

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.

Anonymous Referee #2

Received and published: 11 February 2013

BGD, doi:10.5194/bgd-9-18799/2012

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

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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 undoubtedly 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 supersaturated, 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.

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.

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

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

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- p. 18802, l. 23: change 'Deuterium' to 'deuterium'syringic
- p. 18802, l. 10ff: Some of these terms need explanation, e.g. Pi
- 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.
- p. 18803, l. 27: Maybe the authors want to say 'off' instead of 'of'.
- p. 18803, l. 27: Mention the expedition names here too.
- 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.
- p. 18804, l. 8: Zindler et al.: Clarify if this was found during the same expedition as where the H₂ results derive from.
- 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'.
- p. 18804, l. 23 'concluded': who concluded, Bullister et al., or Setser et al.?
- p. 18804, l. 26: Define CDOM if not already done earlier. In general, check all abbreviations and define them when first used.
- 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.
- p. 18805, l. 11: Suggest to change 'were conditioned' to 'were previously conditioned'.

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- p. 18805, l. 22: Suggest to change 'The mixing ratio' to 'The atmospheric mixing ratio'. Also, change 'was' to 'were'.
- p. 18805, l. 24: Suggest to change 'The measurements consist briefly' to 'Briefly, the measurements consist'.
- p. 18805, l. 26: Suggest to change 'helium cooled' to 'helium-cooled'.
- p. 18806, l. 3: Suggest to change '1/8" ' to '1/8" OD'.
- p. 18806, l. 14: Change 'MPI2009' to 'MPI-2009'.
- p. 18807, l. 6: Change 'oceanographically' to 'oceanographic'.
- p. 18807, l. 23: Remove 'approximately', I presume the mean was exactly 545 ppb when rounded to 3 significant figures.
- p. 18808, l. 13: What is an 'upwelling signal', and was the 'weaker' solely based on temperature arguments?
- 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 — I really couldn't follow as to why that option can be excluded.
- p. 18810, l. 14: m₂ should probably be m⁻².
- p. 18810, l. 19: Suggest to replace 'mean mixed layer' to 'mean atmospheric mixed

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layer'.

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

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

p. 18812, l. 23ff: Would a plot of dD vs 1/H₂ (Keeling plot) help support these findings?

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

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

p. 18824, Figure 1. As with all figures, see major comment of figures. Here, explain, what black dots mean.

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?

p. 18826, Fig. 3. Nearly impossible to recognize anything on this figure. Provide lat/lon as x and y axes.

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.

p. 18829, Fig 6: Is this figure necessary, what is its added value? Could it be combined with Fig. 1?

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

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