

Response to Anonymous Referee # 3

We would like to thank Referee #3 for his/her comments. We have done our best to address each of the points as detailed below. Reviewer comments are in italics and authors responses are in standard font.

#1. A main issue to my opinion is the choice and the representativity of the experimental conditions used here to induce a stress in the phytoplankton cultures. Indeed, due to the seawater absorption coefficient, PAR is rapidly attenuated with depth and reach only 10-20% of the surface irradiance at several tenths meter depth , i.e. at the isoprene maximum level usually observed in seawater (close to the chlorophyll or fluorescence maximum) . Therefore irradiances of 420 and particularly as high as 900 $\mu\text{mol m}^{-2} \text{s}^{-1}$ does not seem to correspond to ambient reasonable figures, their choice should be better justified and discussed (i.e. lines 19 to 22 page 13538.

We agree with the reviewer that irradiances as high as 420 and certainly 900 $\mu\text{mol m}^{-2} \text{s}^{-1}$ will not be representative for the deep chlorophyll maxima. However, the light and temperature conditions here were selected to be representative of phytoplankton exposure at all depths of the oceans, including estuaries. Boreal/austral summer noon surface photosynthetically active radiation (PAR) approaches 2000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ seasonally and regularly from 40°N to 40°S and can do so between 60°N and 60°S (Bouvet *et al.*, 2002). See also our response to the comment #1 from Anonymous Referee #1.

The text now reads: “Therefore, the challenges of abrupt irradiance intensity increases used here are conceivable in the upper ocean due to displacement in the vertical light gradient, however the challenges of abrupt temperature changes become less likely at the extremes of the applied range. For temperature, these experiments represent the natural condition under a limited temperature range ($\pm 4^\circ\text{C}$ around acclimation temperature) but become a test of physiological capability over a larger temperature range. The temperature values were based on the previous works documented in Eppley (1972), Schofield *et al.* (1998) and Staehr and Birkeland (2006).”

#2. Page 13536 Line 7, I don't think that Shaw et al., 1983 were the first to suggest a relationship between gas emissions and climate. To my knowledge J.E. Lovelock was a pioneer in this matter and could be referenced. Authors could also refer to the well-known (and somewhat controversial) CLAW hypothesis of Charlson, Lovelock Andrea and Warren: Charlson, R.J., et al., Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature (326), 1987.

Lovelock and Margulis (1974) introduced a paradigm (the Gaia hypothesis) to account for the remarkable thermal stability of the terrestrial climatic system over time intervals of billions of years. Shaw (1983) has proposed that atmospheric aerosol may also participates in the radiation balance and in particular, the aerosol produced by the atmospheric oxidation of sulphur gases from the oceanic biota. Charlson *et al.* (1987) carried out calculations to show potential feedback loop between ocean ecosystems, cloud condensation nuclei (CCN), cloud albedo and climate (aka the CLAW hypothesis).

The text now reads: “The existence of physical relationships between marine biota, gas emissions, aerosols, clouds, and radiative forcing has been hypothesized for over several decades (Shaw, 1983; Charlson et al., 1987).

#3. Page 13543 Line 26, the MDL is determined as 2.7 to 140 pptv, it would be helpful to precise in which range of isoprene or monoterpene emissions these value correspond. More generally give the MDL and accuracy for the emission rates and not only for the concentrations in the head space.

We thank reviewer for noticing this oversight. The reported range was for all 38 trace gases (with the lowest value of 2.7 ppt determined for 1,1,2-Trichloroethane and the highest value of 140 ppt determined for 1-Bromopentane) measured during the experiment. The total uncertainty (RSD_{Total}) of production rates for each BVOC is given in the last column of Table 1.

The text now reads: “The MDL ranges from 3.83 to 7.15 pptv.”

*#4. Paragraph 2.3- It is announced that some compounds have the affinity to stay in the aqueous phase: what are the compounds concerned precisely. I assume that the Henry Law constant is relatively low for most of the species, what are the species concerned, and what is their Henry law constant . At least the Henry law Constant is relatively low for most of the considered compounds of the order of 2 to $5 \cdot 10^{-2} \text{ M L}^{-1} \text{ Atm}^{-1}$ (isoprene, limonene, alpha pinene (see for example: Leng et al., Temperature-dependent Henry's law constants of atmospheric organics of biogenic origin, *J Phys Chem* , 2013. and <http://www.henrys-law.org/henry.pdf>) Consequently a volume of 14 liter (line 8 in §2.3) of air for the extraction of the dissolved gases in 250 ML of the aqueous phase seems to be more than enough for a 90% efficiency of recovery. Can the authors be more precise on the expected extraction efficiency and the comparison with the measured experimental values.*

We thank the reviewer for pointing out that all the compounds reported in the paper have relatively low Henry law constant.

The text now reads: “The analysis was based on the principle of liberating BVOC from the water samples into the gas stream. To quantify the amount of BVOC recovered by the purging analysis, purging efficiencies were calculated separately for each compound and are reported in Table 1. The purging efficiencies were calculated by spiking seawater with a known concentration of the standards. Successive purging steps from the same sample vial were performed until the compound concentrations were below the detection limit. The purging efficiency was calculated by taking the ratio of the initial purge BVOC concentrations divided by the sum of the BVOC concentrations over all the purging steps. The purging procedure was optimized for >90% purging efficiency for isoprene and monoterpene species. Calculated purging efficiencies were comparable to values of >90% and >95% obtained by a similar analysis from Broadgate et al. (1997) and Shaw et al. (2003), respectively.”

#5. The experimental set up for the head space analysis is simple and classical, I don't think that a figure (such as Figs 1a ad 1b) brings any useful information since it is relatively well

described in the text. On the opposite the full procedure for phytoplankton cultures preparation, conditioning, transfer, is relatively hard to follow, a schematic diagram or a table showing the different steps would be useful.

We have replaced Fig. 1 with a schematic diagram as suggested by the reviewer.

#6. In general, the font sizes for Figures 2 to 5 are too small , also it is difficult to be convinced that the variations are not in the range of the uncertainties, Y scale should be changed i.e. 2×10^{19} instead of $2E-19$

Figures have been changed as suggested by the reviewer.

References:

Lovelock, J. E. and Margulis, L.: Atmospheric Homostasis by and for the Biosphere: The Gaia Hypothesis, *Tellus* 26, 1-10, 1974.