**Biogeosciences
Discussions**

Interactive comment on "Sea-to-air and diapycnal nitrous oxide fluxes in the eastern tropical North Atlantic Ocean" *by* A. Kock et al.

A. Kock et al.

akock@ifm-geomar.de

We thank the referee #1 for the very helpful discussion on our manuscript. We modified our manuscript and added some additional information on the gas exchange parameterization of Tsai and Liu (2003) and its applicability to our budget calculations.

R1: "The final conclusion of the abstract focuses on the finding of Tsa and Liu (2003) that surface ocean surfactants appear to decrease air-sea gas exchange. However, in the actual text very little time and discussion is spent on this topic. In fact, it comes across almost as a default. That is they discuss advection and biological production and when neither of those seem to be they answer they conclude that surfactants might be it. It would be helpful to have more discussion on this topic - especially if they want it to be the main conclusion of the paper. In the discussion section on this

topic they seem very uncertain that surfactants can account for what they observe and conclude that "...quantitative estimates of the surfactant effects on gas exchange reveal large uncertainties, and most field studies report smaller effects of surfactants on gas exchange.." If this is their final conclusion then why do they feel comfortable and compelled to say that surfactants are the explanation here? I don't doubt that they are important - but the argument presented here is not yet convincing. Can they explore the relationships between surfactants and gas exchange more in the text? Perhaps including a discussion of where it seems important and where the relationship falls apart would help the readers have a better understanding."

Author response: We agree with the referee that a more detailed discussion of the relationship between surfactants and gas exchange may help the readers to better assess the contribution of surfactants on our budget calculations. Therefore, we included more information on the wind speed parameterizations by the addition of Figure 2 that shows the wind speed dependence of the gas exchange coefficient of N2O from the parameterizations used in our calculations. Furthermore, the plausibility of the application of this parameterization is discussed in the text:

"However, the gas exchange under the influence of surfactants is not well constrained so far, because a) the distribution of surfactants in natural waters is difficult to determine and b) the influence of surfactants on gas fluxes is not well understood. Biological production has been identified as main source for surface slicks (Lin et al., 2002;Wurl et al., 2011), and SeaWiFs chlorophyll images (not shown) show that the investigated area was highly productive during the sampling periods. The occurrence of surfactants was furthermore associated with high intensities of solar radiation (Gasparovic et al., 1998) which can be found in the tropical upwelling areas. Therefore, the Mauritanian upwelling provides very favorable conditions for the occurrence of surfactants while their extent and individual distribution during the time of the sampling may show large variability, though. The parameterization of Tsai and Liu (2003) is based on the experiments of Broecker et al. (1978), resulting in 70-80% reduced fluxes for CO2. This

is in the upper range of observed reduction rates (Salter et al., 2011;Upstill-Goddard, 2006;Schmidt and Schneider, 2011) and may therefore slightly overestimate the reducing effect of surfactants. However, recent publications point to a relatively large effect of surfactants on gas exchange (Schmidt and Schneider, 2011;Salter et al., 2011), and the applicability of the parameterization of Tsai and Liu (2003) for the budget calculation demonstrates that this effect may have a large impact on gas fluxes in upwelling areas."

We also agree with the author that our conclusion that surfactants substantially reduce the N2O gas exchange may be a bit misleading as we do not have any direct evidence for this effect. To clarify that the main conclusion of our manuscript is not the evidence for a reduced gas exchange by surfactants but the fact that we cannot close the N2O mixed layer budget with the common gas exchange parameterizations, we rephrased the respective sentences in our conclusions:

"Other effects, including a reduced atmospheric turbulence due to a stably stratified boundary layer over cold upwelling waters or the presence of vertical N2O gradients in the oceanic mixed layer due to diurnal varying mixing activities, could also lead to a reduced gas exchange. However, our results suggest that common parameterizations of air-sea gas exchange may lead to a significant overestimation of the oceanic emissions of N2O and other trace gases in highly productive areas."

R1: "Several times the manuscript refers the readers to other papers for more detail. This can be an effective method - especially when text space is limited. However, I found that the details needed to understand this paper were missing and thus I had to read other papers to more fully understand this one. In this case- I had the time to do so - but others might not and it is critical that papers can stand on their own. Thus, it would be helpful for the authors to include a few more details on their method (instead of just referring us to Walter et al.), more information on the diapycnal diffusivities reported in Schafstall et al., and, as I say above, on the surfactant/gas exchange issue."

Author response: We added additional information on the N2O measurement procedure in the methods section:

"Water samples were analyzed for dissolved N2O on board using a GC/ECD system (Hewlett Packard 5890 II during ATA3, Carlo Erba HRGC 5160 Mega Series during P347 and P348) with a static equilibration method. The GCs were equipped with a 6' 1/8" stainless steel column packed with molecular sieve (5Å) (W. R. Grace & Co.-Conn., Columbia, MY) and operated at a constant oven temperature of 190 °C (HP 5890II) and 220 °C (Carlo Erba HRGC 5160). Argon-methane (95/5, 5.0, AirLiquide, Düsseldorf, Germany) was used as carrier gas at a flow rate of 30 mL min 1. Triplicates of bubble free samples were drawn from 10L Niskin bottles mounted on a CTD/rosette, poisoned with mercuric chloride or measured within 24 h after sampling. For analysis, a 10 mL helium headspace was added to each sample using a gas-tight syringe (VICI Precision Sampling, Baton Rouge, LA). A 9.5 mL subsample of the headspace was analyzed for nitrous oxide after an equilibration time of minimum 2 h. The GC was calibrated on a daily basis using at least two different standard gas mixtures (Deuste Steininger GmbH, Mühlheim, Germany) to account for potential drift of the detector. The concentration of N2O in the water phase was calculated using the solubility function of N2O from Weiss and Price (1980). The average precision of the measurements, calculated from error propagation, was ±0.7 nmol L 1."

Several passages were also added to provide more information on the microstructure measurements and diapycnal diffusivities calculation. The last paragraphs of the Methods sections now state:

"Ocean turbulence profiles were sampled using different microstructure profiling systems (MSS) manufactured by Sea & Sun Technology. The MSS consists of a loosely-tethered profiler, a winch with a cable drum attached to the bulwark and a deck unit. The profiler used during the different cruises were equipped with two shear sensors (airfoil), a fast temperature sensor (FP07), an acceleration sensor, tilt sensors and standard CTD sensors. They were adjusted to descent at a rate of 0.5-0.6 ms-1 while

the system records data from 16 channels at 1000 Hz. A detailed description of the instruments is given in Prandke and Stips (1998).

From the high-resolution shear measurements the dissipation rate of turbulent kinetic energy (ε) were determined by integrating vertical wavenumber spectra of individual one-second ensembles assuming isotropy of turbulence at scales smaller than 0.6m. Correction for unresolved spectral ranges and finite sensor tips were applied. For a detailed description of the algorithms used and the instrumental set up during the cruises the reader is referred to Schafstall et al.(2010). Additionally, the different gas exchange parameterizations that were used in our calculations are shown in Figure 2.

R1: "A quick question about the nitrification N2O production. In Clark et al. (2008) they report NH4 oxidation of 1-10 nmol L-1 d-1 and NO2- oxidation of 1-30 nmol L-1 d-1; yet in this paper they use 5 nmol L-1 d-1. I did not read anything more of Clark et al. but the abstract. However, it would be helpful to know more about the nitrification measurements. For example, I am guessing the 5 nmol value must come from the site closest to the one studied here. But nitrification rates can vary widely both spatially and temporally. Including some more discussion on these rates would be helpful and would help convince the reader they are or are not relevant to these findings."

Author response: The paper by Clark et al. (2008) includes a detailed table with nitrification rates from different regions, indeed. In our calculations we used the maximum ammonium oxidation rates from the measurements closest to our study region.

Rees et al. (2011) recently published nitrite oxidation rate measurements from two upwelling filaments off Mauritania that provide higher nitrification rates, indeed. However, by following two upwelling filaments over several days they had a different sampling strategy from our approach where the region was sampled randomly without regard to the upwelling conditions. The high nitrification rates presented by Rees et al. (2011) may thus be not representative for the whole sampling area and period covered in our budget estimate. This is also supported by their estimate of the contribution of surface

nitrification which made up for only a small portion of their sea-to-air N2O emissions. Furthermore, these data provide another argument against biological N2O production as explanation for the observed discrepancy that can be derived from the vertical distribution of nitrification rates in the water column showing higher rates in the subsurface ocean as in the surface. Assuming negligible variations of the N2O yield over the water column, the subsurface N2O production rates would be even higher than in the surface which in turn contradicts the estimates of ocean interior N2O production rates.

The findings by Rees et al. (2011) were included in the discussion section of the manuscript:

"In a more recent publication by Rees et al. (2011), nitrite oxidation rate measurements from two upwelling filaments off Mauritania provide higher nitrification rates in the upper 100m of the water column (25 ± 12 nmol $L-1d-1$ and 115 ± 106 nmol $L-1d-1$ for two different filaments), with a tendency to increase with depth and maximum rates at 100m depth.

Rees et al. (2011) compared the N2O production estimated from their surface water nitrification rates with their sea-to-air fluxes and came the conclusion that surface N2O production could only explain a small portion of the sea-to-air flux of N2O. The majority of the N2O emissions would have to be supplied from below.

Although these nitrification rates are high enough to make a substantial contribution to our mixed layer budget, this may be due to the different sampling strategy applied by Rees et al. (2011), who followed two upwelling filaments with strongly elevated primary productivity and N2O concentrations. In our approach on the other hand we randomly sampled the area without regard to the upwelling conditions, and a large number of our measurements do not indicate pronounced upwelling. The high nitrification rates measured by Rees et al. (2011) are not representative for the regional budget estimate presented here.

Furthermore, their data provide another argument against biological N2O production

as explanation for the missing ML N2O source: Higher nitrification rates at about 100m depth compared to the near-surface layer together with the findings that the N2O yield increases with decreasing oxygen concentrations (Goreau et al., 1980; Löscher et al., 2012) would result in higher N2O production rates at 100m than in the near-surface layer. These high subsurface production rates in turn contradict the estimates of ocean interior N2O production rates, integrated over the age of the water mass (Freing et al., 2012)."

R1: "Finally- figure 2 - is hard to see. The grey stars barely show up and the black dots are too tiny."

Author response: We agree with the referee and changed the figure to different symbols.