

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.

Anonymous Referee #2

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Czerny and colleagues present a straightforward method to quantify the air/sea gas exchange in mesocosm experiments. The method is based on the introduction of known amounts of N₂O into mesocosms and a continuous monitoring of the outgassing of the compound. Assessed gas exchange velocities are then (based on literature data) used to calculate fluxes of CO₂ with maximally reachable precision. This will benefit the quality of field and lab experiments that make use of mesocosms. The paper is well written and it comprehensively conveys the rationale behind the approach. The authors have made great effort to be very exact and to include a maximal number of side-parameters into their considerations. The sensitivities of the methods towards changes in these parameters, however, are seldom stated and an estimation of the

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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. In my opinion this is the only real shortcoming of this manuscript. In the comments, some passages are pointed out that can be optimized with respect to orthography, plausibility and information content, especially regarding quantitative statements of the method's sensitivity to the parameters that are put in. After the authors have approached or rebutted these minor criticisms and questions, the paper is certainly suited for publication in Biogeosciences.

Specific comments: 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...'. .

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 comparable to 'quite windy conditions (L17)'. Please clarify this ambivalence. 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?

P11993 L2: Replace 'covert' by covered'.

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? L22-23 Double use of 'equilibration', I suggest to delete the second one. L24: The mixing ratios of the certified references seem very, very precise (1002 ppb). What is their uncertainty? What is the

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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?

P11995 L5: 'DIC' is not introduced. I assume it refers to 'dissolved inorganic carbon', which was earlier abbreviated as 'CT'. Please make abbreviation consistent. 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.

P11996 L3: Please specify the distance to Zeppelin Mountain. Is this distance negligible in terms of changes in wind speed, direction etc.? L16: Article should be 'an' instead of 'a': 'An N₂O transfer velocity...'. 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.

P11997 L 16-17: The chemical enhancement of air/sea gas exchange is (in the case of CO₂) dependent on the pH. Isn't 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 μ atm) and the uncertainty of that measurement (+/- 10 μ atm) is as large as the absolute correction that is derived from it after applying the equation 7?

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

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look up details in Johnson (1982). L20-25: Many references are given here, please sort them chronologically.

P11999 L9: Please combine the two brackets into a single one. 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.

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. L17: Should read '... too low to bias...'. 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.

P12001 L10: The raw material is referenced as Walopor[®], but it cannot be seen what Desmopan[®] shall mean. Sort out grammar here: 'Estimates for °parameter° based on °method° revealed...'.
°method° revealed...'

P12002 L13: Replace 'wind depended' with 'wind-dependent'. 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 mat-

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ter much more than waves and cosm-material..'. These statements could be conveyed more clearly and strongly. L19: Are you referring to 'enhanced surface renewal' along the air-sea interface or in relation to the surface of the mesocosm material?

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). L26: Reformulate the sentence beginning with "Detailed data on ...".

P12004 L8-10: This sentence is unclearly written. Please specify what you mean here to make the sentence more comprehensive. L25: Please replace 'week' with 'weak'.

P12005 L 11: Please put a comma behind 'oxygen'. L12: more precise: 'surface layer net community primary production', or use abbreviation introduced before.

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. 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.

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