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Discussions

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 #1

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The paper presents novel data on the distributions of CO and NMHCs in the N. Atlantic and Arctic Ocean. This data is valuable, providing greater spatial coverage in the distributions and air-to-sea fluxes of these biogeochemically and atmospherically significant compounds. The authors expand upon the value of the dataset by attempting to define the factors driving variations in CO and NMHC concentrations.

The authors seek to understand the variations in CO and NMHCs by constraining source and sink terms. The microbial oxidation and air-sea gas exchange are considered as sinks. The authors make a compelling case that variations in these sinks minor and thus are not the main cause of CO and NMHC concentrations in the waters

studied suggesting variability must be driven by other factors, most likely variations in production. Before moving to production, it seems the authors did not present a CO sea-to-air emission budget for their study area. As they have done most of the calculations to constrain this term it seems amiss not to present it.

The main sources of CO and NMHCs are proposed to be photochemical degradation of CDOM. This is wholly consistent with the literature. The authors attempt to constrain the production of CO and NMHC rely on literature apparent quantum yields which do not necessarily reflect CDOM photoreactivity in their waters. For instance, the AQY for CO they use derives from Zafiriou et al (2003). This AQY is an average for two transects of the Pacific Ocean, taking in southern, temperate and tropical waters. Yet in that paper it is reported that the most northerly waters (>40oN) have CO AQYs $\sim$10 times lower than the average for the rest of the Pacific. Other studies have reported estuarine gradients in CDOM and CO AQYs, showing that terrestrial CDOM has higher CO AQYs than marine CDOM (Zhang et al 2006; Stubbins et al 2011). The Arctic can be envisioned as a massive estuary with elevated terrestrial CDOM in the water masses, particularly the Polar Waters, studied in current the manuscript (see Opsahl et al. 1999; Amon et al. 2003). Without empirical data for CO AQYs it is hard for the authors to constrain CO photoproduction. They also use a non-spectral model of CO production, adopting an average CO AQY from Zafiriou et al. without including wavelength variations, this introduces a number of assumptions and errors which should be avoided if possible. The lack of local AQYs and inclusion of spectral dependence in their photochemical model does introduce a number of uncertainties, some of which could be avoided (by using a spectral AQY and spectral irradiance data). The lack of AQYs for their water masses cannot be avoided and may introduce errors of a factor of 10 (see Zafiriou et al. 2003; Zhang et al 2006; Stubbins et al 2011). This is likely inescapable, but this limitation should at least be addressed. A sensitivity analysis could be performed using Zafiriou's AQYs to define a minimum likely source and coastal seawater AQYs from Zhang et al and/or Stubbins et al to produce an estimate of maximum production.

CDOM - the instrument defining CDOM needs to be further defined. What is it reporting as CDOM? Absorbance, which is CDOM, or fluorescence which is a fraction of CDOM and better defined as FDOM. Whichever it is reporting, it is important to know the wavelengths it is reporting. For CDOM this has a moderate influence on how the data is interpreted as absorbance at short (e.g. 250 nm) and long wavelengths (e.g. 400 nm) are usually well correlated. For FDOM, this is not the case. Significant fluorescence can occur at long wavelengths, with minimal levels at short, or vice versa. If the "CDOM" sensor is detecting a long wavelength fluorescence excitation emission pair, it likely reflects terrestrially derived heterochthonous CDOM or in some cases microbially processed autochthonous CDOM. As such, it may not pick up the production of CDOM that occurs at or above the chlorohyll max (Kitidis et al. 2006). This CDOM would be expected to be dominated by freshly produced microbial CDOM dominated by blue shifted protein-like fluorescence (e.g. Jorgensen et al 2011; Stedmon and Álvarez-Salgado 2011). These limitations to the "CDOM" data should be introduced.

The above limitations to the CDOM data also influence the interpretation of the correlations between chlorphyll, CO and NMHC which lead the authors to suggest a phytoplankton source for both CO and NMHC. The authors cannot rule out an indirect mechanism, whereby algae produce CDOM and CDOM produces photoproducts (CO + NMHC). The authors do mention this caveat as it is impossible to isolate phytoplankton from the CDOM they produce, or from the light that enables photosynthesis but also photo-degrades CDOM. The possibility of direct and CDOM mediated CO and NMHC production from algae just needs emphasising in order to offer the reader a balanced view of the possible reasons for the observed trends.

Finally, in the above regard, the authors do not discuss whether the variations in chl, CO and NMHC may be driven by physical processes. For instance, sometimes chl and CDOM can be mixed to depth. if this occurs rapidly, then CO and NMHCs would also be mixed with them.

None of the above criticisms are insurmountable with the current data set. They just

require the addition of some extra discussion of the limitations of the analytical and modeling assumptions. After these limitations are addressed, the paper would make a valuable addition to the field.

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