Biogeosciences Discuss., 9, C7089–C7098, 2013
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Biogeosciences Discussions

Interactive comment on "A simple method for air/sea gas exchange measurement in mesocosms and its application in carbon budgeting" *by* J. Czerny et al.

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Received and published: 8 January 2013

We thank anonymous referee #2 for his elaborate remarks on our manuscript "A simple method for air/sea gas exchange measurement in mesocosms and its application in carbon budgeting". Corrections and amendments as suggested by the referee helped to improve the quality of the manuscript substantially.

General comments:

Remark by referee #2: The sensitivities of the methods towards changes in these parameters, however, are seldom stated and an estimation of the uncertainty of the method (not only stating the uncertainties of single measurements, constants etc. but

estimating their combined effect & the propagation of uncertainty; cf. NIST technical note 1297) is missing.

Author's response: We will restructure the manuscript and combine discussed pitfalls and uncertainties into one paragraph. Calculation of one combined effect of uncertainties in all single measurements in the form of a propagation of uncertainty according to NIST technical note 1297 is difficult due to inhomogeneous weighting of uncertainties at different N2O and CO2 gradients or different temperature ranges. Instead of denoted uncertainties of instruments or measurement techniques (e.g. the pt100 thermometer) temporal and special data coverage is problematic in mesocosm experiments (e.g. temperature changes during times between measurements or along vertical or horizontal gradients). An estimate of combined uncertainty would be only applicable to this specific dataset and not of great value to the user of the method. Instead of error propagation we calculated sensitivities of the overall results towards uncertainties in the determination of single components of the presented method. A table with sensitivities will be presented and sensible variables will be highlighted so that the user can optimise his measurement protocol to achieve best results.

Specific comments:

Remark by referee #2: P11991 L1-2: Double use of word 'experimental'. L10: Please change the sentence in a way that it does not start with the word 'but'. L25: Rewrite: 'To directly estimate: : :' .

Author's response: The respective sentences will be rephrased.

Remark by referee #2: P11992 L11-15: The authors state that most equations for air/sea gas exchange are not suitable, and they highlight the work of Smith et al. (1985), who were the only ones that provided an equation that makes sense when wind speed = 0. In the following, Czerny and co-workers argue against this paper as the assumed absence of turbulence is not realistic when dealing with mesocosms in which all the other physical phenomena (convection etc.) lead to turbulence compara-

ble to ‘quite windy conditions (L17)’.Please clarify this ambivalence.

Author’s response:As discussed, gas exchange is not zero at zero wind speed. Other energy inputs than wind might be negligible for gas exchange on a global scale. We will clarify that wind dependent parameterisations by Smith at al. (1985) are not suitable for calculating gas exchange at zero wind speed as they lack alternative energy inputs.

Remark by referee #2: L23-24: Is N2O biologically inert? How large do the authors estimate the risk of biasing the results of the mesocosms by adding precursors of reactive nitrogen species (RNS)? Concentrations of _50 nM may not be negligible for biological responses?

Author’s response: N2O is not biologically inert. It is an intermediate product of suboxic denitrification. It is also a side product of aerobe nitrification at low oxygen conditions. Oxygen levels in pelagic mesocosm experiments are generally high, rather above than below atmospheric equilibrium concentrations. N2O in the ocean is generally oversaturated or close to equilibrium with the atmosphere. Our concern was therefore more directed towards biological production of N2O. A consumption by denitrifies occurs at suboxic oxygen levels below $\sim$10μmol kg-1, wherein N2O is converted to N2. There is no indication that N2O can be utilised as a source for reactive nitrogen by primary producers..In the three analysed experiments (Svalbard/Spitzbergen, Bergen/Norway and Hawaii) changes in N2O concentrations pointing towards biological production or uptake were not observed in the untreated mesocosms or the surrounding.

Remark by referee #2: P11993 L2: Replace ‘covert’ by covered’.

Author’s response: Will be replaced

Remark by referee #2: P11994 L9: How can a sample be drawn that represents the whole 15m water column? Please describe in more detail. Was the water sucked in while the inlet moved vertically through the water column? How was equal sampling ensured?

Author’s response: “Equal amounts of sample are sucked into the sampling bottle at each depth between 0 and 12 m, electronically controlled via hydrostatic pressure sensors. These integrated water samples were assumed to be representative for the 15 m deep water column.” We will include a sentence explaining this principle.

Remark by referee #2: L22-23: Double use of ‘equilibration’, I suggest to delete the second one.

Author’s response: Deleted

Remark by referee #2: L24: The mixing ratios of the certified references seem very, very precise (1002 ppb). What is their uncertainty? What is the estimated uncertainty of the calibration factors obtained with these mixtures and how large may be the resulting possible offset in the finally determined N2O content?

Author’s response: Certified precision of the reference material is $\pm$0.2 ppb calibrated against NOAA standards by the MPI for atmospheric chemistry in Mainz/Germany. Overall uncertainty of N2O analyses following this protocol is specified to be 1.8%. However, variability of, in particular, the strongly oversaturated samples in our dataset seems to be considerably higher. We will include denoted uncertainties citing Walter et al. (2006) who developed the measurement protocol using the same setup in our laboratory.

Remark by referee #2: P11995 L5: ‘DIC’ is not introduced. I assume it refers to ‘dissolved inorganic carbon’, which was earlier abbreviated as ‘CT’. Please make abbreviation consistent.

Author’s response: Will be consistently “CT”.

Remark by referee #2: L14ff: I think it would help the reader’s understanding if you’d move the section 2.4. to the beginning of the methods chapter. This would clarify more strongly in which system the N2O is introduced.

Author’s response: Will be moved accordingly in the revised manuscript.

Remark by referee #2: P11996 L3: Please specify the distance to Zeppelin Mountain. Is this distance negligible in terms of changes in wind speed, direction etc.?

Author's response: The distance is, with about 4.5 km, negligible. Atmospheric concentrations of N2O are rather constant on a large spatial and temporal scale. CO2 concentrations are much more variable on a seasonal scale and can be locally influenced, especially by anthropogenic sources. Atmospheric CO2 is rarely influenced by biological or anthropogenic sources on Svalbard. A steady decrease by 7 μatm during the duration of the experiment can be attributed to summer uptake in more productive areas of the northern hemisphere. We will specify the distance to Zeppelin Mountain.

Remark by referee #2: L16: Article should be 'an' instead of 'a': 'An N2O transfer velocity: : :'.

Author's response: Will be changed accordingly.

Remark by referee #2: Equation 4: The N2O concentrations of bulk water and the N2O equilibrium concentrations are used to express the mismatch of N2O concentrations. It seems that this approach implicitly assumes perfect mixing and homogenous distribution of N2O molecules throughout the mesocosm and does not take into account any delayed resupply of N2O from deeper parts due to stratification of the enclosed volume. Is this simplification valid? The discussion of this issue (later in the ms) may either be moved here or it may at least be indicated that a discussion on this is coming up.

Author's response: We will introduce this issue here and will include a further discussion along with other uncertainties.

Remark by referee #2: P11997 L 16-17: The chemical enhancement of air/sea gas exchange is (in the case of CO2) dependent on the pH. Isn0t it a circular argument to first manipulate seawater chemistry, then assess the carbonate system, and then do an air/sea exchange correction using previously determined parameters of the carbonate

system that are known to be (at least) not perfectly true? How large are the uncertainties we are talking about here? In other words, can it happen that one determines pCO2 in a mesocosm (e.g. 453 atm) and the uncertainty of that measurement (+/- 10 _atm) is as large as the absolute correction that is derived from it after applying the equation 7?

Author's response: We did not correct measured CO2 concentrations using gas exchange estimates. It is therefore no circular argument. Our aim is to detect biologically derived changes in inorganic carbon by subtracting gas exchange from overall measured CT changes. Corrections for chemical enhancement are correcting estimated fluxes towards higher values. An aquatic pCO2 of 453 μatm would cause a low efflux into the ($\sim$395μatm) atmosphere. As the difference to the atmosphere is with $\sim$60μatm quite low, measurement uncertainty of $\pm$10μatm (realistically $\sim\pm$5μatm) would translate to $\sim$30% uncertainty in calculated fluxes. However, overall fluxes of $\sim$1μmol kg-1 within one week would be hardly relevant in comparison to biologically derived fluxes. Chemical enhancement would increase this gas exchange estimate by a fixed percentile, depending on T and pH. Enhancement correction in this dataset of about 5-7% was rather irrelevant, especially in the close to atmosphere treatments.

Remark by referee #2: P11998 L7-11: The authors refer to reactions two and three in Johnson (1982). Please clarify what this means and make this passage comprehensive without the need to look up details in Johnson (1982).

Author's response: We will specify the reactions and restructure this paragraph.

Remark by referee #2: L20-25: Many references are given here, please sort them chronologically.

Author's response: References will be sorted.

Remark by referee #2: P11999 L9: Please combine the two brackets into a single one.

Author's response: We cannot find these brackets.

Remark by referee #2: L 8 -11: Here the authors discuss a bit the sensitivity of the approach and state that T has a larger influence on the enhancement factor than e.g., differences in pH treatment. This comparison of the temperature-effect with the pH-effect is very interesting and helps readers to assess which parameters have major and minor influence on this system. Please also make some statements on the effects of pH, temperature and salinity on the finally calculated corrective values, which are added or subtracted from the calculated carbonate system parameters. Such indications of sensitivity are of major importance for experimentalists as they allow judging the overall profit of the correction method.

Author's response: As mentioned before in general comments, we will include a table with estimates of effects of uncertainties in single measurement parameters on overall calculated CO2 fluxes. (e.g. uncertainties of $\pm 1^{\circ}$C in temperature, ± 1 nmol N2O, 1% of mesocosm volume, 1% in surface area between mesocosms within one experiment.) We will also give a range of cumulative uncertainties in calculated fluxes during the Svalbard experiment, based on approximated uncertainty in above mentioned variables.

Remark by referee #2: P12000 L 5-20: This is interesting information that could a) be extended by the discussion on biological (non-) inertia of N2O and b) would as well fit into the introduction part of the manuscript. It is furthermore unclear how the permeability estimates were developed; please describe this in more detail. Also, some quantification for "considerably higher permeability" (L17) is missing.

Author's response: An equation for the calculation of lateral gas fluxes through the bag material will be given in the revised manuscript. Potential biological production / (non-) inertia will be briefly mentioned in the introduction and extended later in the manuscript. The permeability issue /correction will be extended.

Remark by referee #2: L17: Should read ': : : too low to bias: : :'.

Author's response: Will be changed

Remark by referee #2: L23 –L4 on P12001: Here you elaborate on the gas-exchange when no convection is happening. This consideration might be placed into the methods section, where respective questions have already come up (see according comment). This part is missing a quantification of the differences in wind speed between natural environments and the mesocosms.

Author's response: We will combine paragraphs discussing mixing in mesocosms. Direct wind speed measurements inside the mesocosms were not performed. Due to the 2 m high free board of the mesocosms, wind stress on the water surface can be assumed to be hardly detectable. Apparent wind speed calculated from gas exchange in the mesocosms is about one m s-1 lower compared to measured wind speed on the experimental site. Fitted N2O measurements do not indicate a dependence of gas exchange on wind speed.

Remark by referee #2:P12001 L10: The raw material is referenced as Walopur®, but it cannot be seen what Desmopan® shall mean. Sort out grammar here: 'Estimates for _parameter_ based on_method_ revealed: : :'.

Author's response: Desmopan® is the material Walopur® foils are made of. As there are no permeability measurements for CO2 and N2O published for Walopur®, Desmopan® data were used. We will clarify this.

Remark by referee #2: P12002 L13: Replace 'wind depended' with 'wind-dependent'.

Author's response: Will be replaced.

Remark by referee #2: L13ff: The section on mesocosm proportions is very comprehensive and also bears some interesting and important implications, like 'surface:volume ratio and atmospheric re-equilibration matter much more than waves and cosm-material..'. These statements could be conveyed more clearly and strongly.

Author's response: We will include a respective statement in the conclusion part.

Remark by referee #2: L19: Are you referring to 'enhanced surface renewal' along the air-sea interface or in relation to the surface of the mesocosm material?

Author's response: Along the air-sea surface. We will clarify this. Exchange through the mesocosm material is orders of magnitude slower so that a relevant concentration gradient cannot form even in a low mixing regime.

Remark by referee #2: P12003 L20-24: It is not completely clear under which circumstances these different approaches were tested. Please specify here (not only in the figure legend).

Author's response: We will include a description of the setup.

Remark by referee #2: L26: Reformulate the sentence beginning with "Detailed data on : : :".

Author's response: The sentence will be reformulated.

Remark by referee #2: P12004 L8-10: This sentence is unclearly written. Please specify what you mean here to make the sentence more comprehensive.

Author's response: The sentence is not necessary as the issue is discussed in the following sentences. We will erase it.

Remark by referee #2: L25: Please replace 'week' with 'weak'.

Author's response: Will be replaced.

Remark by referee #2: P12005 L 11: Please put a comma behind 'oxygen'.

Author's response: A comma will be included in the revised version of the manuscript.

Remark by referee #2: L12: more precise: 'surface layer net community primary production', or use abbreviation introduced before.

Author's response: We will replace it by "mesocosm NCP".

Remark by referee #2: F1: Firstly, please specify the characteristics (e.g. height) of the waves. Secondly, the drawing of the mesocosm should be larger to convey more information.

Author's response: We will change figure and legend accordingly.

Remark by referee #2: F2: Instead of the standard deviation of the N2O measurements, it would be much more informative to show some kind of estimate of the overall uncertainty.

Author's response: We agree with the referee's opinion that standard deviation around the fit is not a good basis for estimating overall uncertainties in calculated fluxes. We will include a more realistic estimate of overall uncertainty of fluxes based on calculated sensitivities and approximated uncertainties in major components of the method.

Interactive comment on Biogeosciences Discuss., 9, 11989, 2012.