

Isotopic evidence for biogenic H<sub>2</sub> production in the Atlantic Ocean

S. Walter et al.

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# Isotopic evidence for biogenic molecular hydrogen production in the Atlantic Ocean

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## Abstract

Oceans are a net source of molecular hydrogen ( $H_2$ ) to the atmosphere. The production of marine  $H_2$  is assumed to be mainly biological by  $N_2$  fixation, but photochemical pathways are also discussed. We present measurements of mole fraction and isotopic composition of dissolved and atmospheric  $H_2$  from the southern and northern Atlantic between 2008 and 2010. In total almost 400 samples were taken during five cruises along a transect between Punta Arenas (Chile) and Bremerhaven (Germany), as well as at the coast of Mauretania.

The isotopic source signatures of dissolved  $H_2$  extracted from surface water are highly deuterium-depleted and correlate negatively with temperature, showing  $\delta D$  values of  $(-629 \pm 54)$  ‰ for water temperatures at  $(27 \pm 3)$  °C and  $(-249 \pm 88)$  ‰ below  $(19 \pm 1)$  °C. The results for warmer water masses are consistent with biological production of  $H_2$ . This is the first time that marine  $H_2$  excess has been directly attributed to biological production by isotope measurements. However, the isotope values obtained in the colder water masses indicate that beside possible biological production a significant different source should be considered.

The atmospheric measurements show distinct differences between both hemispheres as well as between seasons. Results from the global chemistry transport model TM5 reproduce the measured  $H_2$  mole fractions and isotopic composition well. The climatological global oceanic emissions from the GEMS database are in line with our data and previously published flux calculations. The good agreement between measurements and model results demonstrates that both the magnitude and the isotopic signature of the main components of the marine  $H_2$  cycle are in general adequately represented in current atmospheric models despite a proposed source different from biological production or a substantial underestimation of nitrogen fixation by several authors.

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## 1 Introduction

Molecular hydrogen ( $H_2$ ) is the second most abundant reduced compound in the atmosphere after methane ( $CH_4$ ).  $H_2$  is not a radiatively active gas itself, but – via its role in atmospheric chemistry – it indirectly influences the lifetime of the greenhouse gas  $CH_4$  and several air pollutants (Prather, 2003; Schultz et al., 2003; Tromp et al., 2003; Warwick et al., 2004; Jacobson, 2008; Feck et al., 2008; Ehhalt and Rohrer, 2009; Popa et al., 2015). The main  $H_2$  sources are photo-oxidation of  $CH_4$  and non-methane volatile organic compounds (NMVOC) in the atmosphere and combustion processes at the surface, whereas soil deposition and oxidation by hydroxyl radicals ( $HO^\bullet$ ) are the main sinks. Oceans are a minor but significant source to the global  $H_2$  budget with a mean estimated contribution of 7%. However, estimates of the oceanic contribution range from 1 to 15% in different studies, indicating high uncertainties (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002; Ehhalt and Rohrer, 2009, and references herein; Pieterse et al., 2013).

Oceanic  $H_2$  production is assumed to be mainly biological, as a by-product of nitrogen ( $N_2$ ) fixation (e.g. Conrad, 1988; Conrad and Seiler, 1988; Moore et al., 2009, 2014).  $H_2$  is produced during  $N_2$  fixation in equimolar proportions, but also reused as an energy source. The  $H_2$  net production rate during  $N_2$  fixation depends on environmental conditions and also on microbial species (Bothe et al., 1980, 2010; Tamagnini et al., 2007; Wilson et al., 2010a). Besides  $N_2$  fixation, abiotic photochemical production from chromophoric dissolved organic matter (CDOM) and small organic compounds such as acetaldehyde or syringic acid has also been found to be a source of hydrogen in the oceans (Punshon and Moore, 2008a, and references therein).

Unfortunately, measurements that constrain the temporal and spatial patterns of oceanic  $H_2$  emissions to the atmosphere are sparse. Vertical profiles display highest concentrations in the surface layer (up to  $3\text{ nmol L}^{-1}$ ) and a sharp decrease with depth towards undersaturation, where the reasons for the undersaturation are not fully understood yet (e.g. Herr et al., 1981; Scranton et al., 1982; Conrad and Seiler, 1988).











indicate that glass flasks equipped with Kel-F valves are stable for H<sub>2</sub> (Jordan and Steinberg, 2011). The mean measurement repeatability between the two measurements on the same flask was between  $\pm 3.2$  ppb (ANT-XXV/5,  $n = 14$ ) and  $\pm 6.4$  ppb (ANT-XXVI/4,  $n = 108$ ) for the mole fraction and  $\pm 3.4\%$  (ANT-XXVI/4,  $n = 108$ ) and  $\pm 5.0\%$  (ANT-XXV/5,  $n = 14$ ) for the isotopic composition.

H<sub>2</sub> and CO mole fractions were also measured by using a Peak Performer 1 RGA with synthetic air as a carrier gas, either continuously on-board (ANT-XXVI/4, see Sect. 2.4.2) or from discrete flasks in the laboratory (ANT-XXV/5 and ANT-XXVI/1). The discrete RGA measurements were performed from the same glass flasks after measurement of the isotope system (see above). Due to a remaining slight overpressure in the flasks, an active pumping of the air into the RGA was not necessary and the flasks were simply connected to the RGA inlet by Teflon tubing. The remaining pressure was mostly sufficient to perform 8 to 10 measurements. A slight memory effect was observed and thus only the last 5 measurements were taken into account when stable. Samples with only three or less valid measurements were not used for evaluation. The standards were the same as those used for the isotope system. For both cruises (ANT-XXV/5 and ANT-XXVI/1), the mean measurement repeatability was better than  $\pm 0.8\%$  (H<sub>2</sub>) and  $\pm 2\%$  (CO). A comparison between the H<sub>2</sub> mole fractions measured with the Peak Performer 1 RGA and the isotopic experimental setup reveals on average slightly lower RGA values of  $(7.5 \pm 23.8)$  ppb (see Fig. 3).

#### 2.4.2 Atmospheric H<sub>2</sub> measured continuously

For the on-board continuous measurements of H<sub>2</sub> mole fractions a Peak Performer 1 RGA was used. The atmospheric air was drawn from the bridge deck to the laboratory in 1/4 inch Decabon tubing. The CO mole fraction was also measured in the same measurement and will be reported here for information, but without further discussion.

In alternating order, 10 air samples and 10 aliquots of reference air were measured, using synthetic air as carrier gas. Due to small memory effects, only the last 5 measurements of each were taken into account when the values were stable. The mole

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2012) model of the National Oceanic and Atmospheric Administration (NOAA, <http://ready.arl.noaa.gov/HYSPLIT.php>).

## 2.5 Modeling

### 2.5.1 TM5 model

5 We performed simulations of H<sub>2</sub> mole fractions and isotopic composition with the global chemistry transport model TM5 (Krol et al., 2005), and compared them with our measurement data (Fig. 5). The simulation setup was similar to the one of Pieterse et al. (2013) and only a short description is given here. The model version used employs the full hydrogen isotopic scheme from Pieterse et al. (2009) and uses ERA-  
10 Interim meteorological data. The chemistry scheme is based on CBM-4 (Houweling et al., 1998), which has been extended to include the hydrogen isotopic scheme (that is, for all chemical species that include hydrogen atoms, HH and HD are treated separately and have different reaction rates). The H<sub>2</sub> sources and isotopic signatures are given as input; these and also the H<sub>2</sub> soil deposition velocities are identical to Pieterse  
15 et al. (2013).

The model has a relatively coarse spatial resolution of 6° longitude by 4° latitude, and a time step of 45 min. Daily average mole fraction fields are used for comparison to observations. The model results were interpolated to the time and location of the observations.

### 2.5.2 Global oceanic emissions

20 The climatological global oceanic emissions were calculated using the protocol of Pieterse et al. (2013), based on the GEMS database and an assumed mean oceanic H<sub>2</sub> source of 5 Tga<sup>-1</sup> as given from global budget calculations (see Ehhalt and Rohrer, 2009, and references therein, Pieterse et al., 2013). The spatial and temporal variability

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season. With approximately 70 % of landmasses in the NH and higher microbial activity in the summer, the mole fraction during this season is lower in the NH than in the SH. Due to the general preference of organisms for molecules with lighter isotopic composition, the  $\delta D$  values increase during summer in the NH and the interhemispheric gradient becomes less pronounced.

The “winter signal” observed in April is defined by almost equal mole fractions and more pronounced differences in  $\delta D$  values between the hemispheres. In winter, molecular hydrogen is accumulating in the NH hemisphere, and the main source is fossil fuel combustion with a depleted isotopic composition of  $-170$  to  $-270$ ‰ (Gerst and Quay, 2001; Rahn et al., 2002). This leads to nearly equal mole fractions in both hemispheres and a more pronounced  $\delta D$  gradient, with isotopically lighter  $H_2$  in the NH. The contribution of source and sink processes in the SH to the seasonal patterns is less pronounced than for the NH (Pieterse et al., 2011, 2013). As a result, the  $H_2$  seasonal cycle in the SH is much weaker compared to the NH. The SH isotopic  $H_2$  signature is caused by mainly emissions and chemical loss with an isotope delta of approximately  $+190$ ‰, which explains the generally higher  $\delta D$  values. The Intertropical Convergence Zone (ITCZ) separates the two hemispheres and is clearly visible, not only in the  $H_2$  distribution, but also in the CO distribution.

Simulations of  $H_2$  mole fractions and isotopic composition using the global chemistry transport model TM5 (Krol et al., 2005) compared with our atmospheric data reveal that the model simulates the  $H_2$  mole fractions quite well (Fig. 5), with a slight overestimate of up to 20 ppb (which means up to 4 %).

The model results are less variable on small spatial scales, due to the low spatial resolution, and possibly to local influences that are not included in the model (e.g. ocean emissions in the model are less variable in time and space than they could be in reality). The largest differences between the modeled and measured  $H_2$  occur between  $30^\circ$  S and the equator. This seems a systematic feature and could be due to a slight overestimation of sources or underestimation of sinks by the model. Despite these small differences, the model is consistent with measured  $H_2$  mole fractions and

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data points a Keeling plot analysis (Fig. 6b) of the data between 15 and 18° S was made with either 5, 7, or 9 data points to get a reasonable range for the source signature. It reveals a mean source signature of  $-561.5$  in a range of  $-530$  to  $-683$ ‰ ( $n = 7 \pm 2$ ,  $R^2 = 0.85 \pm 0.01$ ). The correlation coefficient is a mean of the three analyses.

HYSPLIT trajectories for the samples collected on this transect during the 28 April and 1 May 2010 (21.8 to 15.7° S) reveal the same origin of air masses coming from the direction of Antarctica. Oceanographic parameters such as water temperature and salinity are similar and do not correlate with  $H_2$  mole fractions and  $\delta D$  values. These findings indicate a strong but local source, and the low  $\delta D$  value for the source obtained by the Keeling plot analysis points to biological production (Walter et al., 2012). Such local and temporal patchiness of high  $H_2$  mole fractions in surface waters was reported previously in correlation to high  $N_2$  fixation rates (Moore et al., 2009, 2014). Although reported for other oceanic regions the  $H_2$  mole fractions and  $\delta D$  values here do neither show a diurnal cycle (Herr et al., 1984) nor they are correlated with radiation indicating photochemical production (Walter et al., 2013), and most of the values were observed during night. Wilson et al. (2013) recently showed that  $H_2$  production and uptake rates clearly depends on microbial species, and also on their individual day–night rhythm, but the contribution of different diazotrophs to the marine  $H_2$  cycle is unknown (e.g. Bothe et al., 2010; Schütz et al., 2004; Wilson et al., 2010a, 2010b; Punshon and Moore, 2008b; Scranton, 1983; Moore et al., 2009).

Around 21.2° S one single sample with a low mole fraction of  $(393.9 \pm 3.2)$  ppb in combination with a high  $\delta D$  of  $(322.45 \pm 5)$ ‰ value was observed. As mentioned before HYSPLIT models reveal the same origin of air masses on this transect, thus this sample indicates probably a local sink. However, this interpretation depends on only one single measurement point and although neither instrumental parameters indicated an outlier nor meteorological or oceanographical parameters differed from other samples, we cannot exclude an artefact due to sampling, storage, or analyses. A simple Rayleigh fractionation model reveals a fractionation factor of  $\alpha = 0.646 \pm 0.002$ , which is close to the value of oxidation by  $HO^\bullet$  ( $\alpha = 0.58 \pm 0.07$ , Batenburg et al., 2011). An

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estimate of the  $\delta D$  value by using an  $HO^\bullet$  oxidation fractionation factor would lead to an increase by 125 or 149‰, respectively. The observed increase of  $\delta D$  seems reasonable when assuming oxidation by  $HO^\bullet$ , but with respect to the  $HO^\bullet$  mole fraction and the slow reaction rate of  $H_2 + HO^\bullet$  it is questionable whether the  $H_2$  decrease here can be explained by this.

### 3.3 Dissolved $H_2$

#### 3.3.1 $H_2$ concentration

In total 16 headspace samples were taken during the RV *Polarstern* cruise in April/May 2010 along the transect 32.53° W / 18.79° S to 13.00° W / 36.54° N and 6 samples during the RV *L'Atalante* cruise in February 2008 between 23.00–17.93° W to 16.9–19.2° N to analyse the  $H_2$  mole fraction and the isotopic composition (see Table 4).

Although our setup was a prototype with possibilities for improvement e.g. by adding a heat control or improved pressure monitoring, the mole fractions are in line with previously published data. The  $H_2$  excess,  $\Delta(H_2)$ , exceeds  $5 \text{ nmol L}^{-1}$ , the saturation differ from close to equilibrium to 15-fold supersaturation. Highest supersaturation was found in the Southern Hemisphere between 16 and 11° S and in the Northern Hemisphere around the Cape Verde islands and the coast of Mauretania (Fig. 7a, Table 4).

Herr et al. (1984) reported patchy enhanced  $H_2$  concentrations in the surface water with up to 5-fold supersaturation in the subtropical south Atlantic (18–31° W and 29–42° W). This is comparable to what Conrad and Seiler (1988) found in the Southern Atlantic, on a similar cruise track as the RV *Polarstern*. Around the equator they measured  $H_2$  surface water concentrations up to 12-fold supersaturation. In the Southern Pacific, Moore et al. (2009) combined  $H_2$  surface water measurements with  $N_2$  fixation measurements. They reported a strong correlation between these parameters, a patchy distribution and a steep maximum of  $H_2$  concentrations up to  $12.6 \text{ nmol L}^{-1}$  around 14° S.

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The recently published data by Moore et al. (2014) show similar patterns across the Atlantic as we found, with highest values around the southern and northern subtropics. However, our saturations are lower than the ones given by them, especially in the Northern Hemisphere. Such differences might be caused by experimental issues such as overestimated extraction efficiency or can be due to real temporal variability as the sampling seasons differed. The extraction efficiency has been estimated as 92 % (see Supplement) and was incorporated into the calculation of the original seawater concentration. With respect to the assumption of biological production as main production pathway it is more likely that due to the different sampling seasons less H<sub>2</sub> was produced in April than in October/November because of less microbial activity especially on the Northern Hemisphere in boreal winter.

### 3.3.2 Isotopic composition of H<sub>2</sub>

Additional information about H<sub>2</sub> sources comes from the analysis of the H<sub>2</sub> isotopic composition. In the literature only one experimental value of dissolved marine  $\delta D$  exists,  $\delta D = -628\text{‰}$  (Price et al., 2007; Rice et al., 2010), but the origin of this value is unclear and it is based on unpublished data. Nevertheless, this value has been used as representative for oceanic emission in several global budget calculations (e.g. Price et al., 2007; Pieterse et al., 2011). Other authors (e.g. Rahn et al., 2003; Rhee et al., 2006) used a theoretical value of  $-700\text{‰}$ , as expected for thermodynamic isotope equilibrium between H<sub>2</sub> and H<sub>2</sub>O based on the calculations of Bottinga (1969). The results presented here are the first well-documented experimental results for isotope analysis of dissolved H<sub>2</sub> in seawater.

From the measurement of the isotopic composition of H<sub>2</sub> in the headspace we calculate the isotopic composition of H<sub>2</sub> that was originally dissolved in the sea water as described in Sect. 2.4.3 and in the Supplement, using two different assumptions for fractionation between dissolved H<sub>2</sub> and H<sub>2</sub> in the gas phase. The results shown in Table 4 reveal  $\delta D$  values for the dissolved H<sub>2</sub> that vary within a wide range of  $-112$  to  $-719\text{‰}$  for both fractionation scenarios. Interestingly,  $\delta D$  shows two distinct groups of



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processes. The isotopic enrichment that is expected for removal of H<sub>2</sub> (Chen et al., 2015; Rahn et al., 2003; Constant et al., 2015) is highly unlikely to cause a shift of almost 400‰ in  $\delta$ D from an assumed pure biological source, because in this case the removed fraction would have to be unrealistically large, as also recently argued for soil emitted H<sub>2</sub> (Chen et al., 2015). We suggest that a source of H<sub>2</sub> must exist in these surface waters, which produces H<sub>2</sub> that is out of isotope equilibrium with the water. This can be either one single source with an isotopic signature of approximately  $-250$ ‰, or an even more isotopically enriched source that mixes with the depleted biological source.

Punshon and Moore (2008a, and references therein), reported abiotic photochemical H<sub>2</sub> production from CDOM and small organic compounds such as acetaldehyde or syringic acid. Walter et al. (2013) indicated, that biologically active regions such as the Banc d'Arguin at the coast of Mauritania could act as a pool of precursors such as VOCs for atmospheric H<sub>2</sub> with high  $\delta$ D values. It is thus possible that abiotic photochemical production in the surface water might be an alternative source of H<sub>2</sub> excess, which is not isotopically equilibrated with water, especially in regions with high radiation and biological activity, and less N<sub>2</sub> fixation. Given the fact that the two groups of warm and cold waters are relatively well separated and there is not a continuous mixing curve between two end members, the explanation of a single different source seems more straightforward. Isotope analyses are a powerful tool to distinguish this source from biological production. Additional measurements are needed to determine the isotopic signature of such a source and investigate to which extend photochemical production contributes to the oceanic H<sub>2</sub> budget in colder water masses, and also update the current models. However, with an isotopic signature of approximately  $-250$ ‰, or an even more isotopically enriched, such a source would not significantly impact the current models.

Based on their H<sub>2</sub> measurements, Moore et al. (2014) suggested a substantial underestimation of oceanic N<sub>2</sub> fixation, especially due to high H<sub>2</sub> supersaturations measured in the Southern Hemisphere. By using direct measurements of N<sub>2</sub> fixation rates

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a systematic underestimation by approximately 60 % was also proposed by Großkopf et al. (2012) who suggested a global marine N<sub>2</sub> fixation rate of  $(177 \pm 8) \text{ Tg Na}^{-1}$ . In order to identify a possible significant mismatch between N<sub>2</sub> fixation rates and total marine H<sub>2</sub> production, we calculated the climatological global oceanic emissions from the GEMS database using the protocol of Pieterse et al. (2013), and an assumed mean oceanic H<sub>2</sub> source of  $5 \text{ Tga}^{-1}$  as given from global budget calculations. The estimated emission rates and distributions in the Atlantic Ocean (Fig. 8) are in line with the calculations of Moore et al. (2014), who reported H<sub>2</sub> sea-to-air fluxes mostly in the range of  $(10 \pm 5) \text{ mmol m}^{-2} \text{ a}^{-1}$  and an almost equal distribution between the hemispheres.

Westberry and Siegel (2006) estimated the global nitrogen fixation rate by *Trichodesmium* blooms by using satellite ocean color data at  $42 \text{ TgNa}^{-1}$  and an additional  $20 \text{ TgNa}^{-1}$  under non-bloom conditions, suggesting that *Trichodesmium* is likely the dominant organism in the global ocean new nitrogen budget. The good agreement between our measurements of H<sub>2</sub> concentrations and  $\delta\text{D}$  and the model results from the TM5 model indicate that the oceanic emissions of H<sub>2</sub> to the atmosphere are actually well represented in current atmospheric models (Pieterse et al., 2013 and references herein). The proposed underestimate of oceanic N<sub>2</sub> fixation and a possible additional H<sub>2</sub> release during this process seems already be incorporated in the current atmospheric budgets of H<sub>2</sub>. Thus, supposing that both an assumed total oceanic H<sub>2</sub> source of  $5 \text{ Tga}^{-1}$  to the atmosphere and a total global nitrogen fixation rate of approximately  $175 \text{ TgN a}^{-1}$  are correct, our calculations clearly support the suggestion of Großkopf et al. (2012) that N<sub>2</sub> fixers other than *Trichodesmium* have been severely underestimated in the global picture and that the oceanic release ratio of H<sub>2</sub> to fixed N<sub>2</sub> clearly needs more attention. Besides *Trichodesmium*, several other N<sub>2</sub>-fixing organisms are known for their potential to produce hydrogen (Wilson et al., 2010a; Falcón et al., 2002, 2004; Zehr et al., 2001; Kars et al., 2009; Barz et al., 2010), and even non-N<sub>2</sub>-fixing organisms might play a role (Lilley et al., 1982).

## 4 Conclusions

Identifying sources is important to consider budgets and gain insight in production and consumption processes. Although H<sub>2</sub> has been assumed reasonably to be produced mainly biologically in the oceans, direct evidence was lacking. Our results verify a biological production as a main source of H<sub>2</sub> in oceanic surface water, especially in warmer water masses. As seen from the transects, local sources are difficult to spot due to their patchiness, this should be taken into account when planning the sampling strategy.

The unexpectedly high  $\delta D$  values in colder temperate water masses indicate the significant influence of processes other than biological production, and additional information e.g. by isotopic composition is needed to distinguish and verify possible sources and supersaturations of dissolved oceanic H<sub>2</sub>. Especially the investigation of the isotopic composition of possible production pathways such as abiotic photochemical H<sub>2</sub> production needs further attention and should be an upcoming issue.

The pattern of mole fractions and isotopic composition of H<sub>2</sub> along a north–south Atlantic transect clearly depends on season and hemisphere and are consistent with previous published data and models. A possible significant underestimation of N<sub>2</sub> fixation as assumed by several authors could – providing a net H<sub>2</sub> release rate – go along with higher H<sub>2</sub> emissions. However, a comparison with the TM5 model and the calculation of the climatological global oceanic emissions based on GEMS database reveal that the oceanic contribution to the global H<sub>2</sub> budget is reasonable and in general reproduced well and therefore a proposed underestimation in the oceanic N<sub>2</sub> fixation seems already be corrected (from atmospheric considerations) in the current atmospheric budgets of H<sub>2</sub>. This also indicates, with respect to the proposed source different than biological production in colder temperate water masses, that such a source would probably not significantly impact the current models.

Besides the isotopic composition of photochemically produced H<sub>2</sub> the composition of N<sub>2</sub> fixer communities and the release ratio of H<sub>2</sub> to N<sub>2</sub> fixed needs more investigation to understand the general processes and distributions of oceanic H<sub>2</sub> in more detail.

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The Supplement related to this article is available online at  
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## References

- Barz, M., Beimgraben, C., Staller, T., Germer, F., Opitz, F., Marquardt, C., Schwarz, C., Gutekunst, K., Vanselow, K. H., Schmitz, R., LaRoche, J., Schulz, R., and Appel, J.: Distribution analysis of hydrogenases in surface waters of marine and freshwater environments, *PLoS ONE*, 5, e13846, doi:10.1371/journal.pone.0013846, 2010.
- Batenburg, A. M., Walter, S., Pieterse, G., Levin, I., Schmidt, M., Jordan, A., Hammer, S., Yver, C., and Röckmann, T.: Temporal and spatial variability of the stable isotopic composition of atmospheric molecular hydrogen: observations at six EUROHYDROS stations, *Atmos. Chem. Phys.*, 11, 6985–6999, doi:10.5194/acp-11-6985-2011, 2011.
- Bothe, H., Neuer, G., Kalbe, I., and Eisbrenner, G.: Electron donors and hydrogenase in nitrogen-fixing microorganisms, in: *Nitrogen Fixation, Annual Proceedings of the Phytochemical Society of Europe*, Nr. 18, Academic Press, London, ISBN 0-12-669450-8, 83–112, 1980.
- Bothe, H., Schmitz, O., Yates, M. G., and Newton, W. E.: Nitrogen fixation and hydrogen metabolism in cyanobacteria, *MMBR*, 74, 529–51, doi:10.1128/MMBR.00033-10, 2010.
- Breitbarth, E., Oschlies, A., and LaRoche, J.: Physiological constraints on the global distribution of *Trichodesmium* – effect of temperature on diazotrophy, *Biogeosciences*, 4, 53–61, doi:10.5194/bg-4-53-2007, 2007.
- Bottinga, Y.: Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite–carbon dioxide–graphite–methane–hydrogen–water vapour, *Geochim. Cosmochim. Ac.*, 33, 49–64, 1969.

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- Hauglustaine, D. A. and Ehhalt, D. H.: A three-dimensional model of molecular hydrogen in the troposphere, *J. Geophys. Res.*, 107, 4330–4346, doi:10.1029/2001JD001156, 2002.
- Herr, F. L.: Dissolved hydrogen in Eurasian Arctic waters, *Tellus*, 36B, 55–66, 1984.
- Herr, F. L., Scranton, M. I., and Barger, W. R.: Dissolved hydrogen in the Norwegian Sea: mesoscale surface variability and deep-water distribution, *Deep-Sea Res.*, 28A, 1001–1016, 1981.
- Herr, F. L., Frank, E. C., Leone, G. M., and Kennicutt, M. C.: Diurnal variability of dissolved molecular hydrogen in the tropical South Atlantic Ocean, *Deep-Sea Res.*, 31, 13–20, 1984.
- Houweling, S., Dentener, F., and Lelieveld, J.: The impact of non-methane hydrocarbon compounds on tropospheric photochemistry, *J. Geophys. Res.*, 103, 10673–10696, doi:10.1029/97JD03582, 1998.
- Jacobson, M. Z.: Effects of wind-powered hydrogen fuel cell vehicles on stratospheric ozone and global climate, *Geophys. Res. Lett.*, 35, L19803, doi:10.1029/2008GL035102, 2008.
- Jacobson, M. Z., Colella, W. G., and Golden, D. M.: Cleaning the air and improving health with hydrogen fuel-cell vehicles, *Science*, 308, 1901–1905, 2005.
- Jordan, A. and Steinberg, B.: Calibration of atmospheric hydrogen measurements, *Atmos. Meas. Tech.*, 4, 509–521, doi:10.5194/amt-4-509-2011, 2011.
- Kars, G., Gündüz, U., Yücel, M., Rakhely, G., Kovacs, K. L., and Eroğlu, I.: Evaluation of hydrogen production by *Rhodobacter sphaeroides* O. U.001 and its hupSL deficient mutant using acetate and malate as carbon sources, *Int. J. Hydrogen. Energ.*, 34, 2184–2190, doi:10.1016/j.ijhydene.2009.01.016, 2009.
- Knox, M., Quay, P. D., and Wilbur, D.: Kinetic isotopic fractionation during air–water gas transfer of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>, *J. Geophys. Res.*, 97, 20335–20343, 1992.
- Kock, A., Gebhardt, S., and Bange, H. W.: Methane emissions from the upwelling area off Mauritania (NW Africa), *Biogeosciences*, 5, 1119–1125, doi:10.5194/bg-5-1119-2008, 2008.
- Krol, M., Houweling, S., Bregman, B., van den Broek, M., Segers, A., van Velthoven, P., Peters, W., Dentener, F., and Bergamaschi, P.: The two-way nested global chemistry-transport zoom model TM5: algorithm and applications, *Atmos. Chem. Phys.*, 5, 417–432, doi:10.5194/acp-5-417-2005, 2005.
- Lilley, M. D., Baross, J. A., and Gordon, L. I.: Dissolved hydrogen and methane in Saanieh Inlet, British Columbia, *Deep-Sea Res.*, 29, 1471–1484, doi:10.1016/0198-0149(82)121471-13, 1982.
- Longhurst, A. R.: *Ecological Geography of the Sea*, Academic, San Diego, California, 398 pp., 1998.

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Moore, R. M., Punshon, S., Mahaffey, C., and Karl, D.: The relationship between dissolved hydrogen and nitrogen fixation in ocean waters, *Deep-Sea Res.*, 56, 1449–1458, doi:10.1016/j.dsr.2009.04.008, 2009.

Moore, R. M., Kienast, M., Fraser, M., Cullen, J. J., Deutsch, C., Dutkiewicz, S., Follows, M. J., and Somes, C. J.: Extensive hydrogen supersaturations in the western South Atlantic Ocean suggest substantial underestimation of nitrogen fixation, *J. Geophys. Res.-Oceans*, 119, 4340–4350, doi:10.1002/2014JC010017, 2014.

Nilsson, E. J. K., Johnson, M. S., Taketani, F., Matsumi, Y., Hurley, M. D., and Wallington, T. J.: Atmospheric deuterium fractionation: HCHO and HCDO yields in the CH<sub>2</sub>DO + O<sub>2</sub> reaction, *Atmos. Chem. Phys.*, 7, 5873–5881, doi:10.5194/acp-7-5873-2007, 2007.

Nilsson, E. J. K., Andersen, V. F., Skov, H., and Johnson, M. S.: Pressure dependence of the deuterium isotope effect in the photolysis of formaldehyde by ultraviolet light, *Atmos. Chem. Phys.*, 10, 3455–3462, doi:10.5194/acp-10-3455-2010, 2010.

Novelli, P. C., Lang, P. M., Masarie, K. A., Hurst, D. F., Myers, R., and Elkins, J. W.: Molecular hydrogen in the troposphere: global distribution and budget, *J. Geophys. Res.*, 104, 30427–30444, 1999.

Pieterse, G., Krol, M. C., and Röckmann, T.: A consistent molecular hydrogen isotope chemistry scheme based on an independent bond approximation, *Atmos. Chem. Phys.*, 9, 8503–8529, doi:10.5194/acp-9-8503-2009, 2009.

Pieterse, G., Krol, M. C., Batenburg, A. M., Steele, L. P., Krummel, P. B., Langenfelds, R. L., and Röckmann, T.: Global modelling of H<sub>2</sub> mixing ratios and isotopic compositions with the TM5 model, *Atmos. Chem. Phys.*, 11, 7001–7026, doi:10.5194/acp-11-7001-2011, 2011.

Pieterse, G., Krol, M. C., Batenburg, A. M., Brenninkmeijer, C. A. M., Popa, M. E., O'Doherty, S., Grant, A., Steele, L. P., Krummel, P. B., Langenfelds, R. L., Wang, H. J., Vermeulen, A. T., Schmidt, M., Yver, C., Jordan, A., Engel, A., Fisher, R. E., Lowry, D., Nisbet, E. G., Reimann, S., Vollmer, M. K., Steinbacher, M., Hammer, S., Forster, G., Sturges, W. T., and Röckmann, T.: Reassessing the variability in atmospheric H<sub>2</sub> using the two-way nested TM5 model, *J. Geophys. Res.-Atmos.*, 118, 3764–3780, doi:10.1002/jgrd.50204, 2013.

Popa, M. E., Vollmer, M. K., Jordan, A., Brand, W. A., Pathirana, S. L., Rothe, M., and Röckmann, T.: Vehicle emissions of greenhouse gases and related tracers from a tunnel study: CO : CO<sub>2</sub>, N<sub>2</sub>O : CO<sub>2</sub>, CH<sub>4</sub> : CO<sub>2</sub>, O<sub>2</sub> : CO<sub>2</sub> ratios, and the stable isotopes <sup>13</sup>C and <sup>18</sup>O in CO<sub>2</sub> and CO, *Atmos. Chem. Phys.*, 14, 2105–2123, doi:10.5194/acp-14-2105-2014, 2014.



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- Röckmann, T., Rhee, T. S., and Engel, A.: Heavy hydrogen in the stratosphere, *Atmos. Chem. Phys.*, 3, 2015–2023, doi:10.5194/acp-3-2015-2003, 2003.
- Röckmann, T., Gómez Álvarez, C. X., Walter, S., van Veen, C., Wollny, A. G., Gunthe, S. S., Helas, G., Pöschl, U., Keppler, F., Greule, M., and Brand, W. A.: The isotopic composition of H<sub>2</sub> from wood burning – dependency on combustion efficiency, moisture content and  $\delta D$  of local precipitation, *J. Geophys. Res.*, 115, D17308, doi:10.1029/2009JD013188, 2010a.
- Röckmann, T., Walter, S., Bohn, B., Wegener, R., Spahn, H., Brauers, T., Tillmann, R., Schlosser, E., Koppmann, R., and Rohrer, F.: Isotope effect in the formation of H<sub>2</sub> from H<sub>2</sub>CO studied at the atmospheric simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 10, 5343–5357, doi:10.5194/acp-10-5343-2010, 2010b.
- Schlitzer, R.: Ocean Data View 4, available at: <http://odv.awi.de> (last access: 5 October 2015), 2012.
- Schultz, M. G., Diehl, T., Brasseur, G. P., and Zittel, W.: Air pollution and climate–forcing impacts of a global hydrogen economy, *Science*, 302, 624–627, 2003.
- Schütz, K., Happe, T., Troshina, O., Lindblad, P., Leitão, E., Oliveira, P., and Tamagnini, P.: Cyanobacterial H<sub>2</sub> production – a comparative analysis, *Planta*, 218, 350–359, doi:10.1007/s00425-003-1113-5, 2004.
- Scranton, M., Jones, M., and Herr, F. L.: Distribution and variability of hydrogen in the Mediterranean Sea, *J. Mar. Res.*, 40, 873–891, 1982.
- Scranton, M. I.: The role of the cyanobacterium *Oscillatoria (Trichodesmium) thiebautii* in the marine hydrogen cycle, *Mar. Ecol.*, 11, 79–87, 1983.
- Seiler, W. and Schmidt, U.: Dissolved non–conservative gases in seawater, in: *The Sea*, Vol 5., edited by: Goldberg E. D., John Wiley & Sons, New York, 219–243, 1974.
- Stal, L. J.: Is the distribution of nitrogen-fixing cyanobacteria in the oceans related to temperature?, *Environ. Microbiol.*, 11, 1632–1645, doi:10.1111/j.1758-2229.2009.00016.x, 2009.
- Tamagnini, P., Leitão, E., Oliveira, P., Ferreira, D., Pinto, F., Harris, D. J., Heidorn, T., and Lindblad, P.: Cyanobacterial hydrogenases: diversity, regulation and applications, *FEMS Microbiol. Rev.*, 31, 692–720, doi:10.1111/j.1574-6976.2007.00085.x, 2007.
- Tromp, T. K., Shia, R.-L., Allen, M., Eiler, J. M., and Yung, Y. L.: Potential environmental impact of a hydrogen economy on the stratosphere, *Science*, 300, 1740–1742, 2003.
- Vollmer, M. K., Walter, S., Bond, S. W., Soltic, P., and Röckmann, T.: Molecular hydrogen (H<sub>2</sub>) emissions and their isotopic signatures (H/D) from a motor vehicle: implications on atmospheric H<sub>2</sub>, *Atmos. Chem. Phys.*, 10, 5707–5718, doi:10.5194/acp-10-5707-2010, 2010.

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Vollmer, M. K., Jordan, A., Brand, W. A., Pathirana, S. L., Rothe, M., and Röckmann, T.: Vehicle emissions of greenhouse gases and related tracers from a tunnel study: CO: CO<sub>2</sub>, N<sub>2</sub>O: CO<sub>2</sub>, CH<sub>4</sub>: CO<sub>2</sub>, O<sub>2</sub>: CO<sub>2</sub> ratios, and the stable isotopes <sup>13</sup>C and <sup>18</sup>O in CO<sub>2</sub> and CO, Atmos. Chem. Phys., 14, 2105–2123, doi:10.5194/acp-14-2105-2014, 2014.

5 Walter, S., Laukenmann, S., Stams, A. J. M., Vollmer, M. K., Gleixner, G., and Röckmann, T.: The stable isotopic signature of biologically produced molecular hydrogen (H<sub>2</sub>), Biogeo- sciences 9, 4115–4123, doi:10.5194/bg-9-4115-2012, 2012.

Walter, S., Kock, A., and Röckmann, T.: High-resolution measurements of atmospheric molec- ular hydrogen and its isotopic composition at the West African coast of Mauritania, Biogeo- sciences, 10, 3391–3403, doi:10.5194/bg-10-3391-2013, 2013.

10 Warwick, N. J., Bekki, S., Nisbet, E. G., and Pyle, J. A.: Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model, Geophys. Res. Lett., 31, L05107, doi:10.1029/2003GL019224, 2004.

Westberry, T. K. and Siegel, D. A.: Spatial and temporal distribution of *Trichodesmium* blooms in the world's oceans, Global Biogeochem. Cy., 20, GB4016, doi:10.1029/2005GB002673, 2006.

Wiesenburg, D. A. and Guinasso, N. L.: Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water, J. Chem. Eng. Data, 24, 356–360, doi:10.1021/je60083a006, 1979.

20 Wilson, S. T., Foster, R. A., Zehr, J. P., and Karl, D. M.: Hydrogen production by *Trichodesmium erythraeum*, *Cyanothece* sp., and *Crocospaera watsonii*, Aquat. Microb. Ecol., 59, 197–206, doi:10.3354/ame01407, 2010a.

Wilson, S. T., Tozzi, S., Foster, R. A., Ilikchyan, I., Kolber, Z. S., Zehr, J. P., and Karl, D. M.: Hy- drogen cycling by the unicellular marine diazotrophs *Crocospaera watsonii* strain WH8501, Appl. Environ. Microb., 76, 6797–803, doi:10.1128/AEM.01202-10, 2010b.

25 Wilson, S. T., del Valle, D. A., Robidart, J. C., Zehr, J. P., and Karl, D. M.: Dissolved hydrogen and nitrogen fixation in the oligotrophic North Pacific Subtropical Gyre, Environ. Microbiol. Rep., 5, 697–704, doi:10.1111/1758-2229.12069, 2013.

Yashiro, H., Sudo, K., Yonemura, S., and Takigawa, M.: The impact of soil uptake on the global distribution of molecular hydrogen: chemical transport model simulation, Atmos. Chem. Phys., 11, 6701–6719, doi:10.5194/acp-11-6701-2011, 2011.

5

10

15

20

25

30

Yonemura, S., Kawashima, S., and Tsuruta, H.: Carbon monoxide, hydrogen, and methane uptake by soils in a temperate arable field and a forest, *J. Geophys. Res.*, 105, 14347–14362, doi:10.1029/1999JD901156, 2000.

5 Yver, C. E., Pison, I. C., Fortems-Cheiney, A., Schmidt, M., Chevallier, F., Ramonet, M., Jordan, A., Søvdde, O. A., Engel, A., Fisher, R. E., Lowry, D., Nisbet, E. G., Levin, I., Hammer, S., Necki, J., Bartyzel, J., Reimann, S., Vollmer, M. K., Steinbacher, M., Aalto, T., Maione, M., Arduini, J., O'Doherty, S., Grant, A., Sturges, W. T., Forster, G. L., Lunder, C. R., Privalov, V., Paramonova, N., Werner, A., and Bousquet, P.: A new estimation of the recent tropospheric molecular hydrogen budget using atmospheric observations and variational inversion, *Atmos. Chem. Phys.*, 11, 3375–3392, doi:10.5194/acp-11-3375-2011, 2011.

10 Zehr, J. P., Waterbury, J. B., Turner, P. J., Montoya, J. P., Omoregie, E., Steward, G. F., Hansen, A., and Karl, D. M.: Unicellular cyanobacteria fix N<sub>2</sub> in the subtropical North Pacific Ocean, *Nature*, 412, 635–638, 2001.

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12, 16431–16477, 2015

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**Table 1.** Overview of sample distribution during the cruises: type A are discrete atmospheric samples, type H are headspace samples extracted from the surface water. The sample numbers in brackets give the number of measured samples in the northern (NH) and southern (SH) hemisphere.

Cruise	Date	Position (start–end)	Nr. of Samples (NH/SH)	Type
ANT-XXIV/4	18 Apr–20 May 2008	59.15° W/46.13° S – 06.21° W/47.96° N	95 (44 NH/51 SH)	A
ANT-XXV/5	11 Apr–24 May 2009	50.99° W/40.82° S – 23.05° W/16.55° N	91 (30 NH/61 SH)	A
ANT XXVI/1	16 Oct–25 Nov 2009	12.05° W/37.96° N – 47.28° W/37.43° S	60 (29 NH/31 SH)	A
ANT XXVI/4	07 Apr–17 May 2010	58.14° W/43.75° S – 04.46° E/53.15° N	114 (56 NH/58 SH)	A
ANT XXVI/4	07 Apr–17 May 2010	32.53° W/18.79° S – 13.00° W/36.54° N	16 (10 NH/6 SH)	H
L'Atalante ATA-3	03 Feb–20 Feb 2008	17.83° N/16.56° W – 17.60° N/24.24° W	6 (6 NH/0 SH)	H

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**Table 2.** Hemispheric means of atmospheric H<sub>2</sub> and its isotopic composition along the four meridional Atlantic transects.

Cruise	Southern Hemisphere				Northern Hemisphere				
		IRMS – H <sub>2</sub> mole fraction [ppb]	δD [‰]	RGA – H <sub>2</sub> mole fraction [ppb]	RGA – CO mole fraction [ppb]	IRMS – H <sub>2</sub> mole fraction [ppb]	δD [‰]	RGA – H <sub>2</sub> mole fraction [ppb]	RGA – CO mole fraction [ppb]
ANT-XXI/4 Apr 2008	mean range <i>n</i>	543.4 ± 7.3 528.8–568.5 49 (2 values excluded)	145.4 ± 5.3 135.4–155.7 49 (2 values excluded)	No data	No data	544.1 ± 9.8 522.0–567.8 44	118.6 ± 3.9 110.4–130.9 44	No data	No data
ANT-XXV/5 Apr 2009	mean range <i>n</i>	533.9 ± 38.7 350.2–631.9 60	140.5 ± 21.1 20.9–166.1 60	520.4 ± 24.0 432.5–545.1 21	59.9 ± 17.7 43.6–119.6 21	532.94 ± 19.73 466.9–560.3 28 (2 values excluded)	121.28 ± 7.09 89.1–130.9 28 (2 values excluded)	526.18 ± 12.6 508.9–564.1 29	112.67 ± 21.3 76.9–190.5 29
ANT XXVI/1 Oct 2009	mean range <i>n</i>	548.5 ± 6.8 535.9–563.4 30 (1 value excluded)	143.2 ± 4.2 135.5–149.3 30 (1 value excluded)	546.4 ± 7.4 531.4–563.0 49	59.9 ± 10.5 47.7–85.8 49	532.04 ± 10.65 501.1–551.7 29	133.94 ± 4.43 123.5–141.7 29	526.02 ± 10.53 494.2–548.8 46	76.73 ± 7.43 65.4–96.1 46
ANT XXVI/4 Apr 2010	mean range <i>n</i>	541.6 ± 16.3 496.0–579.6 58	143.7 ± 11.5 89.3–161.8 58	525.1 ± 29.1 481.5–696.8 617	47.2 ± 8.8 36.2–121.8 617	539.4 ± 14.8 505.5–564.6 56	116.2 ± 11.5 93.8–146.6 56	507.8 ± 15.7 481.3–603.8 1339	120.8 ± 11.2 72.7–146.1 1339

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**Table 4.** Overview of headspace sample results from the ANT-XXVI/4 cruise (2010) and the L'Atalante ATA-3 (2008):  $\chi_h$  is the measured mole fraction of the headspace in parts per billion (ppb = nmole mole<sup>-1</sup>),  $\chi_a$  is the corresponding atmospheric mole fraction in ppb,  $D_h$  and  $D_a$  is the measured isotopic composition in permill [‰]. The H<sub>2</sub> equilibrium concentration  $c_{\text{sat}}$  (H<sub>2</sub>) was determined by using the equations from Wiesenburg and Guinasso (1979), the initial dissolved H<sub>2</sub> concentration  $c_{w0}$  is calculated as given in the Supplement, and the excess  $\Delta H_2$  is the difference between them.  $\delta_{w0SC1}$  and  $\delta_{w0SC2}$  show the two scenarios to derive the initial isotope delta of dissolved H<sub>2</sub>.  $S_{(H_2)}$  is the supersaturation of H<sub>2</sub> in the surface water. The calculated extraction efficiency was 92 %. The calculations are given in the Supplement in more detail.

Date/Time [UTC]	Sampling position	$\chi_a$ [ppb]	$\delta D_a$ [‰]	$\chi_m$ [ppb]	$\delta D_m$ [‰]	$c_{\text{sat}}$ (H <sub>2</sub> ) [nmol L <sup>-1</sup> ]	$c_{w0}$ [nmol L <sup>-1</sup> ]	$\Delta$ (H <sub>2</sub> ) [nmol L <sup>-1</sup> ]	$\delta_{w0SC1}$ [‰]	$\delta_{w0SC2}$ [‰]	$S_{(H_2)}$
21 Apr 2010 15:15	–18.79° N –32.53° E	562.0	148.5	653.3	–37.3	0.35	1.68	1.32	–536.2	–535.6	3.75
22 Apr 2010 15:24	–15.91° N –30.49° E	524.2	134.5	750.6	–138.6	0.33	2.89	2.57	–654.8	–654.4	7.80
23 Apr 2010 15:21	–13.06° N –28.51° E	551.6	144.3	754.4	–125.1	0.35	2.91	3.57	–602.9	–602.5	7.41
24 Apr 2010 15:36	–10.71° N –26.92° E	522.0	153.2	797.0	–151.2	0.33	3.52	3.19	–605.6	–605.2	9.74
25 Apr 2010 15:24	–7.97° N –25.02° E	542.9	154.7	674.8	–59.4	0.34	1.97	1.63	–566.1	–565.6	4.81
26 Apr 2010 15:12	–5.16° N –23.11° E	517.8	149.7	584.5	9.2	0.32	0.83	0.51	–654.0	–653.6	1.56
28 Apr 2010 13:54	1.78° N –23.00° E	540.9	144.4	619.8	–33.1	0.34	1.27	0.93	–682.1	–681.8	2.76
29 Apr 2010 14:21	4.99° N –23.00° E	562.8	114.2	615.9	–11.7	0.35	1.25	0.89	–575.4	–574.9	2.53
30 Apr 2010 14:15	8.07° N –23.00° E	550.6	118.6	591.1	–0.6	0.35	0.94	0.60	–680.8	–680.5	1.71
02 May 2010 14:39	14.55° N –23.68° E	541.3	110.5	603.3	–15.0	0.35	1.13	0.78	–680.7	–680.4	2.24
04 May 2010 13:39	17.61° N –24.75° E	523.2	121.5	686.5	–83.6	0.34	2.27	1.93	–630.8	–630.3	5.74
05 May 2010 13:21	20.26° N –22.86° E	559.0	125.7	667.9	–55.3	0.36	2.05	1.69	–572.6	–572.2	4.66

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Date/Time [UTC]	Sampling position	$\chi_a$ [ppb]	$\delta D_a$ [‰]	$\chi_m$ [ppb]	$\delta D_m$ [‰]	$c_{\text{sat}}(\text{H}_2)$ [nmol L <sup>-1</sup> ]	$c_{\text{w0}}$ [nmol L <sup>-1</sup> ]	$\Delta(\text{H}_2)$ [nmol L <sup>-1</sup> ]	$\delta_{\text{w0 SC1}}$ [‰]	$\delta_{\text{w0 SC2}}$ [‰]	$S_{(\text{H}_2)}$
06 May 2010 12:30	23.12° N -20.66° E	550.7	104.3	586.6	-1.1	0.36	0.93	0.57	-719.3	-719.0	1.58
07 May 2010 12:18	26.07° N -17.50° E	539.8	108.9	575.3	20.3	0.35	0.79	0.43	-645.2	-644.8	1.21
09 May 2010 12:51	33.60° N -13.86° E	546.8	104.6	624.2	21.0	0.37	1.51	1.14	-327.2	-326.4	3.10
10 May 2010 12:55	36.53° N -13.01° E	531.8	107.8	571.6	62.0	0.36	0.77	0.41	-230.2	-229.3	1.13
09 Feb 2008 16:05	16.91° N -16.82° E	527.2	118.4	141.7	-224.09	0.35	1.57	1.22	-221.8	-221.0	3.46
11 Feb 2008 17:58	18.77° N -16.81° E	538.5	115.3	550.4	-383.39	0.36	5.91	5.54	-381.6	-380.9	15.28
15 Feb 2008 10:27	17.93° N -16.38° E	536.8	112.2	138.8	-114.85	0.36	1.79	1.42	-112.2	-111.3	3.92
16 Feb 2008 6:05	17.72° N -16.69° E	548.4	120.0	20.3	-180.51	0.37	0.50	0.13	-179.0	-178.2	0.35
16 Feb 2008 17:41	18.01° N -17.01° E	548.4	120.0	31.0	-218.73	0.37	0.72	0.35	-217.3	-216.5	0.94
18 Feb 2008 18:22	18.00° N -23.00° E	541.8	126.5	48.9	-321.61	0.36	1.16	0.80	-320.4	-319.7	2.22

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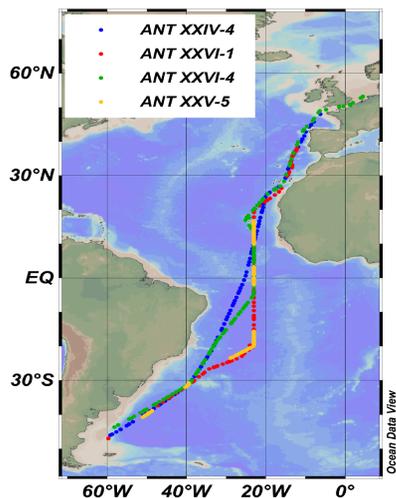
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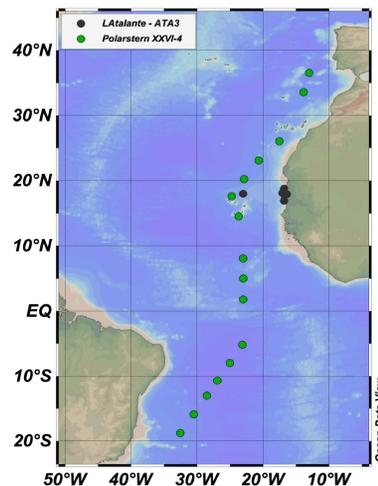
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a)



b)



**Figure 1.** (a) Cruise tracks of the RV Polarstern, dots indicate positions of discrete atmospheric air sampling, (b) positions of surface water headspace sampling during ANT-XXVI/4 ( $n = 16$ , green dots) and the RV L'Atalante ATA-3 cruise ( $n = 6$ , black dots).

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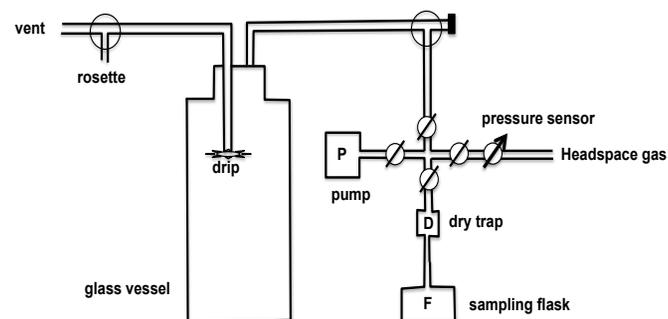
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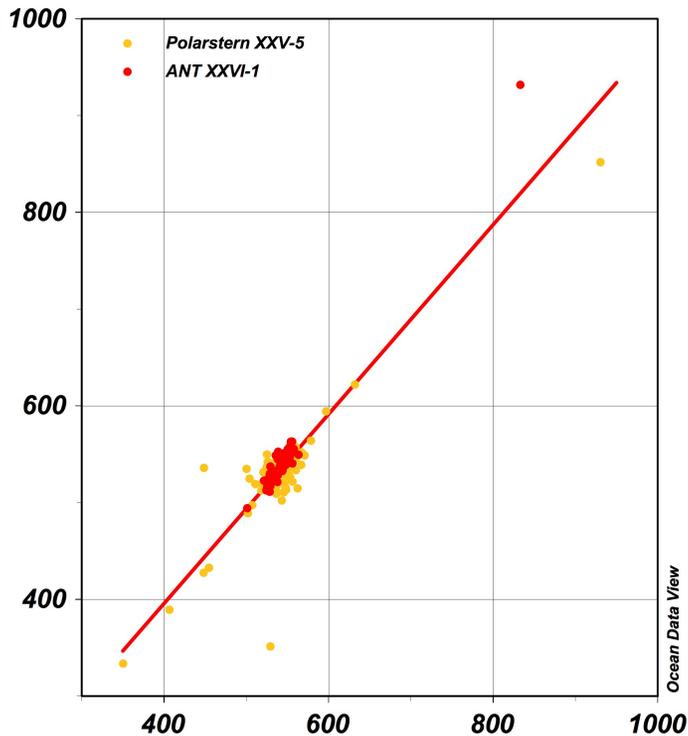
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**Figure 2.** Experimental setup for headspace sampling, **(a)** sampling of the surface water into the glass vessel, connected to the Niskin bottle rosette, **(b)** scheme of the experimental setup.



**Figure 3.** Comparing the H<sub>2</sub> mole fractions [ppb] measured with the isotopic experimental setup (*x* axis) and the Peak Performer 1 RGA (*y* axis) during ANT-XXVI/1 (red labeled) and ANT-XXV/5 (yellow labeled),  $y = 0.979x + 3.96$ ,  $R^2 = 0.81$ ,  $n = 147$ .

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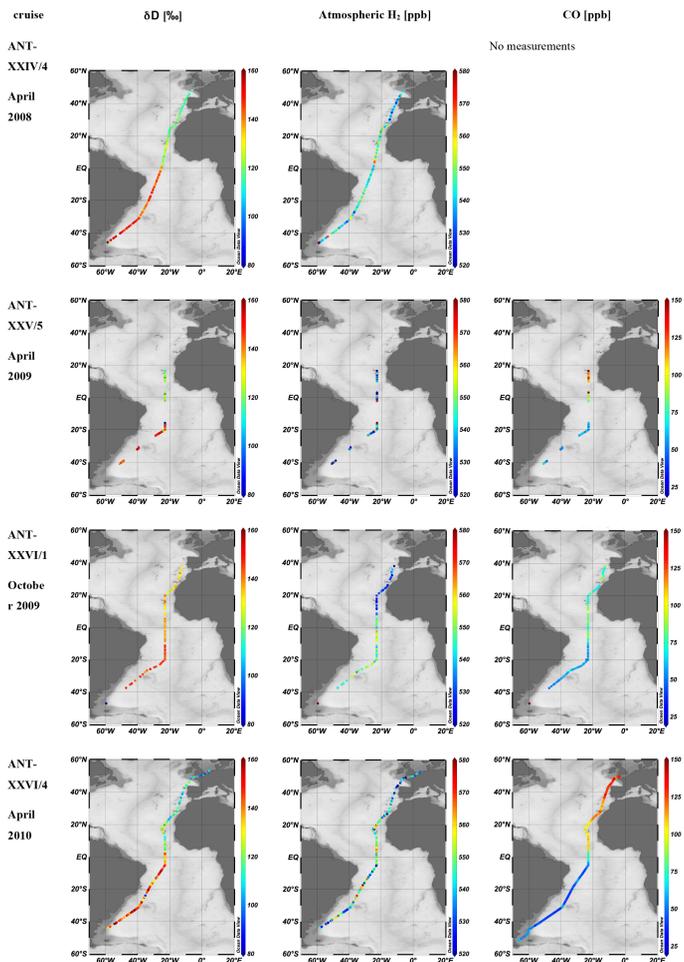
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**Figure 4.**  $\delta D$  ( $H_2$ ) [‰] (first column),  $H_2$  mole fraction [ppb] (second column), and CO mole fraction [ppb] (third column), along the meridional cruise tracks of RV Polarstern, the mole fraction and  $\delta D$  of  $H_2$  are measured by IRMS, the CO mole fraction by RGA.

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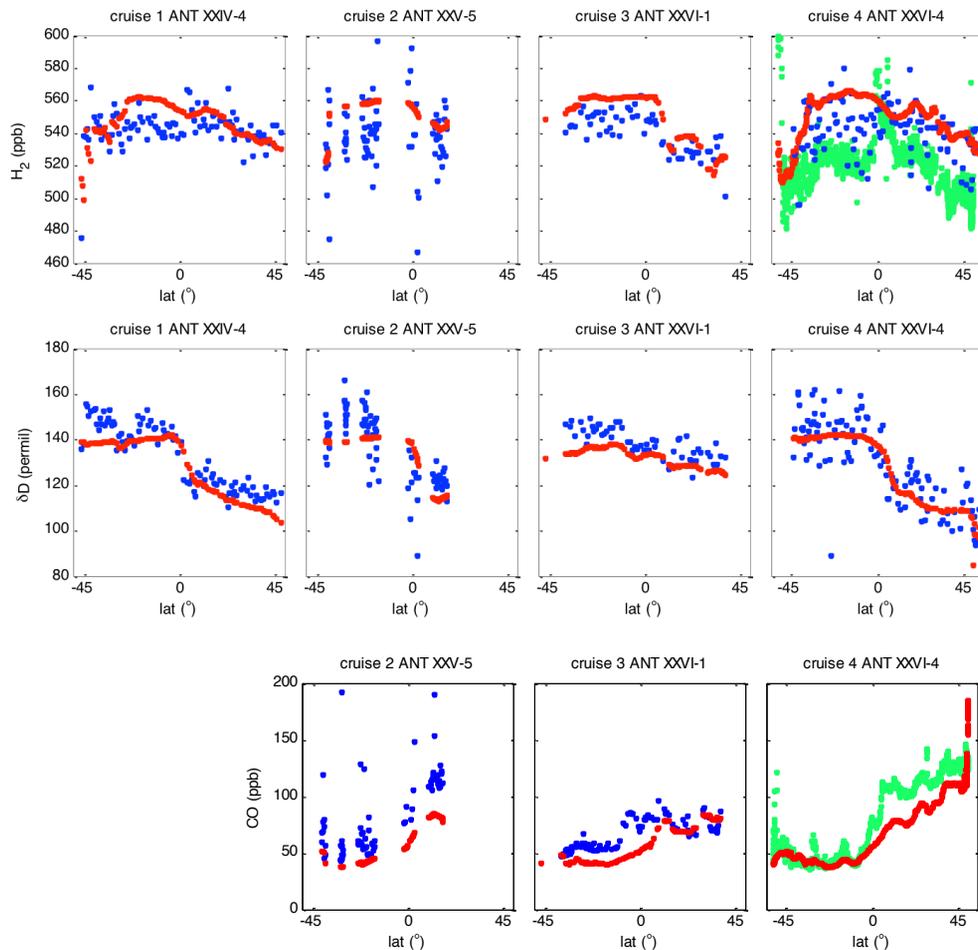


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**Figure 5.** Comparison of measurement results of H<sub>2</sub> and CO mole fractions and  $\delta$ D with TM5 model results (given in red). Data are shown against latitude. The blue markers show results of flask samples, the green markers represent the continuous in-situ measurements (performed with the peak performer instrument on-board). CO has not been analysed in the flasks sampled during the last cruise. The model data were interpolated at the place and time of sampling or measurements.

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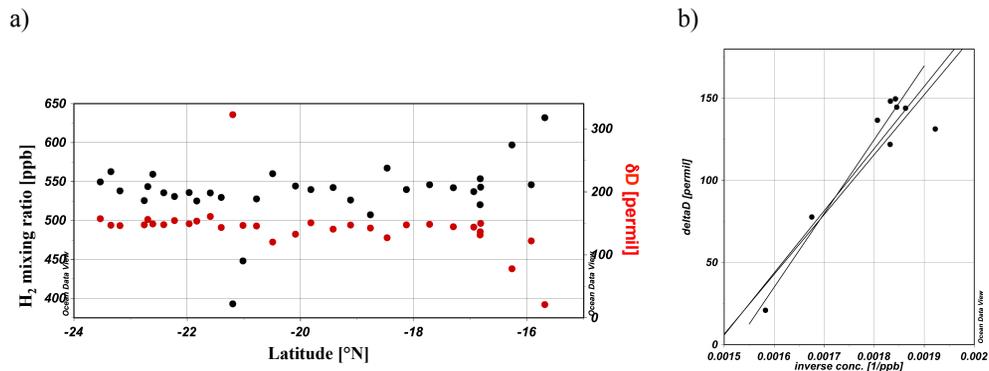


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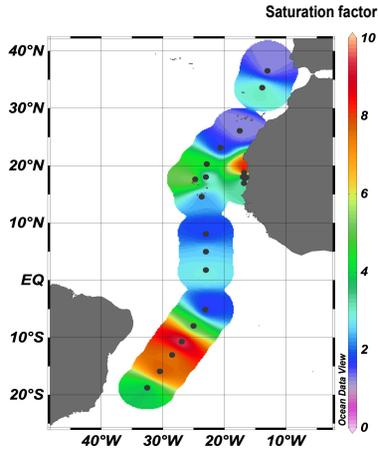
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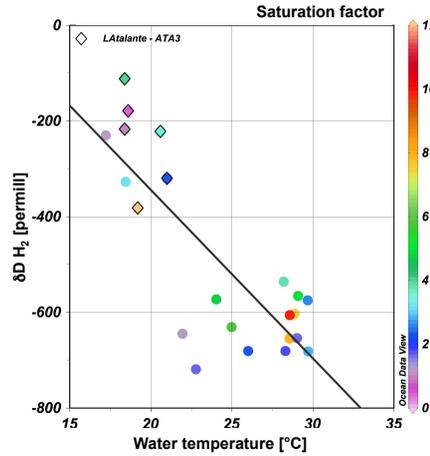


**Figure 6.** (a) H<sub>2</sub> mole fraction [ppb] (black) and δD [‰] (red) along the ANT-XXV/5 high-resolution transect 24–15° S, (b) keeling plot of the samples along the high-resolution transect north of 18° S. The three trend lines indicate the range of the Keeling plot analysis that was applied to determine the source signature.

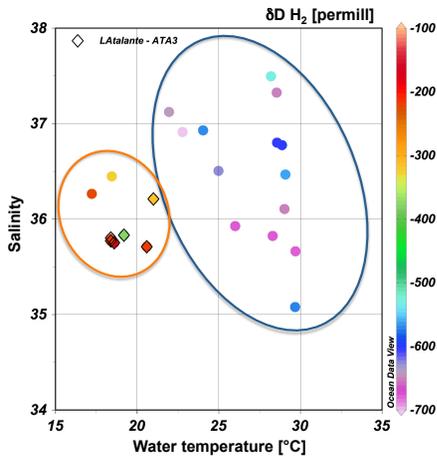
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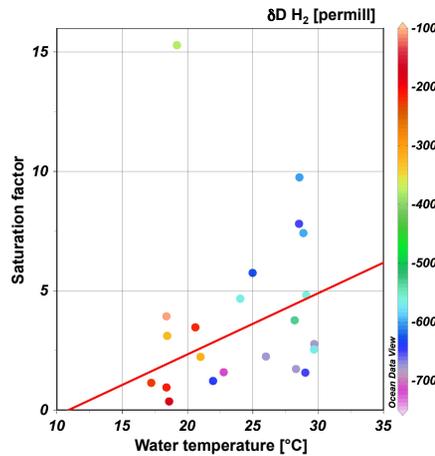
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d)



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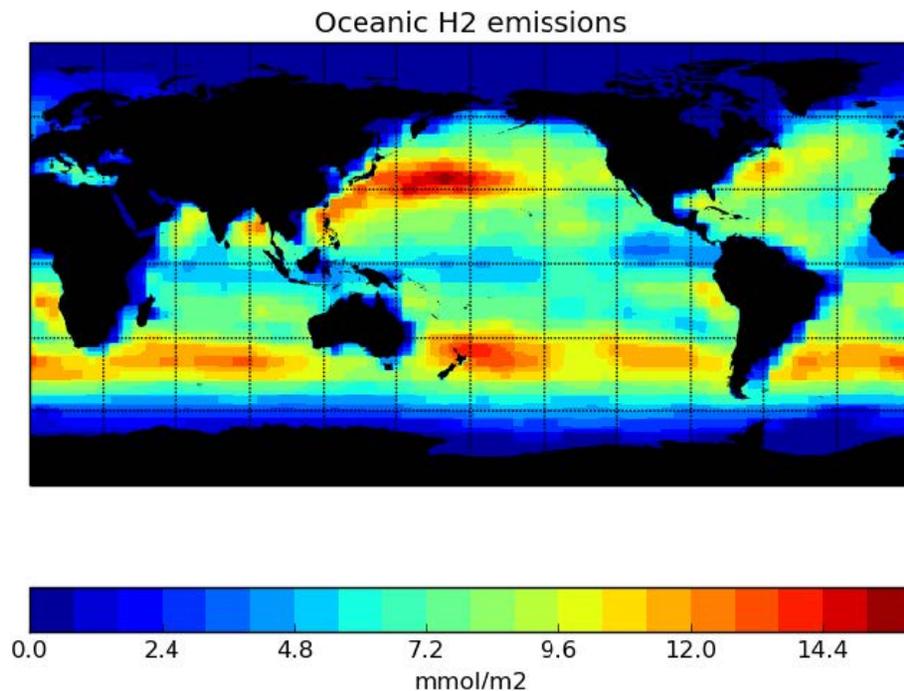


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**Figure 8.** Oceanic H<sub>2</sub> emissions used in the TM5 model simulations ( $\text{mmol m}^{-2} \text{a}^{-1}$ , based on the distribution provided by the project GEMS (Global and regional Earth-system (Atmosphere) Monitoring using Satellite and in-situ data) and scaled to a total oceanic source of  $5 \text{Tga}^{-1}$  (Pieterse et al., 2013).

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