Biogeosciences Discuss., 9, C1529–C1538, 2012
www.biogeosciences-discuss.net/9/C1529/2012/
© Author(s) 2012. This work is distributed under
the Creative Commons Attribute 3.0 License.

Biogeosciences 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 #2**

Received and published: 28 May 2012

This paper presents a relatively large dataset of CO and NMHCs concentrations and distributions in the Norwegian and Greenland Seas. The dataset itself makes an important contribution to understanding trace gas cycling and air-sea exchange in the Arctic Ocean. However, the interpretation of the data in the present status is to a large extent not scientifically sound. It requires major revisions and re-review

Major comments:

1. The budgeting model presented in section 5.1, which is probably the most important part of the Discussion (discussion in sections 5.2-5.4 is derived from this model), is unreliable because of an erroneous assumption about microbial NMHCs consumption,

the use of an unrepresentative microbial CO uptake rate constant, and a biased air-sea gas exchange calculation.

First, the authors claim that there is no reported evidence of biological consumption of NMHCs in seawater. To my knowledge, microbial uptake of hydrocarbons under aerobic conditions, including light hydrocarbons (such as isoprene and propane), is well recognized. Here I just name a few papers in the literature: Brakstad and Bonaunet 2006: Biodegradation 17, 71-82; Alvarez et al. 2009: characterization of marine isoprene-degrading communities, Environmental Microbiology, 11, 3280-3291; Redmond et al. 2010: Appl. Environ. Microbiol. 76, 6412–6422; Shennan 2006: Utilization of C2–C4 gaseous hydrocarbons and isoprene by microorganisms. J. Chem. Technol. Biotechnol. 81, 237–256. Fernando 2009: Degradation of alkanes by bacteria, Environmental Microbiology, 11, 2477–2490.

As a matter of fact, the NMHCs profiles reported in the present manuscript themselves strongly suggest the existence of in-situ consumption, most likely biological consumption, of these NMHCs, since the profiles exhibited rapid decreasing NMHCs concentrations with depth (to negligible levels at the bottom of the euphotic zone, as the authors stated). Note that the NMHCs concentrations would not have fallen to undetectable levels at subsurface depths if there were no in-situ consumption. Molecular and eddy diffusion would be sufficient to maintain significant amounts of NMHCs at the bottom of the euphotic zone, even far below it.

Second, the concentration range (0.1 to 0.8 nM) covered by the samples used for determining the microbial CO uptake rate constant was far below the average surface [CO] of 4.2 nM (range: 0.6-17.5 nM). The average [CO] vertical profile indicates that [CO] was >2 nM in the upper 6 m. Although microbial CO consumption follows first-order at relatively low [CO]s, saturation and inhibition kinetics prevail when [CO] is above a few nanomolars (see Tolli and Taylor 2005: Limnol Oceanogr 50:1205–1212), particularly in cold arctic and sub-arctic waters (see Xie et al. 2009: Limnol Oceanogr & MEPS). Our own group also has a large unpublished microbial CO uptake dataset collected



BGD

9, C1529–C1538, 2012



from both the eastern and western Arctic in summer. The data unequivocally indicate that microbial CO uptake in arctic surface waters in summer always obeys saturation or inhibition kinetics at [CO]>2 nM. As the majority of the [CO]s reported in the present manuscript fall into the saturation or inhibition kinetics category, using a single first-order rate constant for the entire study area/water column would substantially bias the microbial consumption term.

Third, the Wanninkhof (1992) formula was used for calculating the piston velocity. It is well known that this parameterization mainly applies to open ocean with large wind fetches. As described by the authors, their study areas were often partially ice-covered, which makes the Wanninkhof formula undesirable. A better formula would be that of Liss and Merlivat (1986). The piston velocity differs by a factor of 2 between the two formulae for the dominant wind speed range occurring at sea.

2. The "surface" concentrations recorded by the automated system with a water intake of 6 m deep actually did not represent the true surface concentrations. Based on the mean profiles given in the manuscript, it on average underestimated [CO] by a factor of 2 and [propene] by a factor of 1.5 and overestimated [isoprene] by ca. 25%.

3. The authors used a cruise-mean diel [CO] progression to assess if a clear diurnal pattern existed. This approach is valid only if there was no substantial spatial patchiness in CO consumption and production characteristics. As pointed out by the authors, the ship crossed various water masses having diverse physical (e.g. temperature), biological (e.g. biomass), and chemical (e.g. CDOM abundance) properties. It's difficult to envisage that these waters would possess invariable biological CO consumption (which strongly depend on temperature and bacterial species composition and population density) and photoproduction (which depends on CDOM abundance and photoreactivity, solar irradiance, and water column optics). The magnitude and timing of peak [CO] not only rely on the magnitude and timing of solar irradiance (which the authors assessed in Fig. 11) but also on the loss term (microbial plus outgassing). The faster the loss is, the larger the magnitude of CO diurnal amplitude is and the closer of the peak [CO] is



BGD

9, C1529–C1538, 2012



to the peak irradiance. In other words, diurnal patterns might exist in individual areas but averaging could smear or even totally eliminate the diurnal signature, since peak [CO] could vary and occur at different times in different areas. The lack of monitoring [CO] on diel scales thus does not permit evaluating CO's diurnal variability.

4. The authors noted: "We have observed for the first time through in situ measurements that CO was directly produced by phytoplankton" (p4756, line 13-15). This is an exaggerated statement. First, these subsurface maxima were mostly small irregularities. They occurred not only at or close to the chl-a maxima but also at other depths within the upper layer. Second, they were not consistent, i.e. not all chlorophyll maxima having parallel CO maxima. Third, there are a bunch of alternatives to explaining these CO "peaks": a) they might result from erratic CO contamination by the plastic Niskin bottles. It is well known that these plastic samplers could produce variable CO artifacts if no appropriate contamination control measures are taken (see Xie et al. 2002: Mar Chem; Xie et al. 2009: L&O). The negligible CO levels found at deep depths appeared to support the notion that their bottles, at least those for deep-depths sampling, did not pose significant artifacts. However, because the deep samples were analyzed ca. 10 hours after sample collection (p4733, line 19-20), any potential CO contamination could have been smoothed out by microbial consumption. Therefore, potential artifacts cannot be ruled out; b) they might be caused by higher photoreactivity of CDOM produced by local organisms; c) they might stem from particles-based CO photoproduction (see Stubbins 2001: PhD thesis; Xie and Zafiriou 2009: Geophys Res Letts). Particles are often enriched at or near the chl a maxima.

5. The validity of Eq. 6 in section 5.3 is in doubt. First, photoproduction depends not only on the absolute value of the AQY (i.e. phi) but also on its spectral shape. The shapes of AQYs for different compounds could be substantially different. Second, these AQYs are from mid- and low latitude waters and may not apply to Arctic waters (AQYs can differ widely from one region to another, depending on CDOM photoreactivity and environmental conditions, such as water temperature). Also see specific



BGD

9, C1529–C1538, 2012



CC BY

comment#39.

Specific comments

1. p4728, line 14-17: Your CO and NMHCs concentrations were not constant (in fact, they show many big peaks). Lack of diurnal cycles does not necessarily imply a tight coupling of production and consumption. 2. p4729, line 19: please cite Conrad et al. (1982) as well. This is an important paper in the history of seawater CO study.

3. P4729, line 26-27: here you are talking about CO air-sea fluxes. Fitchot et al's value is the global CO photoproduction. Lack of coherence.

4. P4733, line 4: Any biofilms formed on the membrane? Bacteria thriving on water pumping intakes could lead to underestimating concentrations of the measured compounds.

5. P4733, line 21-28: Please specify at what stations/depths the microbial CO consumption rates were determined.

6. Section 3.2.1: I could not find info on how you analyzed the discrete profile samples. Also using the flow-segmentation method? If so, was the 1 L volume enough?

7. P4735, line 19: this is likely the nominal volume. Was the real volume measured? It matters since sample and calibration used separate loops.

8. P4736, line 11: GC column was operated at what temperature?

9. P4736, line 14: The standard's concentration seemed too low compared to the concentrations reported. Was aqueous standard used? If not, how humidity was accounted for (100% humidity in samples vs. almost zero humidity in standard)? Same question for NMHC calibration.

10. P4737, line 5: please give specific numbers of the blanks (not just say "high levels).

11. Section 3.2.4. Give references to pigment measurement.



BGD

9, C1529–C1538, 2012



CC BY

12. P4739, line 3: give makers and models of instruments for wind speed and radiation measurements.

13. P4739, line 7: give details and references about this box system. Why does CDOM have arbitrary units, instead of m-1 as in absorption coefficient? Is this a conventional spectrophotometer? Did it measure absorbance? If not, what did it measure, fluorescence? If not calibrated, how did you know the instrument was stable over the entire cruise?

14. P4740, line: UVA usually refers to 320-400 nm.

15. P4740, line 7: what do you mean by background value?

16. P4740, line 11: Henry's Law constant not Henry's constant.

17. P4740, line 15-16: how did you delimit nearshore and open ocean?

18. P4740, line 26: Table 3 shows means and maxima not "averaged maximum values".

19. P4741, line 6: "in the pack ice"? I think you did not sample sea ice. You mean "in partially pack ice-covered waters"?

20. P4743, line 1-2: Please explicate how bathymetry and pack ice influence [CO].

21. P4744, line 6: These features of profiles are a net effect of production and consumption, not just of light-related production.

22. P4745, line 29: microbial uptake as well.

23. P4746, line 14-15: cited range is incorrect. Reported range by these authors is much larger. These are autumn data (when [CO]s are low). Spring data are different and saturation and inhibition kinetics often dominate in the surface (when [CO]s are high).

24. P4746, line 20: how did you determine NMHC consumption? No info given in the



BGD

9, C1529–C1538, 2012



method section.

25. Eq. 2: was the MLD always >euphotic zone? You said in some areas the MLD was only 0-8 m! (p4744, line 4-5). How did you calculate the mixed layer depths? Give MLD values for all stations in a Table or show averages and ranges for various water masses.

26. Eq. 2: how CML-bar was calculated? Arithmetic mean or depth-weighted mean?

27. Section 5.1: You proposed a budgeting model but did not give any results. Please use a table to show the results of each parameter in Eq. 4 for different water masses if not each station.

28. P4747: line 21-23: I am totally lost here. Why is it more difficult to do budgeting without a significant sink. I think it is the opposite. In addition, even without considering microbial uptake, NMHCs are lost via outgassing.

29. P4748, line 19: Since [CO] decreased approximately exponentially with depth, how could the average [CO] be equal to [CO]surface/2?

30. P4748, line 25: mismatch of eq. number (should be eq. 3). There are many such cases in the manuscript.

31. P4749, line 19-21: This is what I expected. The principal cause is the differing biological consumption rate: low in cold waters and high in warm waters.

32. P4750, line 21-p4751, line 8: [CO] is controlled by both the production and consumption processes. A comparison of CO concentration distribution with photoproduction is thus not justifiable unless there is no CO loss or the loss term is spatially invariant (which is not the case for this study).

33. P4751, line 18: Xie et al. (2009 L&O) measured CO AQYs for arctic seawater. Perhaps more appropriate to use their values.

34. P4752, line 5-7: This is because CO produced at shallower depths is physically



BGD

9, C1529–C1538, 2012



mixed down to deeper depths. Alternatively, light penetration at your stations could be deeper than that used by Fichot's model.

35. P4752, line 11: If the MLD is ca. 20 m, as you claimed, why there was no CO mixed down from the surface. Even within the pycnocline, gases can be transported downwards via molecular and eddy diffusion.

36. P4753, line 12-15: Why would "similar" subsurface distributional features necessarily indicate the same production pathways?

37. P4754, line 20: what do you mean by quasi-exponential? Please show the exact mathematic equation. Please show graphs comparing the fitted profiles with the measured ones. How do you know a purely photochemistry-driven CO profile should follow a quasi-exponential decay? Also, see my comment above on the validity of the assertion of a biological CO source.

38. P4755, line 3: Isoprene is produced mainly by biological processes. How could the approach used for CO be applied to isoprene? Please show the graphs comparing the fitted profiles with the measured ones.

39. Table 5: The phi values used are for what wavelengths? If they are averages, then for what wavelength ranges? Are the same wavelengths or wavelength ranges used for different compounds? I could not find these values from the papers cited. Riemer et al. analyzed samples from various sites showing large ranges of AQYs. Which site did you choose? State the reason of your choice.

40. Fig. 13: I bet this pattern is more related to solar irradiance than to chl a. Peak [CO] lags peak irradiance if microbial consumption is relatively slow, which is the case in the Arctic Ocean. Although irradiance was not measured on 26/7 and afterwards, it can be inferred from previous days that peak irradiance occurred at around 15 UTC (Fig. 7c), which can well explain the CO peak that took place at ca. 2 hours later. The co-variation between [CO] and chl a is likely just a coincidence, since a) such events



BGD

9, C1529–C1538, 2012



CC BY

only occurred two times (only one event is reported) and b) estimate of chl a-based CO production is much smaller than the observed CO production. The maximum-minimum difference in chl a in Fig 13 is ca. 600 ng/L. Using the largest chl a-normalized CO production rate in Table 6, 72 umol CO (g chl a)-1 d-1, this increase in chl a would lead to an increase in CO production of only 0.04 nM d-1. However, [CO] increased by 16 nM in a few hours, suggesting the chl a-based CO production, if any, to be negligible.

It should be noted that this CO peak roughly paralleled the rapid shoaling of the topography (from ca. 2500 m to <1000 m) (Fig. 7d). The CO peak could, therefore, also be caused by contrasting [CO]s across the two areas, which accidentally also had widely differing chl a contents.

41. Please add chl a or chl a fluorescence data to Fig. 5-7 and Fig. C1-C2.

English language

The readability of the manuscript needs to be improved. Here I just picked out a few "eye-catching" errors.

1. p4728, line 11: "UV-induced CO photoproduction" not "CO-induced UV photoproduction".

2. P4737, line 12: Two "becauses", consider revising.

3. P4738, line 3: samples were "analyzed" not "measured".

4. P4738, line 10: transferred "into" not "in".

5. P4754, line 11: awkward sentence.

Suggestions

Because of lack of process study (e.g. photoproduction incubations, microbial consumption incubations [current data are too sparse to be representative] or time-course Lagrangian-mode profiling), the current dataset does not allow to legitimately quantify



BGD

9, C1529–C1538, 2012





the production and loss processes in the water column, as the authors have attempted to do. I suggest that the authors focus on the distributions and regional variability of CO and NMHCs concentrations and air-sea fluxes and their relationships to other parameters. I am surprised that no air-sea fluxes are calculated in the current manuscript, since such calculations could lead to better understanding the role of the Arctic Ocean in regulating the atmospheric chemistry over this region. It should, however, be noted that corrections need to be made if the authors want to use the measurements from the automated system to calculate the fluxes, since the 6-m concentrations do not represent true surface concentrations (see major comment#2).

---

Interactive comment on Biogeosciences Discuss., 9, 4727, 2012.