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Air-sea fluxes of methanol, acetone, acetaldehyde, isoprene and DMS from a Norwegian fjord following a phytoplankton bloom in a mesocosm experiment

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Abstract

The ocean's influence on volatile organic compounds (VOCs) in the atmosphere is poorly understood. This work characterises the oceanic emission and / or uptake of methanol, acetone, acetaldehyde, isoprene and dimethyl sulphide (DMS) as a function of photosynthetically active radiation (PAR) and a suite of biological parameters. The measurements were taken following a phytoplankton bloom, in May/June 2005 with a proton transfer reaction mass spectrometer (PTR-MS), from mesocosm enclosures anchored in the Raunefjord, Southern Norway. The net flux of methanol was always into the ocean, and was stronger at night. Isoprene and acetaldehyde were emitted from the ocean, correlating strongly with light ($r_{avcorr,isoprene}$=0.49 ; $r_{avcorr,acetaldehyde}$=0.70) and phytoplankton abundance. DMS was also emitted to the air but did not correlate significantly with light ($r_{avcorr,dms}$= 0.01). Under conditions of high biological activity and a PAR of ~450 μmol photons $m^{-2}s^{-1}$, acetone was emitted from the ocean, otherwise it was uptaken. The mean fluxes for methanol, acetone, acetaldehyde, isoprene and DMS were −0.26 ng m^{-2} s^{-1}, 0.21 ng m^{-2} s^{-1}, 0.23 ng m^{-2} s^{-1}, 0.12 ng m^{-2} s^{-1} and 0.3 ng m^{-2} s^{-1} respectively. This work shows that compound specific PAR and biological dependency should be used for estimating the influence of the global ocean on atmospheric VOC budgets.

1 Introduction

As the ocean covers some 70% of the Earth's surface area, its potential effect on atmospheric trace gases is enormous. Remarkably, the net primary production of the ocean (48.5 PgC yr^{-1}, P=peta =10^{15}) is comparable to that of the terrestrial environment (56.4 PgC yr^{-1})(Field et al. 1998), despite the total amount of biomass in the surface ocean being 100 times less than on land. Ocean biology influences the concentrations of dissolved gases directly (through photosynthesis and emission), and indirectly (through photochemistry of by-products). Such processes lead to an uptake from, or an emission to, the overlying atmosphere for a suite of organic gases (e.g. CO_2, DMS, isoprene, acetone). These gases are known to significantly impact the atmosphere, influencing ozone photochemistry and aerosol physics (Williams, 2004a and references therein) even at trace concentrations. Dimethyl sulphide and isoprene have both been established as emissions from the surface ocean to the atmosphere and the distribution of these sources has been investigated by several groups (Bonsang et al., 1992; Kettle and Andreae, 2000; Palmer and Shaw, 2005). Many hundreds of atmospherically important species have been characterised and inventoried from terrestrial sources (Olivier et al., 1994; Guenther et al., 1995), but in comparison, very little work has been done on assessing the emission of volatile organic compounds from the ocean.

It was discovered quite recently that the surface ocean can play an important role in the budgets of organic trace gases, particularly oxygenated species such as acetone (propanone), methanol, and acetaldehyde (ethanal) (Singh et al., 2003). These species have been shown to be ubiquitous in the atmosphere (Singh et al., 2001) and to influence radical budgets in the upper troposphere (McKeen et al., 1997; Tie et al. 2003; Colomb et al., in press, 2006). Furthermore, the surface ocean has been shown to be a massive reservoir for oxygenated organic species, both indirectly from aircraft measurements (Singh et al., 2000) and directly from ship borne measurements (Williams et al., 2004b).

There have been several global budget estimates for the oxygenated species methanol (Singh et al., 2000; Galbally and Kirstine, 2002; Heikes et al., 2002), and acetone (Singh et al., 1994; Singh et al., 2000; de Laat et al., 2001; Jacob et al., 2002; Singh et al., 2004). The large range of these budget estimates (75–490 Tg yr^{-1} methanol ; 37–148 Tg yr^{-1} acetone) indicates their currently uncertain nature, and in all these budgets the role of the ocean is the most uncertain factor. In the case of methanol, there is general consensus that methanol is uptaken from the atmosphere to the ocean. The latest budget estimates by Singh et al. (2004) and Jacob et al. (2005) estimate a 10–15 Tg yr^{-1} sink accounting for approximately 20% of the global budget. It is not yet clear as to what is responsible for maintaining an under saturation of methanol in surface waters, although certain methylotrophic bacteria are known to consume methanol (Kiene, 1993). In the case of acetone, there is remarkably poor agreement concerning the effect of the ocean on the global acetone budget. Using an inverse modelling approach, Jacob et al. (2002) deduced an oceanic source of 27 Tg yr^{-1} (some 33% of a total budget of 95 Tg yr^{-1}); Singh et al. (2004) estimated a small net sink (in a total budget of 95 Tg yr^{-1}); whereas Marandino et al. (2005) extrapolate an oceanic sink of 48 Tg yr^{-1} (in a total budget of 101 Tg yr^{-1}), from flux measurements made over the Pacific Ocean. Clearly, further measurements are required in parallel with biological parameters to elucidate these seemingly contrary findings. Moreover, significant median mixing ratios of the reactive species acetaldehyde (204±40 pptv) have been reported by Singh et al. (2003), even after the application of a pollution filter on the dataset. Despite its potential atmospheric importance, no global budget estimate of acetaldehyde has been made to date.

In this study we characterise the effect of the ocean on ambient atmospheric mixing ratios of methanol, acetone, acetaldehyde, isoprene and DMS as a function of light and a suite of biological parameters. The measurements were made under semi-controlled conditions from custom-built mesocosms deployed in the Raunefjord, Southern Norway (see Fig. 1). Mesocosm studies provide a useful interface between laboratory culture studies and open ocean surveys. While laboratory studies cannot generate the community dynamics of natural ecosystems, open ocean studies are complicated by horizontal and vertical mixing in both the air and water phases. Mesocosms therefore offer an excellent opportunity to study natural plankton communities under controlled conditions.

2 Experimental

2.1 The Mesocosms

A total of nine polyethylene enclosures (hereafter referred to as mesocosms) were deployed in a fjord at the University of Bergen Marine Biological Station, 20 km south of Bergen, Norway. The construction and operation of such mesocosms has been described in detail elsewhere (Williams and Egge, 1998; Engel et al. 2005), hence only a brief description is given here. The polyethylene enclosures (~20 m^3 water volume; 9.5 m water depth; ~4.3 m^3 headspace volume) were filled with unfiltered, nutrient-poor, post-bloom fjord water, which was pumped from 12 m depth adjacent to a raft anchored in the centre of the fjord. The enclosures were covered by gas-tight tents made of ETFE foil (Foiltec, Germany), which allowed for 95% light transmission of photosynthetically active radiation (PAR). In order to stratify the water column and avoid re-introduction of sedimented material into the surface sea layer, 0.6 m^3 of freshwater was added and mixed into the upper 5 m of the mesocosms. Throughout the study, the upper 5m layer was gently mixed by means of an aquarium pump. A bloom of the coccolithophore *Emiliania huxleyi* was induced by adding nitrate and phosphate in the ratio of 25:1 yielding initial concentrations of approximately 15 μmol L^{-1} NO_3^- and 0.6 μmol L^{-1} PO_4^{3-}. The development of the bloom is seen in the profile of Chlorophyll a and the trace gas measurements presented herein were conducted in the aftermath of the bloom (see Fig. 2).

The air flow into several mesocosms was dosed with additional CO_2 in order to also study the effects of elevated CO_2 on marine biology (see PeECE study website at http://peece.ifm-geomar.de). In this work, we present measurements only from the duplicate mesocosms which were flushed with ambient air, since these most closely represent the ambient atmosphere of today and are not subject to additional biological responses associated with altering dissolved CO_2. Based on the rate of the ambient air inflow and the volume of the mesocosm headspace (~4.3 m^3), the total headspace-air replacement time was 191 min and 170 min for mesocosms 7 and 8 respectively. The inflow and outflow air from both mesocosms was sampled for a suite of volatile organic compounds.

Irradiance was continuously measured every 10 min throughout the study by using a Li-Cor cosine sensor (LI-192SA), mounted on top of the floating mesocosm laboratory.

2.2 PTR-MS

A proton transfer reaction mass spectrometer (PTR-MS) was employed to measure masses 33, 59, 45, 63 and 69, which have been attributed to methanol, acetone, acetaldehyde, DMS and isoprene respectively. These identifications are in keeping with previous studies although minor contributions from other species, such as propanal to mass 59 cannot be ruled out (Lindinger et al., 1998; Williams et al., 2001). The instrument was positioned on a floating raft to which the mesocosms were attached, in a fjord that opened to the sea some 5 km away (see Fig. 1). Ambient air and air from the headspace of each mesocosm was drawn rapidly (~4.3 L min^{-1}) and continuously through 0.64 cm diameter and 25 m long Teflon lines shrouded from sunlight. The inlet residence time was less than 12 s. A fraction of this flow was sampled online by the PTR-MS. The entire inlet system of the PTR-MS including switching valves comprised of Teflon. Within the instrument, organic species with a proton affinity greater than water are chemically ionised by proton transfer with H_3O^+ ions and the products are detected using a quadrupole mass spectrometer (Lindinger et al., 1998). Further details of the operation of the PTR-MS used here are given elsewhere (Salisbury et al., 2003).

Sequential measurements of ambient air and air from the duplicate mesocosms 7 and 8 were made for 10 min each, in the order–mesocosm 7, ambient air and mesocosm 8. Calibrations were performed during the campaign using a commercial gas standard (Apel-Reimer Environmental Inc.). The total uncertainties of the measurements are estimated to be 21.3%, 15%, 19%, 17% and 14% for methanol, acetone, acetaldehyde, isoprene and DMS respectively. This includes a 5% accuracy error inherent in the gas standard and a 2 σ precision error for all the compounds. Detection limit was defined as the 2 σ error in the instrument signal, while measuring methanol at an average mixing ratio of 1 nmol mol^{-1} and each of the other compounds at an average mixing ratio of 0.5 nmol mol^{-1}. The individually calculated precision errors and detection limits were as follows, methanol (16.3%; 0.24 nmol mol^{-1}), acetone (10%; 0.07 nmol mol^{-1}), acetaldehyde (14%; 0.06 nmol mol^{-1}), isoprene (12%; 0.06 nmol mol^{-1}) and DMS (9%; 0.05 nmol mol^{-1}).

2.3 Biological parameters methods

Chlorophyll a (Chl a) was determined in 250 to 500 ml samples filtered on glass fibre filters (GF/F, Whatman). For pigment extraction, filters were homogenised in plastic vials together with 1 ml acetone (100%) and a mixture of glass beads (2 and 4 mm) by shaking (5 min) in a cooled Vibrogen cell mill (Buehler, Germany). Afterwards the extracts were centrifuged (5000 rpm, 10 min, cooled at −10°C). This procedure corresponds, with minor modifications, to the method of Derenbach (1969).

The content of Chlorophyll-a was then determined by means of HPLC (High Performance Liquid Chromatography), using the method of Barlow et al. (1997).

Phytoplankton cell counts were performed with a FACSCalibur flow-cytometer (Becton Dickinson) equipped with an air-cooled laser providing 15 mW at 488 nm and with a standard filter set-up. The algal counts were obtained from fresh samples at high flow rate (100 μl min^{-1}). The trigger was set on red fluorescence and the samples were run on the cytometer for 300 s. Discrimination of the algal groups was based on dot plots of side-scatter signal (SSC) and pigment autofluorescence (chlorophyll and phycoerythrin).

Samples for enumeration of bacteria were fixed with glutaraldehyde (0.5% final concentration), frozen in liquid nitrogen and stored at −70°C (Marie et al., 1999a). The samples were stained with SYBR Green I (Molecular Probes Inc., Eugene, OR) and analysed according to Marie et al. (1999b). The discrimination of bacteria groups was based on groups observed in scatter plots of SSC signal versus green DNA-dye

(SYBR Green) fluorescence. Fluorescence beads (Molecular Probes) with a diameter of 0.95 μm were added to each sample analysed as an internal reference. Data files were analyzed using EcoFlow (version 1.0.5, available from the authors).

3 Results

3.1 General trends – gas phase species

Figure 3 shows a time series for measurements of methanol, acetone, acetaldehyde, isoprene and DMS measured as masses 33, 59, 45, 69, and 63 respectively. In each case the inflowing ambient air mixing ratio is plotted with the measurements from within mesocosms 7 and 8. Measurements of the inflowing ambient air, including average, median and standard deviation are summarized in Table 1. Variability in the ambient air was highest for methanol followed by acetaldehyde, acetone, isoprene and DMS (see σ values in Table 1). For all species, good agreement can be seen between the two duplicate mesocosms. Where the mixing ratios of a particular species in the mesocosm air were significantly lower than ambient air, we infer that an uptake occurred into the seawater. Conversely when mesocosm air mixing ratios were higher than the inflowing ambient air, an emission from seawater into the air was deduced.

Diel cycles were seen in the mesocosms for acetone, acetaldehyde and isoprene, which exhibited maxima and minima typically from 12:00 p.m.–4:00 p.m. and 12:00 a.m.–08:00 a.m. respectively. In contrast, methanol showed no clear diel cycle in the mesocosms, the variation and absolute values of the mesocosm data being generally suppressed with respect to the ambient air. DMS mixing ratios in the mesocosm air were observed to be generally higher in the evening rather than daytime. We investigate the light and biology dependence of these emissions and uptakes in Sect. 3.2.

3.2 Fluxes of organic species in relation to light (PAR) and biological parameters

At the outset, it should be noted that the emission and uptake fluxes reported here represent the net fluxes from seawater to air and vice versa, inside the mesocosm. Hence the fluxes may be the resultant of separate, strong sinks and sources within the mesocosm system.

Fluxes of the various VOCs were calculated according to Eq. (1),

$$F_{\mathrm{voc}}=\frac{Q}{A}(m_{\mathrm{in,voc}}-m_{\mathrm{out,voc}})\frac{M_{\mathrm{voc}}}{V_m} \tag{1}$$

where F_{voc} is flux of the VOC in μg m^{-2} s^{-1}, $m_{\mathrm{in,voc}}$ and $m_{\mathrm{out,voc}}$ are the VOC mixing ratios (nmol mol^{-1}) in the inflowing ambient marine air and mesocosm air respectively, Q is the flow rate of the ambient air into the mesocosm in m^3 s^{-1}, A is the surface area of the seawater enclosed by the mesocosm in m^2, M_{voc} is the molecular weight of the VOC in kg kmol^{-1} and V_m is the molar gas volume in m^3 kmol^{-1} (= 23.233 at 1013.25 hPa and 283 K).

Figure 4 depicts the time series of the VOC fluxes and PAR in the duplicate mesocosms 7 and 8 while Table 2 gives a summary of the averages, medians and standard deviations of the VOC fluxes in the duplicate mesocosms.

Figure 5 shows daily plankton cell counts of the coccolithophore *Emiliania huxleyi*, the cyanobacterium *Synechococcus sp.*, other nano and picophytoplankton and free-living heterotrophic bacteria. The trace gas measurements covered two subsequent phases of the phytoplankton bloom, from 31 May–5 June – the final phase of bloom decline, and from 6 June–10 June – a post-bloom phase of low phytoplankton standing stocks characterized by an increase in cyanobacterial cell numbers.

The photosynthetically active radiation (PAR) generally ranged from 0 to 1500 μmol photons m^{-2} s^{-1} on most days (Fig. 4). Due to overcast conditions significantly lower daily maxima of ca. 400 μmol photons m^{-2} s^{-1} occurred on the 4 and 10 of June.

From the Figs. 4, 5 and Table 2 we note that there is good consistency in the magnitude and direction of the fluxes as well as the biological parameters in the two mesocosms. The fluxes of the individual organic compounds are examined in detail in the subsequent sections.

Methanol: Throughout the experiment, the net flux of methanol was always into the seawater from the mesocosm air above it. Thus methanol was uptaken both during the day and at night. The average of the Pearson linear correlation coefficients in the duplicate mesocosms (hereafter referred to as r_{avcorr}), calculated for the methanol uptake fluxes and the photosynthetically active radiation (PAR) was 0.18. The period from 31 May–5 June (phase of bloom decline) had stronger methanol uptake compared to 6 June–10 June (post-bloom phase with low phytoplankton abundance). Methanol uptake was generally higher during night-time, indicating that it was not driven by photosynthetic activity. The mean flux in both mesocosms calculated using median values was $-0.26\,\text{ng m}^{-2}\,\text{s}^{-1}$, the negative value indicating the direction from air to seawater.

Acetone: During the daylight sections of the experiment, acetone was emitted from the seawater to the air above it, if PAR exceeded $450\,\mu\text{mol photons m}^{-2}\text{s}^{-1}$, while at night it was always uptaken from the air to the seawater. The acetone flux shows good correlation with PAR ($r_{avcorr,acetone}$=0.70). Furthermore, the emission fluxes were higher in the phase of bloom decline with still relatively high phytoplankton abundances (31 May–5 June) compared to the low biomass post-bloom phase (6 June–10 June). The average of the median uptake fluxes and emission fluxes (uptake from air to sea water and emission from sea water to air) in both mesocosms was $-0.06\,\text{ng m}^{-2}\text{s}^{-1}$ and $0.27\,\text{ng m}^{-2}\,\text{s}^{-1}$ respectively. Overall for the entire measurement period, the flux was an emission of $0.21\,\text{ng m}^{-2}\,\text{s}^{-1}$.

Acetaldehyde and Isoprene: Acetaldehyde and isoprene were emitted from the seawater to the overlying air throughout the measurement period, with almost no evidence of seawater uptake. The fluxes of acetaldehyde and isoprene show strong correlation with each other (r_{avcorr}=0.86). The flux of acetaldehyde shows greater correlation with PAR ($r_{avcorr,acetaldehyde}$ =0.70) compared to isoprene flux and PAR ($r_{avcorr,isoprene}$ =0.49). There was a decrease in the flux of both acetaldehyde and isoprene during the second phase of the measurement period, from 6 June–10 June. Mean emission flux strengths calculated from median values in the duplicate mesocosms were 0.23 ng m^{-2} s^{-1} and 0.12 ng m^{-2} s^{-1} for acetaldehyde and isoprene respectively.

Dimethyl sulphide (DMS): In both mesocosms, DMS was always emitted from the seawater to the air above it. DMS fluxes showed negligible correlation with PAR ($r_{avcorrdms}$=0.01). Emission occurred at similar rates irrespective of light intensity, as seen on 4 June, which was particularly overcast. Remarkably, among all the measured organic species' fluxes, only the DMS flux did not decrease in the second phase i.e. from 6 June–10 June. The mean DMS emission flux calculated using median values from both mesocosms was 0.3 ng m^{-2} s^{-1}.

Discussion This is the first time that air-sea fluxes of organics have been analyzed and quantified during a mesocosm experiment. While previous oceanic flux studies of these compounds have been based on either air-sea flux models (Liss and Merlivat, 1986) or inverse modelling (Jacob et al., 2002; de Laat et al., 2001), in this study we infer fluxes from the difference in direct measurements of the air, before and after controlled interaction with the underlying seawater. Thus, assumptions and uncertainties pertaining to the model based studies are absent in this approach. On the other hand, the mesocosm system has low, almost constant air flow, subdued wave activity and possible wall effects from the enclosures, which might cause deviance from conditions in the natural environment. For investigating the role of light and biology in the emission and uptake of compounds, mesocosm studies are probably better suited than laboratory or in-situ open ocean studies. In the laboratory, it is difficult to establish the composition and simulate the succession of a natural plankton community, while in the open ocean mixing, dispersal and advection of the water mass complicate the interpretation of the data.

From the observations presented in Sect. 3.2 we now examine the light and biology dependence of our derived fluxes within the context of the available literature. In this study, it is extremely difficult to implicate specific biological parameters for the emission or uptake of a particular trace gas, as the biological parameters were measured only once a day and the measured flux represents a net process due to possibly different sources and sinks. We have therefore restricted ourselves to general trends in the populations of the measured biological species.

Day-time emission of acetone from seawater to the air occurred during the period of bloom decline, when phytoplankton biomass was still high, and comparatively low or absent during the post-bloom period of low phytoplankton abundances. Light-dependency of acetone emission was indicated on 4 June, when maximum light intensities below ~350 μmol photons $\mathrm{m}^2\ \mathrm{s}^{-1}$ shifted day-time acetone emission to acetone uptake. Can we reconcile these results with the study by Marandino et al. (2005), which reported that acetone is always uptaken from the air to the seawater? It is well established that dissolved organic matter produces acetone by solar irradiation (Zhou and Mopper, 1997). During both phases of plankton succession covered by our measurements, i.e. from 31 May–5 June and 6 June–10 June, the dissolved organic matter (DOM) in the seawater did not show significant variance. Concentrations of dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) were more or less constant during the measurement period with mean values of DOC = 100±7μmol L^{-1}; DON = 8±3μmol L^{-1} and DOP = 0.26±0.04 μ mol L^{-1} (Wohlers et al., personal communication, 2006). However, since the second phase had considerably less emission of acetone (see Figs. 4 and 5), despite similar PAR and DOM concentrations as during the first phase, the implication is that acetone production in seawater is biologically mediated and light dependent. In the absence or under low activity of the relevant production pathway, acetone consumption in seawater can exceed its production, leading to net acetone uptake by the ocean. This was the situation during the second phase of this study and may have been the conditions during the study of Marandino et al. (2005) in the oligotrophic N.W. Pacific.

Net uptake of methanol from air into seawater appears to be attenuated by light, and biological dependence can be inferred from the decrease in the second phase, as plankton abundance and biomass declined. As mentioned in the results section, we also observed reduced uptake during daylight hours in the first phase, which was characterized by higher plankton abundance. Heikes et al. (2002) report that methanol has been observed in the headspace of laboratory phytoplankton cultures. Either the biological uptake of methanol from air to seawater is less during the day, or methanol is produced in seawater by phytoplankton during the day or both processes together result in the reduced uptake of methanol, from air to seawater during the day. The second phase has higher *Synechococcus sp* and free living heterotrophic bacteria but the methanol uptake flux does not increase. This suggests that the cyanobacteria *Synechococcus sp* and the free living heterotrophic bacteria do not consume methanol significantly under these conditions.

Acetaldehyde and isoprene are generally emitted from the seawater to the overlying air. The emissions correlate well with both photosynthetically active radiation, as well as the measured biological parameters and decrease in the second phase of the measurements. It should also be noted that some isoprene and acetaldehyde production occurs under overcast conditions and even at night. Like acetone, acetaldehyde is also produced by the photochemical degradation of dissolved organic matter (DOM) in seawater (Zhou and Mopper, 1997), while plankton are known to produce isoprene (Milne et al., 1995). The high degree of correlation between isoprene and acetaldehyde (r_{avcorr}=0.86) and the decrease in both isoprene and acetaldehyde emissions in the second phase, coupled with the insignificant variance in the dissolved organic matter (DOM) during both phases, suggest that there might be some biologically mediated production of acetaldehyde in seawater, from which emission then occurs to the overlying air.

DMS emissions do not seem to depend on light and the emission rate is quite comparable in both phases. It is well established that DMS is produced in seawater both by direct release from phytoplankton and by bacteria and zooplankton mediated grazing (Dacey and Wakeham, 1986; Gabric et al., 2001). Thus, DMS emission in the first phase is probably due to direct release from phytoplankton while grazing processes seem to be responsible for the DMS emission during the second phase.

In Table 3, we compare the mixing ratios and fluxes measured here with previous studies on methanol, acetone, acetaldehyde, isoprene and DMS in the marine boundary layer. The general level of the ambient air mixing ratios of the oxygenates presented here are consistent with earlier studies, while for isoprene and DMS, they are somewhat higher. Proton transfer reaction mass spectrometry measurements are upper limit estimates because of possibly more than one species contributing to the measured mass. It should be noted that the high mixing ratios of isoprene and DMS in the ambient air were probably due to a local source of macro algae, which were growing near the raft. Isoprene might additionally have been impacted by trees on the coast and the nearby islands.

The relative abundances of the organic trace gases reported in this work and measured using the same instrument, fit with the trend discerned from measurements in previous studies (Zhou and Mopper, 1993; Mao et al., 2006 and other references in Table 3). The trend is: methanol > acetone > acetaldehyde > isoprene ~DMS. The reported median values also show that the sum of the oxygenates is approximately six times higher than the sum of isoprene and DMS in the marine boundary layer. Compared with direct methanol, acetone and acetaldehyde fluxes reported from a terrestrial pine plantation (Karl et al., 2005), the oceanic fluxes reported here and in previous works (see Table 3) are 2–3 orders of magnitude lower.

From the discussion above it is clear that the air-sea flux of each trace gas depends differently on light and biological activity. Therefore on a global scale, extremely large variations in such fluxes can be expected as a consequence of the range of solar and biological conditions over the oceans. From the extensive ocean studies done on DMS emission fluxes, it is also apparent that seasonality and biological hotspots are very important factors. Nonetheless it is informative to extrapolate the fluxes derived here to the global scale for comparison with previous budget estimates and to gauge which species are most significant for atmospheric chemistry.

It should be noted that although this study took place in coastal waters, chlorophyll a (2.28–1.050 μg L^{-1}, nutrient values (PO$_4^{3-}$ = 0.05 μmol L^{-1}; NO$_3^-$ = 1 μmol L^{-1}; SiO$_3^-$ = 0.25 μmol L^{-1}, Riebesell et al., personal communication, 2006) and dissolved organic matter (DOM; 97–110 μmol L^{-1}) measured in the mesocosm seawater between 31 May and 10 June are representative of vast areas of the global oceans. The up-scaling of the fluxes was based on the entire global ocean surface area of 3.61×10^{14} m^2, and all results are summarized in Table 3.

For methanol we estimate a net oceanic sink of 2.97 Tg yr^{-1}. This is higher than the 0.3 Tg yr^{-1} oceanic sink proposed by Galbally and Kirstine et al. (2002) and lower than the estimates reported by Singh et al. (2003), Heikes et al. (2002) and Jacob et al. (2005). Based on the same measurements but different models, methanol oceanic sinks of 8 Tg yr^{-1} and 15 Tg yr^{-1} were proposed by Singh et al. (2003) and Singh et al. (2004) respectively, showing that different model parameterizations give quite different results.

Except for Jacob et al. (2002), all previous studies have estimated a net oceanic sink for acetone. We estimate an emission flux and uptake flux of 3.13 Tg yr^{-1} and 0.68 Tg yr^{-1} respectively. It should be mentioned that during the period of our field study in Norway, there was 18 h of daylight and only 6 h of darkness. As established in this study, acetone emissions are influenced by both a critical PAR threshold and biological activities, parameters that have not been incorporated in up-scaling the measurements obtained in this or previous studies.

Measurements of acetaldehyde are currently viewed with some scepticism due to recently reported potential sampling problems for this species. Apel et al. (2003) reported an artefact for acetaldehyde could occur within inlets, even on inert surfaces. Interferences in stratospherically influenced air have been reported by Northway et al. (2004) and Singh et al. (2004) for PTR-MS and GC systems respectively, suggesting an interfering surface related phenomenon affecting all instruments. Furthermore, acetaldehyde measurements appear to be inconsistent with simultaneously measured species such as PAN and ethane when compared with models (Singh et al., 2004; Lewis et al., 2005). However, by measuring the difference in the acetaldehyde mixing ratios, for the inflowing ambient air and the mesocosm air, we have minimized possible systematic artefacts. As an additional precaution, all the Teflon inlets used for sampling ambient air and mesocosm air, had the same dimensions and were shrouded from sunlight, using black tubing. The case for acetaldehyde emission not being an artefact is strengthened as it correlates with both isoprene and the independently measured biological trends. Our estimate of a global acetaldehyde oceanic source of 2.62 $\mathrm{Tg\,yr^{-1}}$ is significantly lower than the only other estimate of 125 $\mathrm{Tg\,yr^{-1}}$ reported by Singh et al. (2003). It should be noted that a direct emission of acetaldehyde through biological processes as suggested here is a good explanation why acetaldehyde levels were not consistent with ethane (formerly considered the main precursor) in the marine boundary layer.

Estimated global marine isoprene fluxes extrapolated from in-situ measurements range from 0.1–1.4 $\mathrm{Tg\,yr^{-1}}$ (Bonsang et al. 1992; Broadgate et al., 1997; Matsunaga et al., 2002; Shaw et al., 2003; Broadgate et al., 2004). The latest estimate based on satellite chlorophyll observations totals 0.12 $\mathrm{Tg\,yr^{-1}}$ (Palmer and Shaw, 2005). This is small in comparison with terrestrial emissions of ca. 500 $\mathrm{Tg\,yr^{-1}}$ and the results of this study (1.4 $\mathrm{Tg\,yr^{-1}}$) are in agreement with this estimate.

Dimethyl sulphide fluxes reported in this study (3.42 $\mathrm{Tg\,yr^{-1}}$) are significantly lower than those reported in previous open ocean studies (25–104 $\mathrm{Tg\,yr^{-1}}$ Nguyen et al. 1978; Andreae, 1990; Kettle and Andreae, 2000; Sciare et al., 2000; Huebert et al., 2004). Two factors may contribute to the difference between the flux estimates of this study and previous studies. Firstly, measurements being in the aftermath of a phytoplankton bloom, characterized by depleting nutrients and generally moribund phytoplankton populations, DMS emissions are expected to be low. Alternatively it could be that the predominant biological species during our measurement period were not prolific DMS emitters.

4 Conclusions

In conclusion, it is clear that parameterizing the fluxes of the various organic species requires individual treatment, because they depend quite differently on light and biological activities. Thus, specifically parameterized models constrained by measurements from locations that represent the varied geographical areas of the global ocean are needed to form more accurate estimates of the oceanic contribution to the global budgets of different volatile organic compounds.

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Table 1. Average, Median, Standard Deviations, Minima and Maxima for Measurements of the Ambient Marine Air flushed into the Mesocosms.

	Units (nmol mol^{-1})					
	Ave.	Med.	Min.	Max.	σ	n
Methanol	2.26	1.86	B.D.L	7.99	1.56	1171
Acetone	0.87	0.80	0.28	2.40	0.29	1228
Acetaldehyde	0.60	0.55	B.D.L	3.96	0.45	1099
Isoprene	0.18	0.18	B.D.L	2.38	0.17	1123
DMS	0.17	0.40	B.D.L	1.15	0.18	651

B.D.L = Below Detection Limit

Table 2. Comparison of Fluxes in the Duplicate Mesocosms 7 and 8.

	Units (ng m^{-2} s^{-1})					
	Ave.(7)	Ave.(8)	Med.(7)	Med.(8)	σ(7)	σ(8)
Methanol (U)	0.33	0.39	0.26	0.27	0.29	0.30
Acetone (U)	0.08	0.10	0.05	0.07	0.06	0.08
Acetone (E)	0.21	0.26	0.19	0.34	0.23	0.29
Acetaldehyde (E)	0.34	0.49	0.19	0.26	0.49	0.70
Isoprene (E)	0.14	0.14	0.12	0.12	0.12	0.17
DMS (E)	0.30	0.35	0.30	0.27	0.17	0.29

U = Uptake from atmosphere to seawater; E = Emission from seawater to atmosphere

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Table 3. Comparison with earlier works on Marine Emissions and Uptake of VOCs.

Med./Ave*. (nmol mol^{-1})	Sea-Air flux (ng m^{-2} s^{-1})	Oceanic Source (Tg yr^{-1})	Oceanic Sink (Tg yr^{-1})	Location	Reference
Methanol					
0.87	-12.5^a	–	–	Tropical Atlantic	Williams et al., 2004b
0.57	-0.6^a	–	8	Pacific Ocean (0–2 km)	Singh et al., 2003
0.57	–	–	15	Pacific Ocean (0–2 km)	Singh et al., 2004
2.0	-2.81^a	–	–	New England Marine Coast	Mao et al., 2006
0.9	–	30^b	85	–	Heikes et al., 2002
–	–	–	0.3	–	Galbally and Kirstine et al., 2002
–	–	–	10	-	Jacob et al., 2005
1.86	-0.26^+	–	2.97	Raunefjord, Norway	This work
Acetone					
0.52	5.71^a	–	–	Tropical Atlantic	Williams et al., 2004b
1.3	-3.22^a	–	–	New England Marine Coast	Mao et al., 2006
0.47	-1.2^a	–	14	Pacific Ocean (0–2 km)	Singh et al., 2003
0.36	-2.92^a	–	48	North Pacific Ocean	Marandino et al., 2005
0.38	–	–	–	Caribbean Sea	Zhou et al., 1993
–	–	27	14	–	Jacob et al., 2002
0.5	–	–	–	Mace Head	Lewis et al., 2005
0.8	-0.06^+(U) 0.27^+(E)	3.13	0.68	Raunefjord, Norway	This work
Acetaldehyde					
0.2	11^a	125	–	Pacific Ocean (0–2 km)	Singh et al., 2003
0.44	–	–	–	Mace Head	Lewis et al., 2005
0.50	–	–	–	Caribbean Sea	Zhou et al., 1993
0.55	0.23^+	2.62	–	Raunefjord, Norway	This work
Isoprene					
0.04	$0.02–0.24^a$	0.26–2.7	–	NW Pacific Ocean	Matsunaga et al., 2002
–	0.02^a	0.22	–	Near shore North Sea	Broadgate et al., 1997
–	0.12^a	1.4	–	NW Pacific Ocean	Bonsang et al., 1992
< 0.01	$0.01–0.08^a$	0.08–0.9	–	Florida Straits	Milne et al., 1995
–	–	0.1–0.7	–	North Atlantic	Baker et al., 2000
–	–	0.12	–	–	Palmer et al., 2005
0.18	0.12^+	1.4	–	Raunefjord, Norway	This work
Dimethyl sulphide					
0.05	1.79^a	–	–	Tropical Atlantic	Williams et al., 2004b
–	$1.44\text{-}4.3^a$	–	–	Equatorial Pacific Ocean	Huebert et el., 2004
0.03–0.34	–	–	–	Southern Indian Ocean	Sciare et al., 2000
–	–	$29–104^d$	–	–	Andreae et al., 1990
–	–	$25–72^d$	–	–	Kettle et al., 2000
–	–	50.37^d	–	–	Nguyen et al., 1978
0.4	0.3^+	3.42^d	–	Raunefjord, Norway	This work

a= converted from original units to (ng m^{-2} s^{-1});
b = best estimate; + = average of median values in duplicate mesocosms
d = converted from (Tg S yr^{-1}) to (Tg DMS yr^{-1}) ;
* = where both median and average are available, median has been used

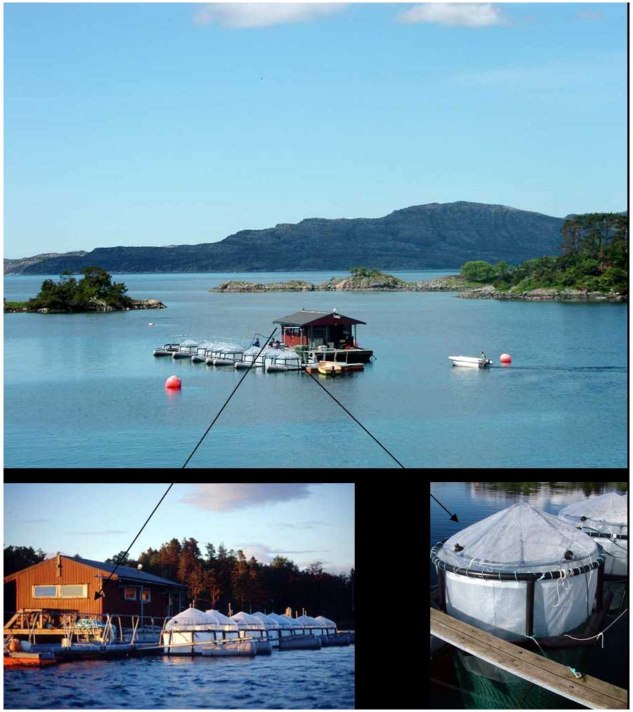

Fig. 1. View of the University of Bergen raft facility with attached mesocosms, located in a fjord 20 km south of Bergen. The enlarged views show the mesocosms and the raft in detail.

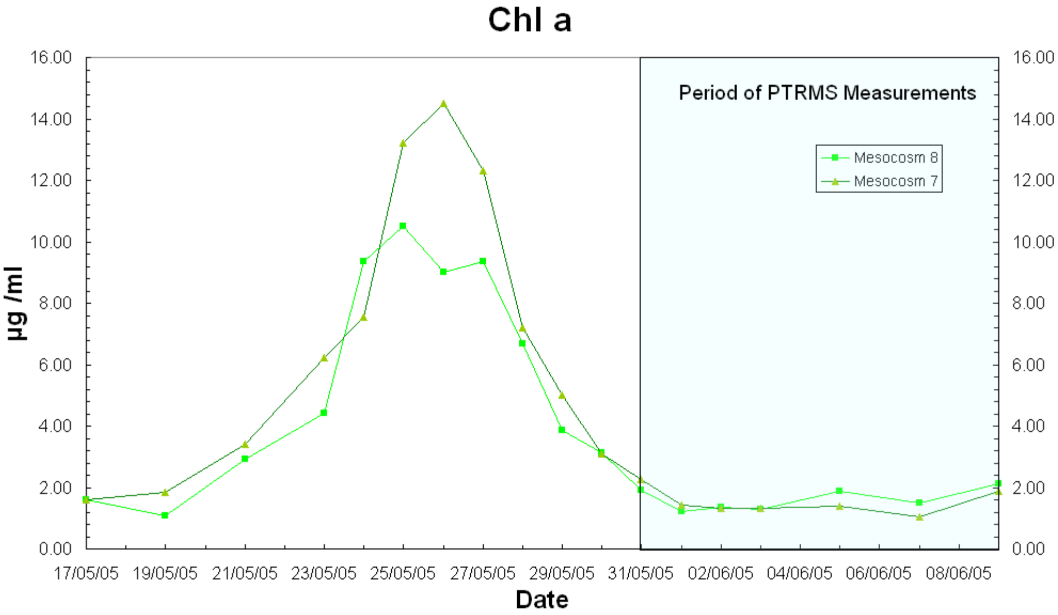

Fig. 2. Time series of Chlorophyll a in mesocosms 7 and 8.

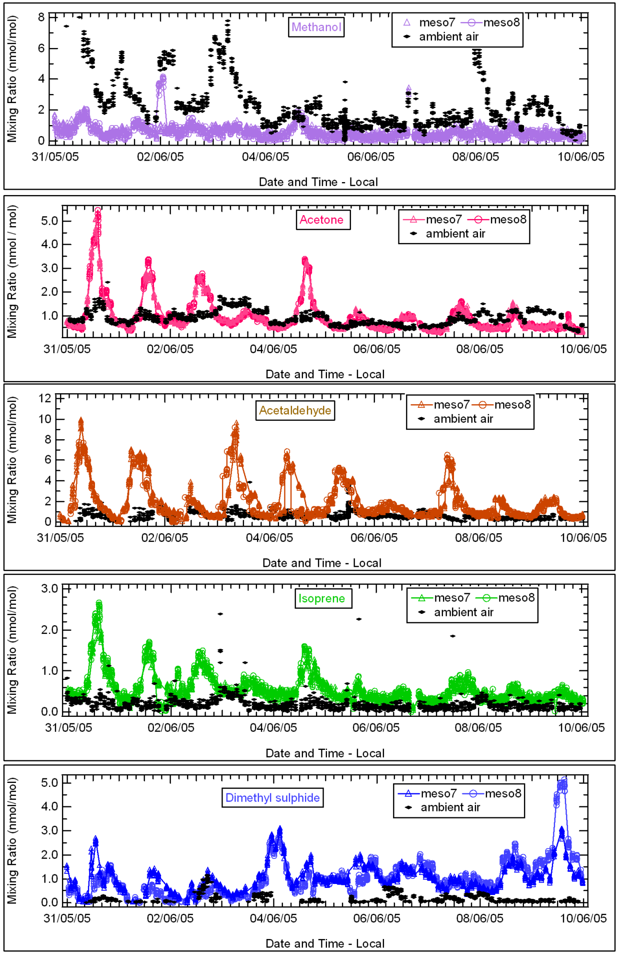

Fig. 3. Time series of methanol, acetone, acetaldehyde, isoprene and DMS from inside and outside the duplicate mesocosms 7 and 8.

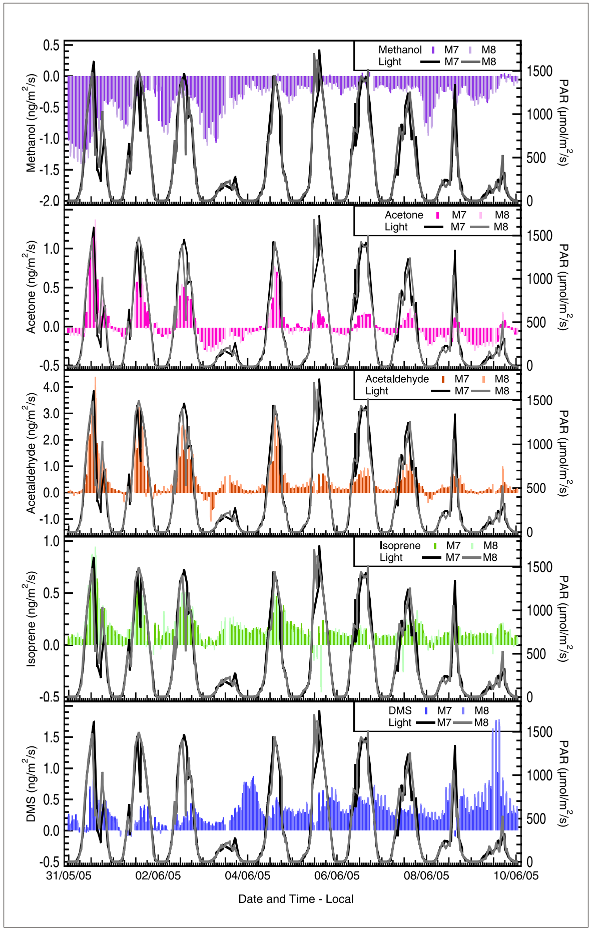

Fig. 4. Flux profiles of methanol, acetone, acetaldehyde, isoprene, DMS and photosynthetically active radiation (PAR) as a function of time in the duplicate mesocosms 7 and 8.

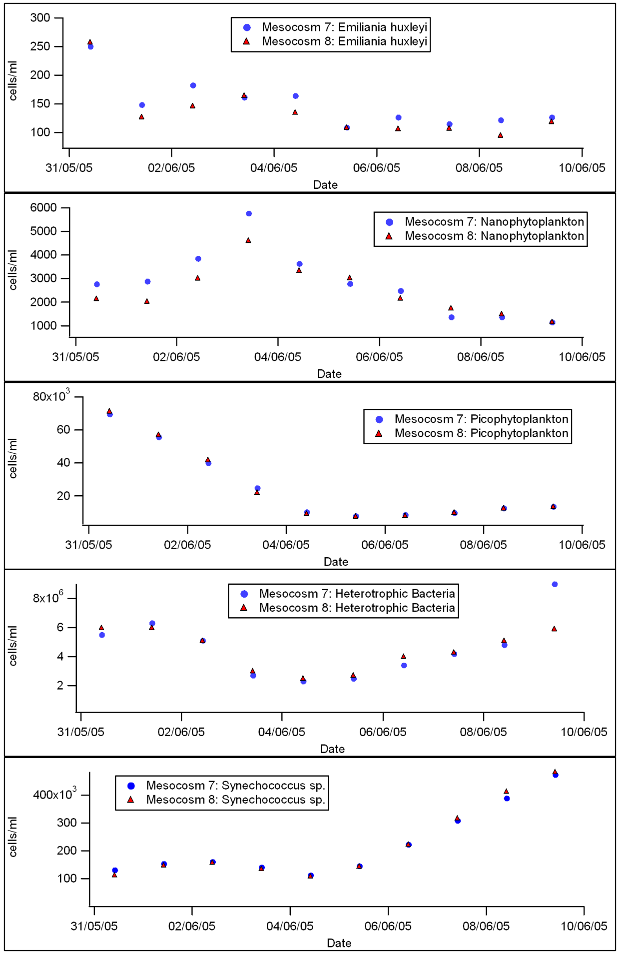

Fig. 5. Daily variation of selected phytoplankton and bacteria over the measurement period for the duplicate mesocosms 7 and 8.