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Biogeosciences
Discussions

Interactive comment on "High-resolution measurements of atmospheric molecular hydrogen and its isotopic composition at the West African coast of Mauritania" *by* S. Walter et al.

S. Walter et al.

s.walter@uu.nl

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Reply editor and reviewers

Dear Editor, dear reviewers,

Thanks for your critical and helpful comments and ideas, which helped to improve the quality of the manuscript. Please find our reply to them in a point–by–point discussion below.

Referee 1:

General comments In view of the role of hydrogen (H2) as potential new energy source,

there is an increasing interest to identify its natural formation and consumption pathways as well as to quantify the atmospheric budget of H2. Walter et al report a new data set of atmospheric H2 and its isotope signature in the atmospheric boundary layer over the eastern tropical N Atlantic (ETNA). Measurements from two cruises are presented. The ms is well written and the results are well presented and discussed. The conclusions are justified by the presented results. Therefore I recommend publication with a few minor corrections.

Specific comments 1) Overwhelming (and necessary) information about H2 is presented in the introduction. In order to clarify the major points I suggest a re-organization of the introduction along the following outline: - atmospheric chemistry/new energy source, - global budget (please give an estimate about the oceanic contribution, in %, to the atm. H2 budget), - oceanic pathways, - isotope signatures of H2, - major aims of the ms.

Reply: We agree that this order will help to clarify the major aims of the manuscript and will change it to the suggested one.

2) Please compile the information about the hydrographic and biological settings of the ETNA in a separate section (e.g. study area description)

Reply: We agree that the information about the hydrographic and biological settings better fit in a study area description and will shift them.

3) I can see that for the 2008 cruise measurements of marker pigments do exist. However, I am wondering if a similar set of data exists for the 2007 cruise? This is especially important to assess whether the two upwelling events encountered may have had different biological settings (c.f. interannual variability?).

Reply: For the cruise in 2007 marker pigments for phytoplankton distribution were measured and we got them by personal communication. The marker pigment data give the typical distribution of phytoplankton species with dominating diatoms in the upwelling region and cyanobacteria in the more open ocean waters as described for 2008 by Zindler et al. (2012). To our knowledge, the data of 2007 are not published or further validated, thus we have not taken them into account.

4) I am wondering whether the measurements of atmos. compounds such as CO, CH4, NMHC or OVOCS (incl. acetaldehyde) could be used to get additional information for the atmos. H2 distribution. These data are measured at the Cape Verde Atmos. Observatory, CVAO; data are available from http://www.ncas.ac.uk/index.php/en/cvaohome.

Reply: We compared our high–resolution data with the CH4 data of POS348 (published by Kock et al. 2008 and personal communication). The distribution of atmospheric and dissolved CH4 is similar to the atmospheric H2 data, and, although the water column is supersaturated, emissions from surface waters are not sufficient to explain the full increase of atmospheric CH4 mixing ratios. Therefore, the authors assume a possible contribution of the Banc d′Arguin. We will include this feature in the revised version. For the other gases we haven′t noticed relevant changes during these days, but will carefully check again.

Referee 2:

The manuscript describes results of H2 mixing ratios and stable isotopes from two expeditions off the coast of Mauretania. The authors are trying to explain their observations and to derive the source and sink patterns for the H2 in this region.

Major Issues: The aim of this study was to identify areas of H2 production [in the ocean] and to distinguish them by isotope analysis, in particular the source from N2 fixation (p. 18800, l. 11, p. 18003, l 24ff, p. 188004, l. 11ff). Considering this aim it is absolutely unclear as to why this analysis was not conducted on water samples, by profiling and lateral sampling and analysis of dissolved H2. With at least a few measurements of dissolved H2 from surface water samples, many of these questions and vague statements could have been very clearly and presumably undoubtely answered. Combined surface water and atmospheric sample analysis for both H2 concentrations and isotopes

should have been the campaign design of choice for the scientific questions addressed in this project. The authors don't even know if H2 in the surface waters of their study area was supersatured, or maybe at equilibrium or undersaturated! With the aims of the project as currently stated in this paper, the approach taken to investigate these appear to be inadequate, unless there is something the reader doesn't know such as e.g. measurements of H2 in the water columns are not possible to make with the current technology. But then, there is published H2 water column work that dates many years back, so this could not have been a show stopper. I strongly advice to find justifications other than investigation of oceanic H2 production for the discussion of these measurements. Nevertheless the data set as presented in this manuscript may still be worth to disseminate but not under the scientific questions as they are currently put forward. The figures are of very poor resolution and the legends are not readable without a lot of figure processing tricks. This is also something that should have been detected during the first screening by Copernicus and is an affront to the reviewers. Figures need improvement such that all parts are easily readable also without magnifying glasses.

Reply: The major aim of this study was the detection and identification of H2 sources to the atmospheric budget by using primarily atmospheric samples. We agree with the referee that the combination of atmospheric samples and headspace samples of surface waters for isotopic analysis would be the experimental design of choice. The analysis of H2 isotopes at atmospheric mixing ratios is a challenge, even more on oceanic headspace samples. To our knowledge a protocol on surface water isotope measurements does not exist. Rice et al. (2010, and personal communication) mentioned two data points from the ALOHA station, but the experimental setup of these data is not published yet. We tried to establish such a protocol to get additional information, but failed for 2007. Only for 2008 a few results are available, however, still with some question marks. Thus, they were not taken into account for this publication. A measurement system for only dissolved mixing ratios, e.g. a RGA was not available at that time. We therefore focussed on an area with expected H2 emissions from the ocean. We know from previous studies, that: âĂć the tropical surface waters are in general supersaturated with H2 âĂć the production pathway for H2 in the ocean is mainly biological, with potentially some minor contributions of photochemical production âĂć the isotopic signature of biologically produced H2 in thermodynamic equilibrium with water is approximately –700‰ independent of the biological pathway itself (Bottinga 1969, Walter et al. 2012) âĂć fractionation between the phases is, estimated according to Muccitelli and Wen (1978) or Knox et al. (1992), around 3 to 4 % and therefore will not change the overall picture of released biologically produced hydrogen with its exceptionally low δD values compared to atmospheric H2

Based on these assumptions, we assume that if H2 from this oceanic region is released to the atmosphere in measurable amounts, it would show highly depleted isotopic compositions close to the values of a biological production pathway. Thus while we agree that a combination of atmospheric and water data would be desirable, we do not agree with the referee that the approach is inadequate without the information from the surface water data. While we were unsuccessful in providing these data, our experimental approach includes isotope analysis of the atmospheric samples, which has never been performed in this region before. We will state the aim and intention of the study more clearly regarding to this, but we see no need to change it in general.

Minor Issues: p. 18800, l.1 The sentence is structured a little unfortunate and very difficult to understand. It could be improved by replacing 'besides' by 'followed by'. Also, how solid is that very first statement that oceans are a net source. Concluding from p 18802 l. 21ff, the scientific evidence for that seems to still be moderate. Reply: The sentence will be rearranged to make it clearer. Regarding the statement, that oceans are a net source: The scientific evidence is based on several global bottom–up studies, which all indicate the oceans, especially the tropical ones as a net source (see detailed review by Ehhalt and Rohrer, 2009, and references herein). This is generally accepted in the atmospheric community. However, due to a general lack of H2 measurements and uncertainties regarding the production processes, e.g. N2 fixation, we see the need for more detailed investigations.

p. 18800, l. 23: suggest to replace 'just' by 'only'. Reply: changed

p. 18800, l. 27: define 'VOC' Reply: changed

p. 18802, l. 23: change 'Deuterium' to 'deuterium'syringic Reply: changed

p. 18802, l. 10ff: Some of these terms need explanation, e.g. Pi Reply: changed

p. 18802, l. 28: Undersaturation probably means that there is a sink of H2 in the water, either in-situ or during advection of the water from where it was last in contact with the atmosphere. Can you, for completeness, mention the sink processes that lead to this undersaturation. Reply: The sink processes have not been investigated in detail yet, but advection / mixing processes are assumed to be the most probable reason. It will be mentioned.

p. 18803, l. 27: Maybe the authors want to say 'off' instead of 'of'. Reply: changed

p. 18803, l. 27: Mention the expedition names here too. Reply: changed

p. 18804, l. 10: It is mentioned that Trichodesmium is a dominant in the oligotrophic waters in the study area but P. 18803 states that Trichodesmium is mostly restricted to warm (>22 C) waters. SST (see Table 1) seems to be well below 20C, so this appears to be a contradiction. Reply: no contradiction, Trichodesmium is dominant in the oligotrophic open waters west of 18°W, the data in table 1 are belonging to stations east of 18°W, towards the coast in the upwelling region.

p. 18804, l. 8: Zindler et al.: Clarify if this was found during the same expedition as where the H2 results derive from. Reply: it was, will be clarified

p. 18804, l. 16: Clarify if this is in the atmosphere or in the ocean, e.g. by ' .... diel cycle in surface water' (if true). Check if 'dial' is the correct word, might be 'diel'. Reply: see p. 18804, l.15, dial has been changed to diurnal

p. 18804, l. 23 'concluded': who concluded, Bullister et al., or Setser et al.? Reply: Setser et al. concluded

p. 18804, l. 26: Define CDOM if not already done earlier. In general, check all abbreviations and define them when first used. Reply: see p. 18802, l.18

p. 18805, l. 3: Confusingly enough, the authors here state that water samples were taken, but maybe not for H2 analysis. Again given that this expedition had an oceanographic water component, it appears inexcusable to not have measured dissolved H2. State what air and water samples were measured for during these expeditions. Reply: For the above-mentioned reasons we do not agree with the referee that the lack of surface water measurements is “inexcusable”. We apologize for the confusion by using the term “water samples”, it remained from a former version and has been removed.

p. 18805, l. 11: Suggest to change ’were conditioned’ to ’were previously conditioned’. Reply: changed

p. 18805, l. 22: Suggest to change ’The mixing ratio’ to ’The atmospheric mixing ratio’. Also, change ’was’ to ’were’. Reply: changed

p. 18805, l. 24: Suggest to change ’The measurements consist briefly’ to ’Briefly, the measurements consist’. Reply: changed

p. 18805, l. 26: Suggest to change ’helium cooled’ to ’helium-cooled’. Reply: changed

p. 18806, l. 3: Suggest to change ’1/8" ’ to ’1/8" OD’. Reply: changed

p. 18806, l. 14: Change ’MPI2009’ to ’MPI-2009’. Reply: changed

p. 18807, l. 6: Change ’oceanographically’ to ’oceanographic’. Reply: changed

p. 18807, l. 23: Remove ’approximately’, I presume the mean was exactly 545 ppb when rounded to 3 significant figures. Reply: changed

p. 18808, l. 13: What is an ’upwelling signal’, and was the ’weaker’ solely based on temperature arguments? Reply: the upwelling is indeed characterized by the surface temperature, will be stated more clearly

p. 18808, l. 15: According to e.g. Moore et al., 2009, a sink of H2 is co-located with the biological source, so how can one assume that the resulting signal has the typical biological -700 permil? The entire argumentation on l. 16 ff is based on the assumption that the net N2-fixation derived signal is at -700 permil. It is also assuming that there is no fractionation during air-sea gas exchange/transfer. There is a lot of arm-waving here, I suggest to rephrase more cautionary, as again, not a single surface water measurement is available to back up any of these conclusions. The authors don’t even know at what equilibrium state the H2 in water/air is at that time. Also, can the authors exclude a mixture of a biogenic production and photochemical abiotic production that would give a somewhat ’mixed’ isotope signal âĂŤ I really couldn’t follow as to why that option can be excluded. Reply: We will rephrase this part more cautionary with respect to the following arguments: – Biogas experiments, which confirmed the depleted values for biologically produced H2 were also done in aqueous–gas systems, and uptake/recycling could also not be excluded there. The value of app. –700% is thus reasonable. – fractionation between the phases is possible and probable (Knox et al. 1992, Mucitelli and Wen 1978, Vignais 2005), but would result in less than 2‰ thus in the range of measurement uncertainties. We will include this in the discussion. – a contribution of photochemical sources and thus a mixed signal would be possible, and we will discuss this option. Due to the expected (based on models) isotopic signature we would not be able to distinguish here between the two possibilities: starting from the coast with lower mixing ratios due to the soil sink from the African continent and increase the mixing ratio by mixing with remote air, or release of precursors and photochemical production towards the open ocean. However, an enhanced production of precursors would rather be expected in the more biologically active upwelling areas towards the coast. Beside this, the hypothesis of reduced values due to a soil sink is supported by an α = 0.89 for this 18°N transect.

p. 18810, l. 14: m2 should probably be m-2. Reply: corrected

p. 18810, l. 19: Suggest to replace ’mean mixed layer’ to ’mean atmospheric mixed layer'. Reply: changed

p. 18811, l. 1: Change 'would probably visible' to 'would probably be visible'. Reply: changed

p. 18811, l. 22: The term 'negative estuary' is not very commonly used, a brief definition would help. Reply: included

p. 18812, l. 23ff: Would a plot of dD vs 1/H2 (Keeling plot) help support these findings? Reply: We tested the data with both Keeling plots and Rayleigh plots, and they support our findings.

p. 18819, l. 8, and l. 11. subscript the '2' in H2. Check entire reference list. Reply: changed

p. 18823, Table 1. Mention in the caption what expedition this was, what year etc. Reply: included

p. 18824, Figure 1. As with all figures, see major comment of figures. Here, explain, what black dots mean. Reply: we will improve the quality of the figures, black dots will be explained

p. 18825, Fig. 2: First, clearly state, which of the correlations and fits are considered statistically significant. Include the measurement uncertainty in this figure, e.g. as vertical bars (1 or 2 sigma). In the caption, state if the intense day sampling results are included here also. If not, why are they not included? In this figure it would help to include the 'background' H2 at that time and at that latitude so the reader can compare it with the present results. Can the background H2 be taken from other resources/ publications, maybe extrapolated? Is the background ratehr near 540 ppb or 520 ppb, or has it changed between the years of the expeditions? Reply: we will include the standard deviation and the background H2 mixing ratio for the Cape Verde in the figure. The high resolution days are not included, because they are not laying on the 18°N transect

p. 18826, Fig. 3. Nearly impossible to recognize anything on this figure. Provide lat/lon as x and y axes. Reply: the figure will be improved

p. 18828, Fig. 4: If these are the high-resolution results, then say so. It is unclear why Schlitzer et al., 2012 are cited here, it implies that the listed correlations are from this source. Reply: explanation will be included in Fig. 5, correlations are indeed done with the programme "ODV", developed by Schlitzer, 2012.

p. 18829, Fig 6: Is this figure necessary, what is its added value? Could it be combined with Fig. 1? Reply: the added value is a better visualization of the Banc d′Arguin and the biological activity of this area. We will try to combine it with Fig. 1.

Interactive comment on Biogeosciences Discuss., 9, 18799, 2012.