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Interactive comment on “A survey of carbon monoxide and non-methane hydrocarbons in the Arctic Ocean during summer 2010: assessment of the role of phytoplankton” by S. Tran et al.

Anonymous Referee #3

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This paper describes distributions of CO and NMHCs in the Arctic Ocean during a summer field campaign. Based on the dataset, the authors generally well discussed the factors controlling the distributions, production processes, and sea-surface fluxes of the trace gases. Although a number of systems have recently been developed for continuous dissolved trace gas measurements, this work provided the first dataset in the Arctic Ocean with the high temporal and spatial resolutions. Therefore, the data obtained in this study would be valuable and worth publishing in the journal Biogeosciences. However, I consider this manuscript has a few serious issues, especially in methodology, and those need to be clarified before publication. My major and minor comments are described below.

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Major comments:

1. Equilibration in the system

If the target gas is in equilibrium between gas and liquid phases, the experimental extraction efficiency should be the same as the theoretical value. For example, in Table 2, ethene, propene, propane, n-butane and n-pentane achieved almost complete equilibriums between gas and liquid phases. In general, it is considered that degree of equilibration between the two phases depends on not only the contact time between the carrier gas and the water in the equilibrator used, but also the solubility of the target gases (e.g., Johnson, 1999). Therefore, gases with higher solubility can reach complete equilibriums faster. In this sense, isoprene is able to achieve the complete equilibration more rapidly, compared to the other species (Table 2). Furthermore, while ethane, propene, 1-butene, and isobutene have almost the same solubility ($4.7\text{--}4.8 \times 10^{-3} \text{ mol l}^{-1} \text{ atm}^{-1}$, described as Henry's Law constant), their extraction efficiencies were obviously different in this study. These inconsistencies could be attributed to uncertainties of this measurement system. Please clarify these points.

I speculate that the equilibrator used in this study could not be thermo-controlled (Figure 1). It is well known that solubility is one of the key factors for the achievement of equilibrium. The authors described differences in temperature over $10 \text{ }^\circ\text{C}$ during the cruise. The difference might change the solubility of the target gases. For example, the Henry's Law constant of ethene at $-1.4 \text{ }^\circ\text{C}$ (minimum temp.) and $11.5 \text{ }^\circ\text{C}$ (maximum temp.) are 8.4×10^{-3} and $6.3 \times 10^{-3} \text{ mol l}^{-1} \text{ atm}^{-1}$, respectively, using the Henry's Law constant and the temperature dependent equation ($k_H = 4.7 \times 10^{-3} \text{ mol l}^{-1} \text{ atm}^{-1}$, $-\text{d} \ln k_H/\text{d} (1/T) = 1800 \text{ K}$) described in Wilhelm et al. (1977), which is also listed in Sander (1999). As a result, the solubility at the minimum temperature becomes almost twofold higher than that at $25 \text{ }^\circ\text{C}$. When the authors conducted lab experiments to obtain the experimental extraction efficiencies, how was the temperature condition? Ethene, propene, propane, n-butane and n-pentane, which can reach equilibriums completely between the gas and liquid phases, still keep their equilibra-

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tions even if temperature conditions are changed. However, the extraction efficiencies of other species such as CO and isoprene would vary due to changes in temperature. These matters may be responsible for the inconsistencies between the degree of equilibrium and solubility mentioned above.

Another related point is the contribution of the temperature dependence of Henry's Law constants to the air-sea exchange estimations. According to the authors, temperature dependence for the air-sea exchange yields only ~10% contributions for the CO variability (page 4749, lines 8–12). In this calculation, have authors considered the temperature dependence of Henry's Law constant? If so, please describe how the temperature dependence is assumed.

2. Biological consumption of NMHCs

According to the authors, the microbial consumption has never been reported in the literature and could therefore be negligible (page 4746, lines 20–22). There are, however, some reports on the microbial consumption of NMHCs. For example, Rojo (2009) and Alvarez et al. (2009) pointed out the alkane and isoprene consumptions by microbial organisms, respectively. These literatures must be cited in this paper, and their results should be included in the production/consumption models of NMHCs as well as CO.

3. Statistical comparisons

The trace gas data with high spatiotemporal frequencies have been compared with other parameters in this manuscript. However, I am wondering why the authors did not show any scatter plot for their comparisons. It is important to evaluate the consistency between profiles of target gases and other biological or physical parameters for the production mechanisms of the target gases. I consider that the authors should make the comparisons more quantitatively. Scatter plot with regression analysis is an easy way to estimate the significance of the relationship.

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Minor comments:

Page 4733 Line 25 – “The flasks were perfectly sealed”. How were the flasks sealed? Did the authors use rubber stoppers or O-rings? If so, have the authors checked any contamination from the materials?

Page 4735 Line 4 – Silicon tubing has a potential of permeation and/or dissolution of gases. Although a membrane type equilibrator with silicon tubing for trace gas measurements has been reported (e.g., Ooki and Yokouchi, 2008), have the authors examined such errors as well?

Page 4738 Lines 27–29 – The authors should explain how initial pigment ratios were selected for the CHEMTAX analysis, because the initial values would largely influence the outputs obtained in this study. If the authors do not have any grounds of the initial ratios, it could be worthwhile performing multiple runs of CHEMTAX using a range of initial marker pigment:Chl a ratio matrices (see Latasa, 2007). Also, I consider the authors need to justify the output pigment ratios using such data published previously.

Analytical methods & Table 2 – The authors used the terms “extraction efficiency” and “extraction yield”. Please unify the terminology.

Appendix A – I consider that it is not easy for readers to understand the equation A1 in Appendix A. This equation is important to calculate the theoretical extraction efficiency. Please add conscientious explanations for the equation.

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