

Answer to referee 3

1-Equilibration in the system

We don't agree with the referee's comments on this section, since one should clearly make the distinction between the thermodynamic of the equilibrium between two phases (case of infinite dilute solutions) and the kinetics of transfer at a water/gas interface.

It is true that the degree of equilibration depends on several factors and not only of the contact time between the gas and the water phase. Theoretical extraction efficiencies given in our paper are calculated for an infinite time of contact between the two phases. Gas solubilities are the main term to be considered, the Henry's law constant as expressed in the paper in $\text{mol L}^{-1} \text{atm}^{-1}$ represents the solubility of the gas, a gas with a high solubility (high Henry's law constant) will remain preferentially in the water phase and will be hardly transferred by molecular diffusion (after an equilibration period) from the water phase to the gas phase.

However the transfer occurring within a relatively short time (typically 10 mn: the residence time of a segment of water in the equilibrator) the equilibrium is not reached, and the kinetic of the transfer becomes an important parameter. One important factor is therefore the gas diffusivity coefficient in water, which drives the resistance to the transfer between the water to the gas phase (the other parameters being the thickness of the diffusion layers). This has been nicely described by Liss and Slater (1974)* on the two layers (or 'thin film') model of transfer. An important point is that the diffusivity decreases with the molar mass of the compound.

Taking into account the example of isoprene compared to other NMHCs: isoprene has a diffusivity coefficient 30% lower than ethane at the same temperature and a Henry's law constant 3 to 5 times greater, it is consequently more soluble (due to its Henry's law constant) and less rapidly exchanged (due to its diffusivity lower), both effects lead to a lower extraction efficiency. The same remark can be done in a lesser extent for the group ethane, propene, butene, they have similar Henry's law constant but their diffusivity in seawater differ by 10 to 30 % for a C_2 to a C_4 Hydrocarbon

Concerning the effect of temperature on the sea air exchanges estimations, if we consider again the two film layer model of transfer (Liss and Slater, 1974), the flux across the air sea interface depends both on the piston velocity and the supersaturation of the sea surface with respect to the atmosphere according to the formula:

$$\text{Flux } K_w = (C_w - K_H C_g) \quad (1)$$

Where K_w is the piston velocity depending on the diffusivity of the gas in seawater (more precisely on its Schmidt number).

C_w is the concentration in bulk surface seawater,

C_g the concentration in bulk air above the interface

K_H the Henry's law constant,

As the surface seawater is largely supersaturated, of at least of one order of magnitude, i.e.

$C_w \gg 10 \times K_H C_g$ (on the average, $C_w \sim 40 \times K_H C_g$)

The second term of equation 1 depends on a first approach of C_w . This is why generally the flux at the sea air interface is described in a first approach for most of the supersaturated species as :

Flux = $K_w \cdot C_w$

(Nota: the uncertainty on K_w can be very large; it is much more greater than the approximation $C_w \sim C_w - K_H C_g$, for highly supersaturated species, this is why this formula is considered as a very good approximation, and that the solubility is generally not taken into account)

However we can roughly compute the variability due to the effect of temperature on the solubility: considering a variation of K_H of about 30% due to the temperature effect as pointed out by the referee, and considering only this effect, the variation of the second term of equation (1) will be lower than 3 % and on the average of 0.8 %.

On the opposite the flux exchanged with the atmosphere is dependent on K_w which is strongly affected by diffusivity of the gas in seawater, and consequently by the temperature, this piston velocity is directly dependent on the gas diffusivity or more precisely on the Schmidt number (ratio of kinematic viscosity to mass diffusivity) at the power $\frac{1}{2}$ or $\frac{2}{3}$.

The influence of temperature acts principally on the piston velocity and not on the supersaturation term.

*References:

Liss, P. S. 5 and Slater, P. G.: Flux of Gases across the Air-Sea Interface, *Nature*, 247, 181–184, doi:10.1038/247181a0, 1974.

The equilibrator used in the experiment was initially equipped with a thermo-controlled system. However we decided not to use this system since the equilibrator remained opened for a quasi continuous visual inspection of the water level in the gas phase separator. However, the laboratory was thermo regulated at 22°C, and this was constant during the cruise. Concerning the extraction temperature, water was slowly transferred into the

equilibrator and its temperature reached during the transfer time delay the laboratory temperature.

2- Biological consumption of NMHC's

We include data about microbial consumption of NMHC's if such values are available.

3- Statistical comparisons.

As stated before, there are several production processes for the various trace gases and simple regression statistics will not solve the complex nature of these processes. We would need much more detailed studies, to be able to apply multivariate statistics to extract statistical significant data from our result. We also feel that this is beyond the scope of our paper

4- Minor comments

Page 4733 Line 25. Flasks were sealed with plastic caps and O rings (Schott Durand flasks). Contamination was checked from the analysis of samples stored from several hours (see also our answer to the referee 2)

Page 4738 Lines 27–29. We are aware of the input ratio problem for the Chemtax analysis as last reviewed by Higgins et al. (2011). Particular in the Arctic where the identification of haptophytes from diatoms is difficult since the common available haptophyte *Phaeocystes* sometimes lacks its diagnostic marker pigment 19-hexanoyl-oxy-fucoxanthin (Wassmann et al. 1990). In close cooperation with Eva Maria Nöthig and Katja Metfies both AWI we used microscopic and 454 sequencing of some samples to derive appropriate ratios for the Arctic Ocean. One co-author is currently preparing a paper "Investigation of phytoplankton distribution along a west/east transect across Fram Strait via molecular techniques" where we do a detailed comparison of all the various methods.

Analytical methods and Table 2. We agree to use some consistent term.

Appendix A - Equation A1

Equation A1 is derived from a mass balance in the extraction cell, i.e. the initial quantity (in moles) of a compound in the water phase is the sum of the quantity transferred in the gas phase (expressed as a partial pressure P_g) with the quantity remaining in the water.

Considering:

V_w = volume of the water phase, C_w = concentration in the water phase (typically mol L⁻¹)

V_g = Volume of the gas phase, P_g = Partial pressure in the gas phase (atmosphere)

K_H = Henry's law constant. (typically: mole L⁻¹ atm⁻¹)

n_w = number of moles in the water phase at the equilibrium, n_g = number of moles in the gas phase at the equilibrium.

At the equilibrium we have the Henry's law formula : $C_w = K_H P_g$

In the gas phase : $P_g V_g = C_w V_g / K_H = n_g RT$

$$n_g = C_w V_g / K_H RT$$

in the water phase: $n_w = C_w V_w$

Hence n_{total} (initially in the water phase)

$$n_{total} = n_g + n_w = C_w (V_g / K_H RT + V_w) = P_g K_H ((V_g / K_H RT + V_w))$$

Therefore the extraction efficiency equals to n_g / n_{total}

$$C_w (V_g / K_H RT) / C_w (V_g / K_H RT + V_w) = V_g / K_H RT / (V_g / K_H RT + V_w)$$

Which can be also written:

$$(V_g / V_w) / (V_g / V_w + K_H RT)$$

This can be included in the paper (as appendix), however we think that it could be a little bit beyond the scope of our paper.