

Global modelling of methyl iodide production in the open ocean

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Motivation

Methyl iodide (CH_3I) is ubiquitously detected in water and air in the marine boundary layer. It is a major carrier of iodine to the atmosphere and plays a considerable role in the tropospheric ozone chemistry. It alters the atmospheric oxidative capacity and partly also affects new particle formation with possible implications for the radiative budget and climate forcing. There are a number of uncertainties concerning the production of methyl iodide in the open ocean related to origin of the source and production rates. Two types of sources are suggested: direct production by phytoplankton and photochemical production in presence of organic matter. Information in the literature on CH_3I production by picocyanobacteria is either inconsistent or contradictory. There is several orders of magnitude difference between the rates of CH_3I production by *Prochlorococcus marinus* reported by Smythe-Wright et al. 2006 and Brownell et al. 2010. Hughes et al. 2011 show, that CH_3I production in a single *P. marinus* culture can vary by at least one order of magnitude depending on the physiological state. They argue that the large range of average production rates derived from laboratory studies could be due to the different physiological state of the cell. Here, we take into account the different production mechanisms to investigate distribution patterns and air-sea exchange of CH_3I .

CH_3I modelling

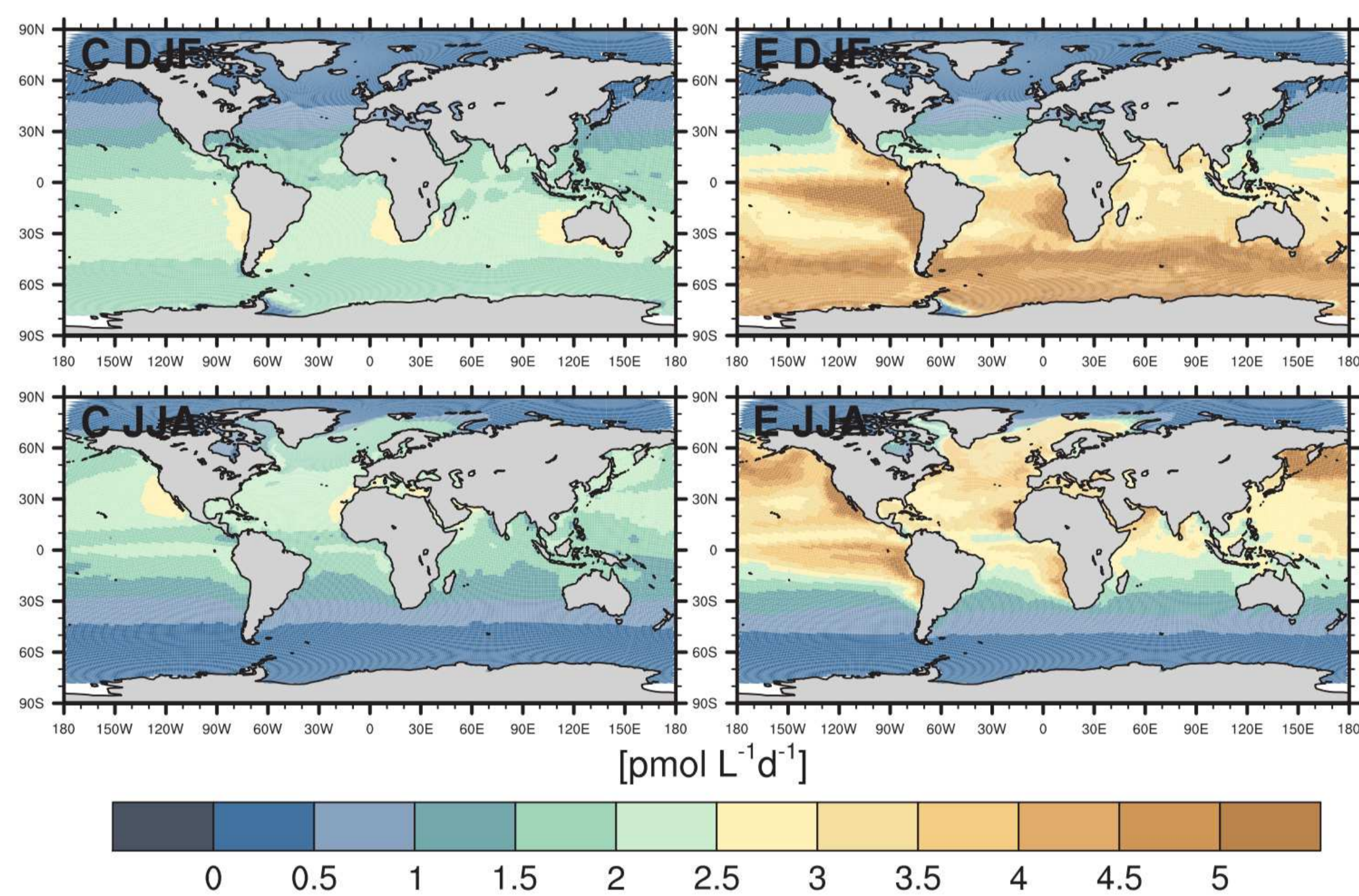
- CH_3I chemistry is embedded into the carbon cycle model HAMOCC (Six & Maier-Reimer 1996), which is coupled to the ocean GCM MPIOM (Marsland et al. 2003)
- CH_3I production:
 - photochemical production by radical recombination between methyl groups and iodine atoms, implemented as a linear function of either semi-labile (from HAMOCC) or refractory (constant) DOC and radiation
 - biological production by phytoplankton, implemented as linearly coupled to primary production
 - to mimic enhanced CH_3I production by stressed picocyanobacteria an adaptive biological production rate is implemented that uses nutrient availability as a proxy for picocyanobacteria abundance and stress
- CH_3I degradation: nucleophilic substitution with chloride, hydrolysis, photolysis
- gas exchange is calculated using a time-invariant field of atmospheric concentrations

Tab.1: Experiments differing in production mechanism included

	A	B	C	D	E
biological production		+			+
photochemical production (SLDOC)			+		+
photochemical production (RDOC)				+	+
biological production (with stress)				+	

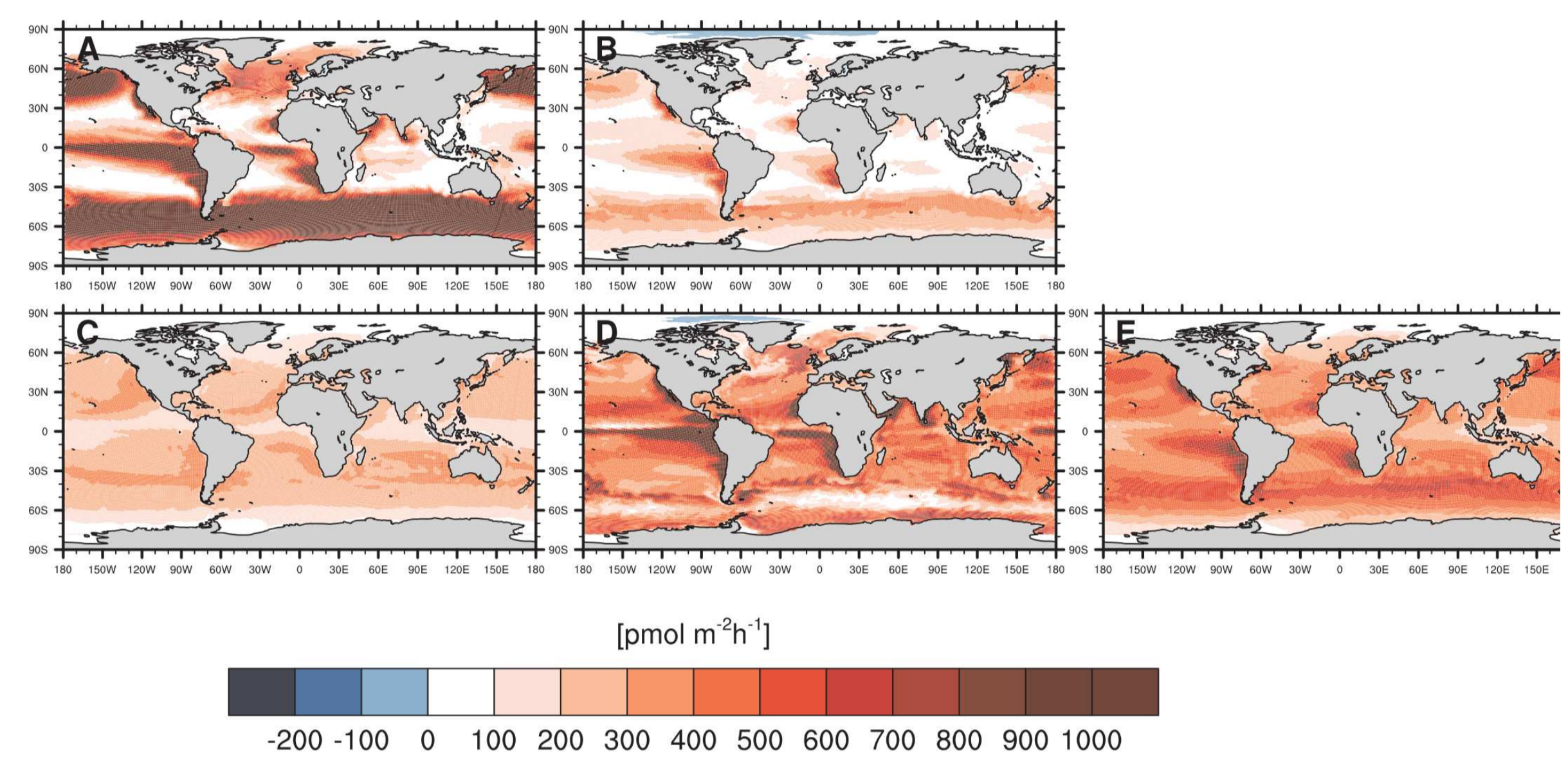
CH_3I production

Daily surface ocean production rates in regions dominated by photochemical production (Fig. below, simulations C,E) are of the same magnitude as the ones estimated previously for this production pathway (Richter & Wallace 2004).



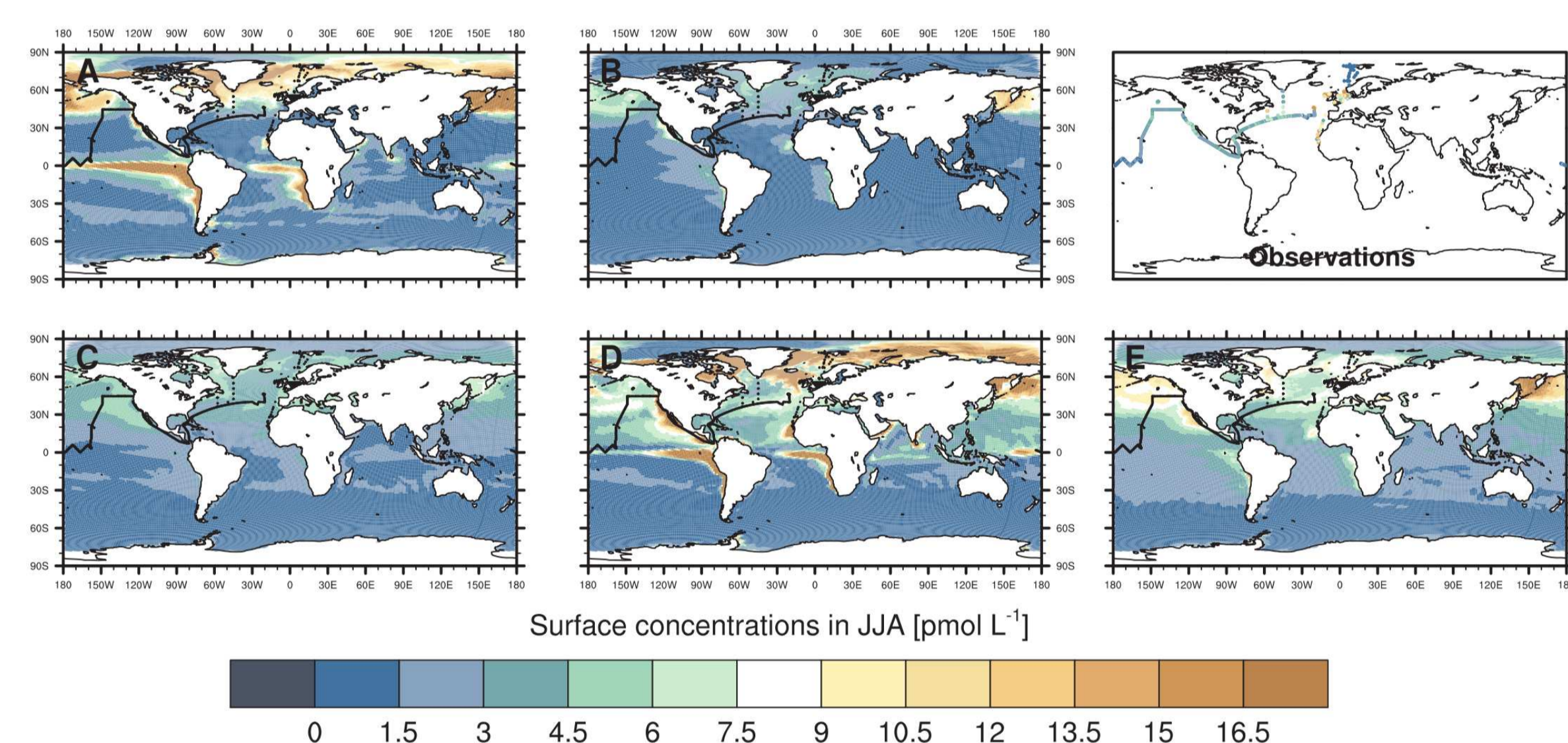
Air-sea gas exchange

Global annual CH_3I fluxes range between 70 and 260 Gg yr^{-1} , i.e. the ocean is a net source of methyl iodide for the atmosphere. These values are at the lower edge of previously estimated global emissions (130-1300 Gg yr^{-1} see Bell et al 2002 and references therein). Local air-sea fluxes can be both positive and negative, depending on season and location, and source processes considered (see Fig. below for annual mean). For all of A-D negative fluxes, i.e. from air to sea, are predicted in the North Atlantic ($> 50^\circ\text{N}$) in DJF (not shown).



Model evaluation

Neither biological production (A, D) or photochemical production from semi-labile DOC (B) alone represent CH_3I surface concentrations satisfactory (Fig. below, JJA). Best representation is achieved when considering either photochemical production from refractory DOC (C), or mixed biological and photochemical sources (E). Globally 8.46%, 12.37%, 37.09%, 18.19%, 23.89% of the CH_3I observations are best represented by experiment A, B, C, D, and E, respectively.



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Conclusions

The model results suggest:

- The ocean can act both as a source and a sink of methyl iodide to the atmosphere.
- There is no universally dominating mechanism of marine CH_3I production, but methyl iodide in the ocean is likely to originate from mixed sources.
- For modelling CH_3I surface ocean concentrations a parameterization based on production by photochemical degradation of refractory DOC is appropriate to represent a large fraction of the observations.

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