₃Cl or CH₃I. It was discovered after the experiment that a mixed standard of higher molecular weight halocarbons, containing CH₂Cl₂, CHCl₃ and CH₂Br₂, and used for supplementary analyses during the cruise, had slowly accumulated some CH₃Br, though initially none had been present. Dibromomethane, as the only brominated compound in the original mixture, had to be involved in the reaction that generated CH₃Br within the electropolished stainless steel standard tank. Since the level of CH₃Br contaminant in that standard was measured, it was subsequently possible to correct the CH₃Br calibra-

tions for this artifact. However, making this correction inevitably contributed a small additional uncertainty to the absolute accuracy of the CH₃Br measurements in both water and air samples. All measurements were corrected for blanks, which were run with the purge vessel empty; values for CH₃Cl, CH₃Br, CH₃I, and isoprene were typically equivalent to 2.2±0.5, 0.2±0.05, 0.16±0.08, 0.15±0.03 pmol L⁻¹ (1σ), respectively.

Four of air samples were collected in 0.8-L stainless steel, internally electropolished canisters and analysed on board. The method was similar to that for water samples but with the purge vessel replaced with a steel loop (volume 207 ml). Blanks for CH₃Cl, CH₃Br and CH₃I were 8, 1, 0.7 pptv, respectively. In the case of CH₃I, the average atmospheric concentration was only twice the detection limit, so for flux calculations the atmospheric concentration was approximated at zero.

Wind speeds were measured at a height of 26±1 m above sea level and were corrected to a standard height of 10 m. The cubed wind speeds were averaged and used to calculate exchange velocities using the cubic formulation of Wanninkhof and McGillis (1999). The day numbering used here starts with Day 0 on July 9 (UTC).

3. Results

3.1. Concentrations and depth profiles

The stimulation of isoprene production inside the fertilized patch is well illustrated by three pairs of depth profiles measured at intervals of about 5 days through the experiment (Fig. 1).

These profiles show an increasing divergence of concentrations in the mixed layer, with concentrations in the patch being higher than outside, while beneath the mixed-layer concentrations remain similar inside and out. The maximum seen in all of these profiles beneath the mixed layer is typical of oceanic isoprene profiles and is interpreted as an effect of the non-ventilation of this layer. Thus, while production remains significant at this level in the euphotic zone, the rate of loss is substantially lower than in the overlying, ventilated mixed layer. The losses must include some mixing downwards and upwards away from the maximum, and, it is assumed, heterotrophic consumption.

An unexplained anomaly is the almost exact coincidence of isoprene profiles measured inside and outside the patch on day 5 (profiles not shown).

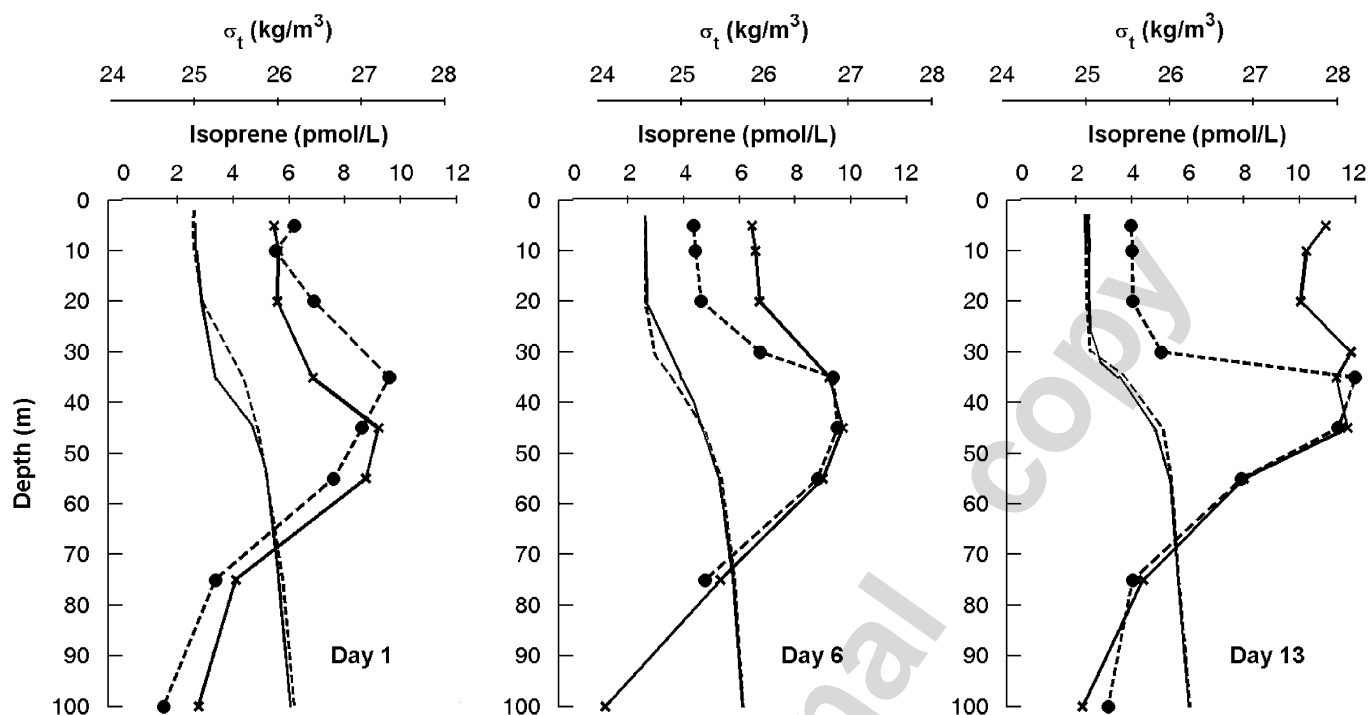


Fig. 1. Three pairs of profiles illustrating the growth of isoprene within the fertilized patch at 1, 6 and 13 days after fertilization; filled circles represent samples from outside the patch, and crosses samples within. The corresponding density (σ_t) profiles are shown.

The near-identity of these two profiles is supported by the optical transmission values from 5 to 25 m that were very similar to each other and more characteristic of water from outside the patch than in. SF_6 measurements appear to rule out incorrect placement of the vessel with respect to the patch as a possible reason for this anomaly: a single mixed-layer SF_6 measurement from the supposed “out” profile shows a concentration 73 times lower than inside. At this stage of the experiment, just prior to the second iron infusion, it is possible that as the patch spread, SF_6 was being added to water around the periphery with little dissolved Fe, but any explanation of the anomaly is highly speculative. A time-series of mixed-layer concentrations of isoprene inside and outside the patch is shown in Fig. 2. The concentrations plotted are the average of the samples within the mixed layer, which varied in depth between 5 and 35 m (average 23 m); in most cases the points are the average of 5- and 10-m samples, but samples from up to 30 m are included where the mixed-layer depth was greater. These results will be used below to estimate the change in production rate of isoprene and its efflux to the atmosphere.

In presenting results for the methyl halides, those for CH_3I will be presented first and in most detail. There are several reasons for this, an important one

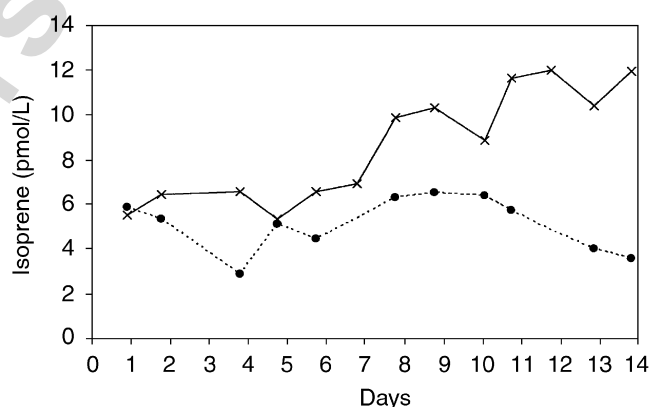


Fig. 2. A time-series of mixed-layer concentrations of isoprene inside and outside the patch; symbols as in Fig. 1.

being that it is the simplest compound to interpret. Being readily subject to photolysis in the troposphere, its atmospheric concentration approximates to zero so that the atmosphere itself does not support a significant concentration in seawater. This is not the case for CH_3Cl and CH_3Br for which average measured atmospheric concentrations were 513 and 9 pptv, respectively. Also, CH_3I is not produced in seawater by halogen exchange reactions with other methyl halides; in contrast, methyl chloride has some production from reaction of both CH_3I and CH_3Br with chloride ions. Finally, the

measurements of CH_3I have a higher precision than the other two compounds.

The surface concentrations of CH_3I both inside and outside the patch are shown as a function of time in Fig. 3. It is immediately apparent that there is no obvious pattern of enhanced concentrations in the patch to match the increasing isoprene. The time series might appear noisy, but reference to vertical profiles inside and outside the patch indicates that there are real differences between certain pairs of profiles, for example, 10 days after the fertilization (Fig. 4(A)). Additional support for the quality of the measurements is provided by CFC 11 profiles that were measured on exactly the same samples (Fig. 4(B)). These profiles are typically identical as

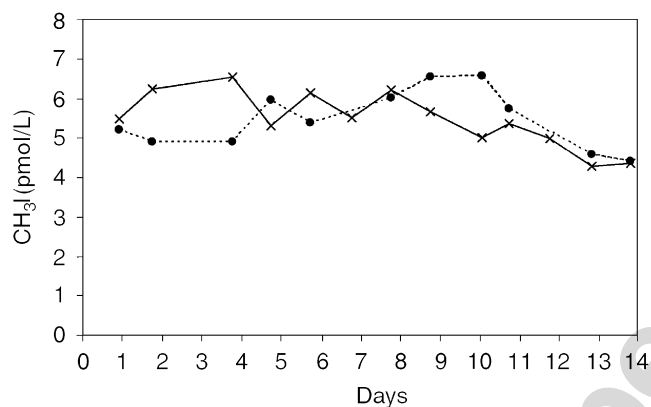


Fig. 3. A time-series of surface (5 m) concentrations of CH_3I inside and outside the patch; symbols as in Fig. 1.

expected for a gas that has concentrations in water controlled only by physical factors such as water temperature, and a constant atmospheric mixing ratio. The differences in the profiles are likely to reflect significant horizontal variability within both regions, which may result from physical and/or biological processes affecting the balance between production and loss of these gases.

Examples of CH_3Cl and CH_3Br profiles are shown for 9 days after the fertilization (Fig. 5(A), (B)). The pair for CH_3Cl show no difference between the patch and outside, while the CH_3Br profiles, though of similar form, at first glance suggest slightly higher concentrations (4–12%) outside the patch. Examination of samples in the same profile from 150 to 200 m, where concentrations were typically close to zero, suggests that the apparent difference arises from instrumental drift equivalent to 0.2 pM/L between the measurement of the two profiles. Typically, CH_3Br concentrations have decreased to close to zero by 200 m. It is concluded that no significant difference can be discerned between the profiles for CH_3Br .

The time series of mixed-layer CH_3Cl and CH_3Br concentrations (Fig. 6(A), (B)) show no evidence of significant differences between the fertilized and unfertilized waters. Methyl chloride was found to be always supersaturated in the surface waters, the degree of supersaturation calculated depending on the value used for the atmospheric concentration. A small number of air samples measured gave an

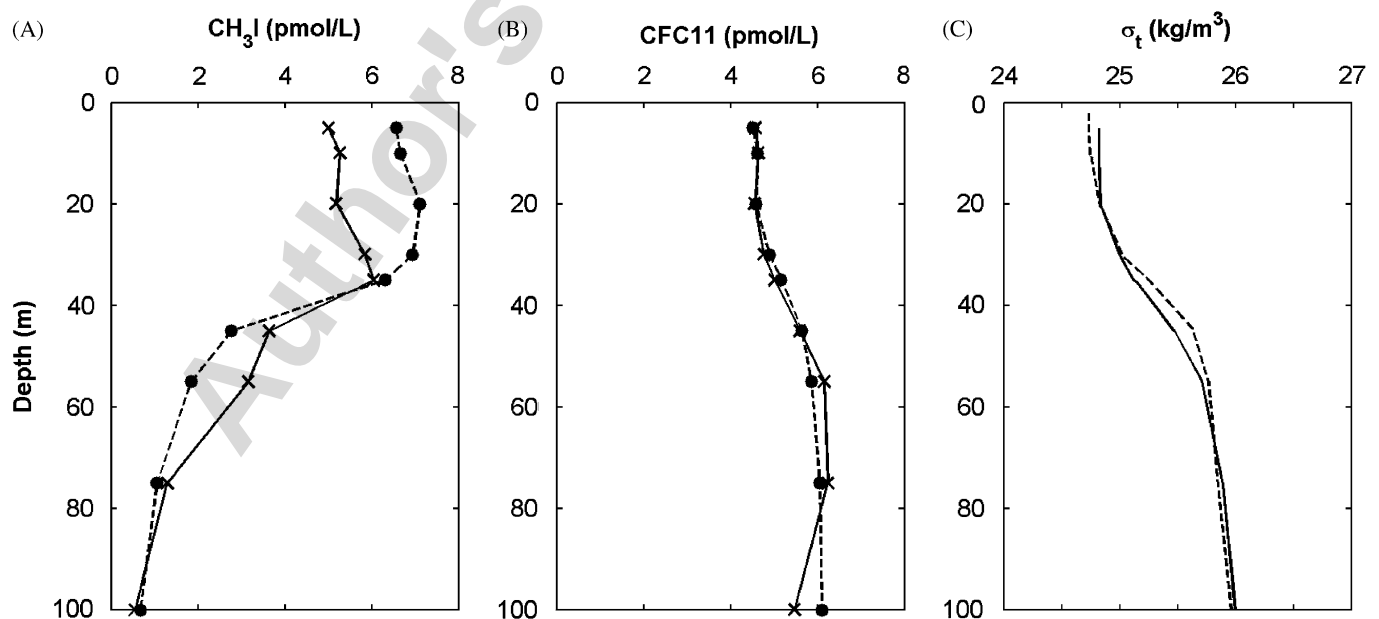


Fig. 4. Vertical profiles of (A) CH_3I , (B) CFC11 and (C) potential density on Day 10; symbols as in Fig. 1.

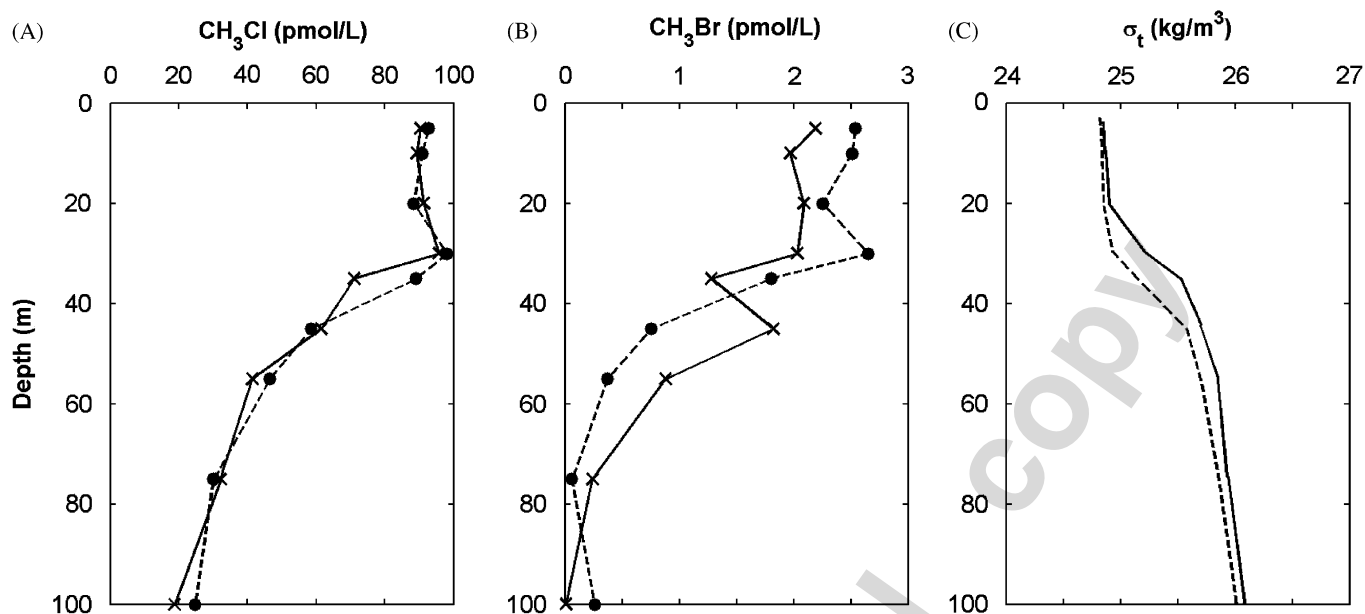


Fig. 5. Examples of (A) CH_3Cl , (B) CH_3Br and (C) potential density profiles from nine days after the fertilization; symbols as in Fig. 1.

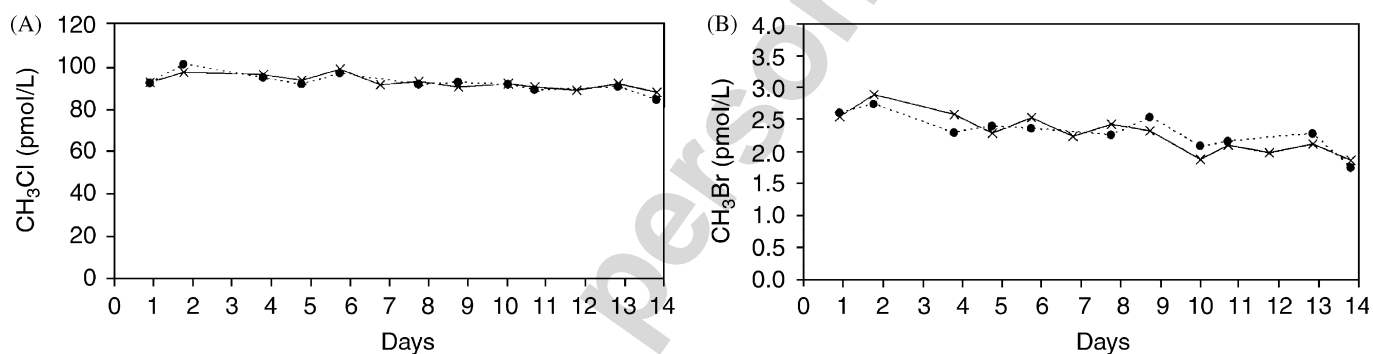


Fig. 6. CH_3Cl and CH_3Br times series inside and outside the patch; symbols as in Fig. 1.

average mixing ratio of 513 pptv, and this value would give an oceanic supersaturation averaging 21% (range 12–31%). It is possible that this estimate is a little high: the work of Khalil and Rasmussen (1999) suggests that the summertime mixing ratio of CH_3Cl at 50°N would be around 550 pptv, which gives a lower average supersaturation of 12% (range 5–22%). But in support of our higher supersaturations, it can be pointed out that saturation values are independent of calibration.

Supersaturation values for methyl iodide have little meaning: the atmospheric concentration is normally so low, on account of the short tropospheric lifetime of CH_3I with respect to photolysis, that surface ocean waters can have large supersaturations even at water concentrations much lower than those reported here. In the case of CH_3Br , it is found that the average saturation level

in surface waters was 97% (range 73–123%) referenced to a small number of atmospheric measurements. So we can say little about the air–sea exchange of this gas other than there was no evidence for either a strong source, or strong sink relative to the atmosphere.

3.2. Fluxes and production rates

From the data obtained we are able to calculate fluxes of the gases to the atmosphere, and then, with appropriate assumptions, production rates. This is done for isoprene, CH_3I and CH_3Cl , but is not feasible for CH_3Br because of the large uncertainty in the saturation values. Fluxes to the atmosphere are calculated using exchange velocities calculated from wind speed using the cubic relationship proposed by Wanninkhof and McGillis (1999).

Since the gas concentrations were measured only daily, while the wind speeds were recorded at a relatively high frequency, the latter were averaged over the time period between each sampling of the dissolved gases and that value was used for the flux calculation. Schmidt numbers for the three gases were obtained from the literature (Groszko, 1999) or, in the case of isoprene, calculated from a molar volume estimated by the method of Le Bas (Reid et al., 1987), and a diffusion coefficient calculated from the revised Wilke and Chang equation (Hayduk and Laudie, 1974).

On account of the extremely low concentrations of isoprene measured in air samples (close to detection limit), the flux of isoprene from the ocean to atmosphere is dependent only on the mixed-layer concentration and exchange velocity. Its variation with time is shown in Fig. 7. The average production rates of isoprene have been calculated for two time periods, days 1–9 and 11–14, based on two calculable quantities: the loss to the atmosphere, and the change in the mixed-layer reservoir. It is in part the difficulty in accounting for short-term (day-to-day) mixed-layer depths that has led us to make

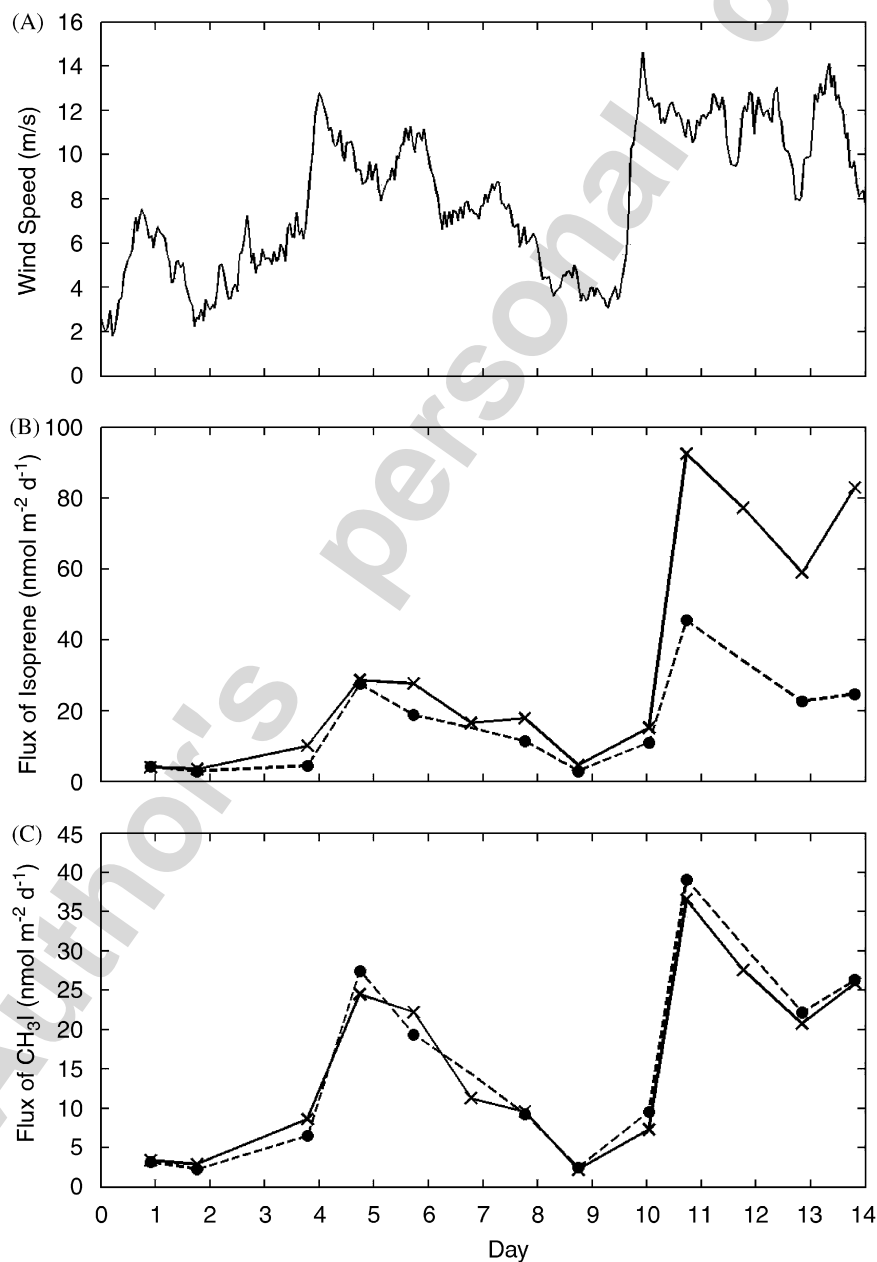


Fig. 7. (A) Wind speed as a function of time after fertilization, (B) ocean–atmosphere flux of isoprene, (C) ocean–atmosphere flux of methyl iodide as a function of time from fertilization; symbols as in Fig. 1.

this calculation for just two periods, rather than for each day. The two periods selected were a low-flux period that covered the first 9 days after iron fertilization, and the high-flux period at the end of the experiment. There is no information on the rate of consumption of isoprene within the mixed layer, though the form of the vertical profile, with concentrations decreasing to low values beneath the upper 50 m or so, demonstrates that consumption must be occurring. Consequently our production estimates are conservative. There are major uncertainties in the calculated gas fluxes of all the trace gases referred to in this work due to uncertainties in the relationship between flux and wind speed which makes it difficult to assign possible errors to our estimates of production rates. These could be of the order $\pm 50\%$, but the ratio of calculated production within the patch to outside is less sensitive to the uncertainties in the flux formulation.

A potential source for isoprene in the mixed layer is from diffusion from the subsurface maximum, the magnitude of which depends on the vertical eddy diffusivity, a quantity that it is difficult to estimate. The vertical diffusive flux (F_v , $\text{nmol m}^{-2} \text{day}^{-1}$) of isoprene across the bottom of the mixed layer may be expressed as $F_v = D_z (d[\text{iso}]/dz)$, where D_z is the vertical diffusion coefficient in $\text{m}^2 \text{day}^{-1}$, and $(d[\text{iso}]/dz)$ denotes the concentration gradient of isoprene across the bottom of the surface mixed layer in nmol m^{-4} . Using values for D_z in the range of $8.6\text{--}13.0 \text{m}^2 \text{day}^{-1}$ (estimated from St. Laurent and Schmitt, 1998), the vertical diffusive flux of isoprene is calculated to be 3–5% of the efflux to the atmosphere. An even smaller vertical flux is estimated using the relationship between D_z and Brunt–Väisälä frequency given by Law et al. (2003). This effect is thus minor and may be neglected.

Table 1 gives the averaged fluxes to the atmosphere for both IN and OUT stations for the two periods, normalized to the average mixed-layer thickness (20 and 25 m for the first and second

period), and also an estimate of the rate of change in the concentration in mixed layer. The sum of these two quantities is the best estimate of the net production rate of isoprene. It would be expected that the unfertilized area would have a roughly constant rate of production, and this is reflected in the results that indicate that the higher efflux to the atmosphere during the second, windier period, is largely balanced by a decline in the mixed-layer inventory. The fertilized patch shows an approximately 3-fold increase in flux during the second period relative to the first, and the mixed-layer concentration continues to increase. Over the first 9 days the rate of production of isoprene is on average about twice as high in the patch as outside, and the ratio grows to an average of 6-fold during the last 4 days. The results do not point to a large rate of biological consumption in the mixed layer. During the windier period the reduced concentrations outside of the patch should lead to lower biological consumption, and therefore a higher rate of net production than during the low wind period: the data do not reveal such a change. It is acknowledged that other effects of changing wind speed, such as altering the mixed-layer thickness, may act to obscure the role played by biological consumption.

The variation of flux with time is shown for methyl iodide in Fig. 7 (concentrations are shown in Fig. 3). Fluxes from inside and outside the patch are indistinguishable, but they change with wind speed and are generally higher during the last 4 days of measurements. Averaging the fluxes for the same two time periods as for isoprene gives values of 10.1 and $28.3 \text{nmol m}^{-2} \text{d}^{-1}$. The elevated flux is mostly accounted for by a decline in the mixed-layer concentration of $0.4 (\pm 0.07) \text{pmol L}^{-1} \text{d}^{-1}$; prior to that period the mixed-layer concentration was almost constant (increasing by only $0.06 \pm 0.05 \text{pmol L}^{-1} \text{d}^{-1}$). Combining the efflux and changes in mixed-layer inventories yields a mean net production rate of $0.65 \text{pmol L}^{-1} \text{d}^{-1}$ with little change between the two

Table 1

An estimate of the rate of production of isoprene based on a balance with loss to atmosphere and change in the mixed-layer inventory

	Flux/(mixed-layer depth), $\text{nmol m}^{-3} \text{d}^{-1}$	Delta C/time, $\text{pmol l}^{-1} \text{d}^{-1}$	Net production, $\text{pmol l}^{-1} \text{d}^{-1}$
Days 1–10 IN avg	0.71	0.47	1.18
Days 1–10 OUT avg	0.52	0.17	0.69
Days 11–14 IN avg	3.12	–0.08	3.04
Days 11–14 OUT avg	1.24	–0.73	0.51

periods. At the temperature of 11 °C, the loss rate of CH₃I due to reaction with Cl⁻ is less than 1% d⁻¹ (Elliott and Rowland, 1993) and hydrolysis is smaller still, so both are ignored. Moore and Groszko (1999) calculated minimum production rates of methyl iodide in warm ($T > 17$ °C) Pacific Ocean waters of 0.5 pmol L⁻¹ d⁻¹ (range 0.4–0.7) based on an assumed steady state between production beneath the mixed layer and chemical loss processes. Fluxes to the atmosphere for the northernmost latitudes of that study (30–40°N) were in the range 10–18 nmol m⁻² d⁻¹, which is in good agreement with the values reported here for the SERIES site.

For methyl chloride, the average flux is calculated as 55 nmol m⁻² d⁻¹ (range: 1–127, σ 42). While this is only about half the typical flux that was previously reported for the Pacific Ocean (Moore et al., 1996), it is rather high for waters having a temperature close to 10 °C. Our earlier observations indicated that waters cooler than 12 °C were typically undersaturated, while warmer waters were increasing supersaturated (Moore et al., 1996). The value is consistent with the view that the ocean is a modest source of atmospheric methyl chloride and not the predominant source as the earliest reports suggested.

4. Discussion

4.1. Isoprene

The observations for isoprene are qualitatively what would be predicted on the assumption that it is a model biogenic gas, meaning that it is produced by all marine algae. Laboratory studies (Moore et al., 1994; Shaw et al., 2003) have shown that isoprene is produced by all of the phytoplankton species tested and, furthermore, that the production rate varies positively with cell volume (Shaw et al., 2003). Shaw et al. also reported that the production rates that they measured in the laboratory for a limited number of species were of the right order of magnitude to account for field-measured fluxes in areas where algal species larger than those tested in the laboratory would have predominated. Our results give an average production rate of isoprene of 1 ± 0.3 pmol ($\mu\text{g chl a}$)⁻¹ d⁻¹ which compares well with the range of 1–1.8 pmol ($\mu\text{g chl a}$)⁻¹ d⁻¹ reported by Shaw et al. (2003) for laboratory cultures. Typical isoprene fluxes outside the patch were 3–30 nmol m⁻² d⁻¹ during the first 10 days of the experiment, and 50–100 nmol m⁻² d⁻¹ in the

patch during the last few days of measurement. There are few reported isoprene flux measurements for ocean waters, but Milne et al. (1995) reported similar fluxes ranging from 10–100 nmol m⁻² d⁻¹ for a study in the Florida Straits. In the Southern Ocean Iron Enrichment Experiment (SOFeX) Wingerter et al. (2004) found that its concentration increased 4-fold in the patch and was strongly correlated with productivity.

4.2. Methyl halides

An objective of this study was to shed light on the source of methyl iodide, chloride and bromide in ocean waters. At present there is evidence for some production of these compounds by marine algae grown in laboratory cultures, though the rates of production are typically far short of those that would be required to account for observed fluxes from the ocean (Manley and de la Cuesta, 1997). A possible reason is the small selection of phytoplankton that can be grown in culture, or alternatively the abnormal conditions under which they grow. There is at least one example of a more prolific microalgal producer of CH₃I from a laboratory study (Porphyridium purpureum), but it is not an organism that occurs in the open ocean (Scarratt and Moore, 1999). In this discussion, it is important to realize that the methyl halide and isoprene sampling continued up to 13 days after the first Fe addition at which time chlorophyll concentrations and diatom biovolume were still about 3 days short of their maxima. Consequently, nothing can be said about the effect of the bloom decline on these gases. The results of this study show that there is no simple relationship between total primary production and production of methyl iodide, chloride, and probably bromide also, though the record is more noisy.

The phytoplankton groups that showed a clear response to the iron addition were: Coccolithophorids that showed an approximately 5-fold increase in cell numbers over the first 10 days, Thalassiosiraceae, which showed a roughly 4-fold increase during the 10 days, and Prasinophytes that appear to increase rapidly about 20-fold in cell numbers, then remain steady for about 5 days before beginning a rapid decline (Marchetti et al., 2006a). The measurements of prymnesiophytes other than coccolithophores showed such a high degree of variability (Levasseur et al., 2006) that it seems most reasonable to assume that their distributions were

spatially non-uniform: this would make it more difficult to discern a true influence of the iron addition. Diatoms other than Thalassiosiraceae showed a gradual increase from initial low abundances over about 17 days following the fertilization. Notable amongst the diatoms were *Thalassiothrix*, accounting for 33% of the diatom carbon, and *Pseudonitzschia* accounting for 42% of the diatom numbers (Marchetti et al., 2006a). Wong and Crawford (2006) report that fucoxanthin, a marker for diatoms, was one of the most strongly enhanced pigments. The apparent absence of any significant increase in the methyl halides strongly suggests that none of these stimulated groups could be major producers of methyl halides. The absence of a role by diatoms is consistent with the observation of relatively high concentrations of methyl iodide and chloride in the Sargasso Sea in comparison to the more nutrient-rich high-chlorophyll waters lying to the north (Moore et al., 1996; Moore and Groszko, 1999).

The observed increases in the biomass of various algal groups in the fertilized patch was not associated with any perceptible change in methyl iodide, but the region in which this experiment was conducted does support substantial production of this gas. It appears that any link with biological processes might lie in the background low-chlorophyll environment that is characterized by small cells whose numbers are controlled by micrograzers (Boyd and Harrison, 1999). Marchetti et al. (2006a) give as examples of the indigenous algal assemblage *Synechococcus*, *Phaeocystis* and *Emiliana*. These authors report that *Synechococcus* numbers increased by a factor of 3 during the first 10 days, and such a degree of enhancement might be expected to be reflected in an increase in methyl halides were this species a significant producer. *Phaeocystis* remains a candidate as an important source because it is a component of the indigenous assemblage, and because its patchiness obscures any clear enhancement due to the iron fertilization. There are several reports from both field (Baker et al., 1999) and laboratory (Saemundsdottir and Matrai, 1997) studies of relationships between *Phaeocystis* species and methyl halides, particularly CH_3Br . These are referred to below. The coccolithophorids showed an especially clear enhancement over the first 10 days after fertilization, so these also do not appear to be important producers.

Can this study provide any further insight into the proposed photochemical source of methyl iodide

for which there is evidence from laboratory (Moore and Zafriou, 1994) and field (Richter and Wallace, 2004) studies? The fact that samples were collected only during the day, and that there were no significant periods of sun, means that our data set offers very limited means for identifying photochemical effects. Clearly, there was no difference in the surface light flux between the patch and its surroundings, so to that extent no change in photochemical production would be expected. However, regardless of the details of the mechanism, there has to be an organic moiety that supplies the methyl group, either directly from the light absorber, or from a secondary reactant. If photochemical production is important beyond the coastal zone and shelf seas, it must be the case that the methyl group ultimately has its source in marine primary production. Therefore, it might be expected that the fertilized patch would have supported a higher photochemical production rate of CH_3I unless the process were light limited as opposed to substrate limited. However, it is known that coloured dissolved organic matter was not perceptibly enhanced within the patch over the period spanned by our measurements (W. Miller, personal communication). Its involvement as a major or minor source of methyl iodide via photochemical processes by acting as both primary photo-reactant and methyl source would be consistent with the absence of a response in methyl halides.

The interpretation of results is more difficult for CH_3Br and CH_3Cl because of the lower measurement precision for the former, and the influence of an atmospherically supported background concentration for both. For neither compound is there any clear influence of Fe addition. Previous studies have appeared inconsistent with respect to whether CH_3Br is correlated with chlorophyll-*a* in ocean waters. Moore and Webb (1996) reported that they found no correlation between CH_3Br production rates and chlorophyll-*a* concentrations in the Labrador Sea, while Baker et al. (1999) found a positive correlation between CH_3Br concentrations and this pigment in the northeastern Atlantic. However, this might be explained by the stronger correlation that Baker et al. found between CH_3Br and the accessory pigment, 19'-hexanoyloxyfucoxanthin that is characteristic of prymnesiophytes. As indicated above, the abundance of prymnesiophytes other than coccolithophores during SERIES showed signs of major patchiness that tended to obscure any influence of iron addition.

4.3. Comparison with other Fe addition experiments and conclusions

As part of the SOFeX experiment, CH₃I was measured inside and outside the fertilized patch 4 weeks after the iron addition (Wingenter et al., 2004). Methyl iodide showed a 23% decline in concentration within the patch in marked contrast with a 3-fold increase in isoprene and a 4-fold increase in dimethyl sulphide. Methyl bromide changed from being undersaturated outside the patch to almost neutral inside, representing a concentration increase of 14%. Such undersaturation has been previously reported for high latitude regions (Moore and Webb 1996; Lobert et al., 1997).

In the springtime Eisenex experiment, carried out in the Atlantic sector of the Southern Ocean, CH₃I showed a doubling of its initial low concentration of about 1.4 pmol L⁻¹ (A. Chuck, personal communication). It is apparent that the effect of iron fertilization on methyl halide production rates is unpredictable. This situation reflects the current lack of understanding of what exactly are the production mechanisms of these gases. It is possible that there are multiple sources, including some or all of photochemistry, algae, bacteria and zooplankton. The SERIES results appear not inconsistent with a photochemical source that is dependent on CDOM and independent of freshly produced dissolved organic carbon.

In contrast, isoprene production appears to be directly linked to the rate of primary production and, as such, was enhanced during the SERIES experiment and led to increased evasion of this gas to the atmosphere.

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