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 5 cruises along a transect between Punta Arenas (Chile) and Bremerhaven (Germany), as well as at the coast of Mauritania.

The isotopic source signatures of dissolved H$_2$ extracted from surface water are highly deuterium-depleted and correlate negatively with temperature, showing δD values of $(−629 ± 54)$ ‰ for water temperatures at $(27 ± 3)$ °C and $(−249 ± 88)$ ‰ below $(19 ± 1)$ °C. The results for warmer water masses are consistent with the 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.

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, 2005, 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 (NMVOCs) in the atmosphere and combustion processes at the surface, whereas soil deposition and oxidation by hydroxyl radicals (HO*) 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, esti-
mammalian species and their metabolic processes. The kinetic isotope fractionation in the two main respiratory pathways is also influenced by environmental conditions and microorganisms. Various studies have shown that mammalian species, such as bacteria, fungi, and plants, can produce hydrogen gas under anaerobic conditions. This gas can be released into the atmosphere and contribute to the global hydrogen cycle. The aim of the study was to determine the δD of dissolved H₂ and gain more information about possible sources, and to get a high-resolution picture of the distribution of atmospheric H₂ along meridional Atlantic transects during different seasons and compare it with global model results. Samples were taken on four cruises along meridional Atlantic transects in the Southern Hemisphere and the Northern Hemisphere and on one cruise at the coast of Mauritania. A total of almost 400 atmospheric and 22 ocean surface water samples were taken, covering two seasons between 2008 and 2010.

2 Methods

2.1 Cruise tracks

During four cruises of RV Polarstern and one of RV L’Atalante between February 2008 and May 2010, air and seawater samples were collected (see Fig. 1, Table 1). The cruises of RV Polarstern were part of the OceaNET project (autonomous measuring platforms for the regulation of substances and energy exchange between ocean and atmosphere, Hanschmann et al., 2012).

They covered both hemispheres, between Punta Arenas (Chile, 53°S/71°W) and Bremerhaven (Germany, 53°N/8°E). South–north transects were carried out in boreal spring (April/May) and north–south transects in boreal autumn (October/November). The transects followed similar tracks as the Atlantic Meridional Transect (AMT) program (http://amt-uk.org/) and crossed a wide range of ecosystems and oceanic regimes, from sub–polar to tropical and from euphotic shelf seas and upwelling systems to oligotrophic mid–ocean gyres (Robinson et al., 2009; Longhurst, 1998).

The RV L’Atalante followed a cruise track from Dakar (Senegal) to Mindelo (Cape Verde), covering a sampling area along the coast of Mauritania and a transect to the Cape Verde Islands. This area is characterized by strongly differing hydrographical and biological properties with an intensive seasonal upwelling. Area and cruise track are described in more detail in Walter et al. (2013) and Kock et al. (2008).

2.2 Atmospheric air sampling

Discrete atmospheric air samples were taken on-board RV Polarstern at the bridge deck, using 1 L borosilicate glass flasks coated with black shrink-hose (NORMAG), with 2 Kel-F (PCTFE) O-ring sealed valves. The flasks were preconditioned by flushing with N₂ at 50°C for at least 12 h; the N₂ remained in the flask at ambient pressure until the sampling. During sampling the flasks were flushed for 4 min with ambient air at a flow rate of 12 L min⁻¹ using Teflon tubes and a membrane pump (KNF VERDER PM2874-...
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).

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 Hemisphere (NH) and Southern Hemisphere (SH).

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Date</th>
<th>Position (start–end)</th>
<th>Nr. of Samples (NH/SH)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANT-XXIV/4</td>
<td>18.04.–20.05.2008</td>
<td>59.15° W/46.13° S–06.21° W / 47.96° N</td>
<td>95 (44 NH/51 SH)</td>
<td>A</td>
</tr>
<tr>
<td>ANT-XXV/5</td>
<td>11.04.–24.05.2009</td>
<td>50.99° W/40.82° S–23.05° W/16.55° N</td>
<td>91 (30 NH/61 SH)</td>
<td>A</td>
</tr>
<tr>
<td>ANT XXVI/1</td>
<td>16.10.–25.11.2009</td>
<td>12.05° W/37.96° N–47.28° W/37.43° S</td>
<td>60 (29 NH/31 SH)</td>
<td>A</td>
</tr>
<tr>
<td>ANT XXVI/4</td>
<td>07.04.–17.05.2010</td>
<td>58.14° W/43.75° S–04.46° E/53.15° N</td>
<td>114 (56 NH/58 SH)</td>
<td>A</td>
</tr>
<tr>
<td>L’Atalante ATA-3</td>
<td>03.02.–20.02.2008</td>
<td>17.83° N/16.56° W–17.60° N/24.24° W</td>
<td>16 (10 NH/6 SH)</td>
<td>H</td>
</tr>
</tbody>
</table>

The sample air was dried with Drierite® (CaSO$_4$). The flasks were finally pressurized to approximately 1.7 bar, which allows duplicate measurements of the H$_2$ isotopic composition of an air sample.

Table 1 gives an overview of the sampling scheme for discrete H$_2$ samples. In total 360 samples were collected, regularly distributed over the transects at 4 to 6 h intervals. In 2009 the resolution of sampling was enhanced to one sample per 2 h and focused on five sub-sections of the transect, in an attempt to resolve dial variability.

Samples were always taken at the downwind side of the ship to exclude a possible contamination by ship diesel exhaust. One atmospheric sample was taken directly inside the ship’s funnel of RV Polarstern to determine the mole fraction and $\delta^D$ of ship diesel exhaust as a possible contamination source. This first measurements for ship diesel exhaust gave an H$_2$ mole fraction of (930.6 ± 3.2) nmol mol$^{-1}$ and a $\delta^D$ of $(-228.6 ± 5.0)$ ‰. In the following, we will use the abbreviation “ppb” = $10^{-9}$ in place of the SI unit “nmol mol$^{-1}$”.

2.3 Headspace sampling from surface waters

In addition to the atmospheric air samples, 16 headspace samples from surface water were taken during the RV Polarstern cruise ANT-XXVI/4 in April/May 2010 and 6 samples during the RV L’Atalante cruise in February 2008. The experimental setup (Fig. 2) was a prototype, and deployed for the first time to extract headspace air from surface water for isotopic composition measurements of molecular H$_2$. It consists of a glass vessel (10 L) and an evacuation/headspace sampling unit.

The glass vessel was evacuated for at least 24h before sampling, using a Pfeiffer vacuum DUO 2.5A pump, with a capacity of 40 L min$^{-1}$ (STP: 20°C and 1 bar). Water sam-
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.

samples were taken from 5 m depth (RV Polarstern cruises) or 10 m depth (RV L’Atalante cruise) using a 24-Niskin-bottle rosette with a volume of 12 L each. Sampling started immediately after return of the bottle rosette on-board and from a bottle dedicated to the H2 measurements. The evacuated glass vessel was connected to the Niskin bottle by Teflon tubing, which was first rinsed with approximately 1 L surface water. Then, 8.4 L water streamed into the evacuated flask (Fig. 2), using a drip to enhance the dispersion of the sample water. After connection of the headspace-sampling unit, the lines were first evacuated and then flushed with a makeup gas several times. During the RV L’Atalante cruise a synthetic air mixture with an H2 mixing ratio below threshold was used as makeup gas. The makeup gas used during the RV Polarstern cruises was a synthetic air mixture with an H2 mole fraction of (543.9 ± 0.3) ppb and a δD of (93.1 ± 0.2) ‰. The mole fraction of the makeup gas was determined by the Max Planck Institute for Biogeochemistry and is given on the MPI2009 scale (Jordan and Steinberg, 2011). The glass vessel was pressurized to approximately 1.7 bar absolute with the makeup gas and the total headspace (added makeup gas plus extracted gas from the water sample) was then flushed to a pre-evacuated sample flask. The flasks were of the same type as for the atmospheric sampling: 1 L borosilicate glass flasks (NORMAG), coated with black shrink-hose to minimize photochemical reactions inside and sealed with 2 Kel-F (PCTFE) O-ring sealed valves. All flasks were previously conditioned by flushing with N2 at 50 °C for at least 12 h and evacuated for at least 12 h directly before use. The whole sampling procedure took around 15 min: (4.0 ± 0.5) min flushing surface water to the evacuated glass vessel, (8.0 ± 1.0) min to connect the glass vessel to the sampling unit and evacuate the lines, and (3.0 ± 0.5) min to add and pressurize the glass vessel with the makeup gas and take the headspace sample. The surface water temperature was on average (0.9 ± 0.6) °C higher than the air temperature. Given that most of the apparatus was at air temperature and that the headspace will adjust to ambient temperature relatively quickly during equilibration the air temperature was used for calculations. Since the temperature dependence of H2 solubility is less than 0.3 % per K for seawater between 16 and 30 °C (as encountered here) and view of the large H2 saturations (see below), the error associated with this assumption is negligible. Flasks were stored in the dark until measurement. Additionally, atmospheric samples were taken at the same location of headspace sampling (Table 4).

2.4 Measurements

2.4.1 Atmospheric H2 and δD (H2) in discrete samples

The mole fraction and isotopic composition of molecular H2 was determined using the experimental setup developed by Rhee et al. (2004) and described in detail in Walter et al. (2012, 2013) and Batenburg et al. (2011). The D/1H molar ratio in a sample, Rsample(D/H), is quantified as the relative deviation from the D/1H molar ratio in a standard, Rstandard(D/H), as isotope delta δD value, and reported in per mill (%):  

\[
\delta D = \frac{R_{\text{sample}}(\text{D}/\text{H})}{R_{\text{standard}}(\text{D}/\text{H})} - 1.
\]

The isotopic standard is Vienna Standard Mean Ocean Water (VSMOW). H2 mole fractions are reported as mole fractions in nmol mol⁻¹, abbreviated ppb (10⁻⁹, parts per billion) and linked to the MPI2009 calibration scale for atmospheric hydrogen (Jordan and Steinberg, 2011). As working standards, atmospheric air from laboratory reference air cylinders and synthetic air mixtures were used (Walter et al., 2012, 2013; Batenburg et al., 2011); the H2 mole fractions of the air in these cylinders were determined by the
Max Planck Institute for Biogeochemistry, Jena, Germany. The atmospheric reference air and the synthetic isotope reference air were measured daily (atmospheric reference air at least twice) and results were used for correction of the sample measurements. The uncertainties reported here reflect random (i.e., repeatability) errors only and do not include possible systematic errors (Batenburg et al., 2011; Walter et al., 2012, 2013). Samples were measured in random order and analyzed within 3 months (ANT-XXIV/4, ANT-XXV/5, ANT-XXVI/1) up to 2 years (ANT-XXVI/4) after sampling. Storage tests indicate that glass flasks equipped with Kel-F valves are stable for H$_2$ Storage tests indicate that glass flasks equipped with Kel-F valves are stable for H$_2$ and CO mole fractions were also measured by using a Peak Performer 1 RGA (Reduced Gas Analyzer) 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 ±0.8 (H$_2$) and ±2 % (CO). A comparison between the H$_2$ mole fractions measured with the Peak Performer 1 RGA and the isotopic experimental setup reveals on average slightly lower RGA values of (7.5 ± 23.8) ppb (see Fig. 3).

2.4.2 Atmospheric H$_2$ measured continuously

For the on-board continuous measurements of H$_2$ 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 fractions of H$_2$ and CO were calculated by using the mean of the enclosing standard measurements, with an estimated maximal error of ±5 %. For more details see Popa et al. (2014). The mean measurement repeatability for the air samples was ±1.7 % for H$_2$ and ±3.6 % for CO in ambient air, respectively ±0.8 (H$_2$) and ±0.9 % (CO) for the reference air. Comparing the H$_2$ mole fractions measured continuously on the RGA with discrete samples measured on the isotope system and collected close in time, we found a mean offset of (−18.8 ± 16.4) ppb for the RGA results.

2.4.3 Dissolved H$_2$ extracted from surface water

The discrete samples of extracted dissolved H$_2$ were measured as described for the discrete atmospheric samples in Sect. 2.4.1. Details about assumptions and calculations to determine dissolved H$_2$ concentrations and isotope delta values and quantity symbols are given in detail in the Supplement. We define the extraction efficiency $\eta$ as

$$\eta = \frac{c_h V_h}{c_{w0} V_w}$$

(2)

where $V_h$ and $V_w$ are the volume of the headspace and the water fraction, and $c_h$ the concentration of H$_2$ in the headspace. The initial concentration of H$_2$ in seawater, $c_{w0}$, can be calculated from

$$c_{w0} = \frac{c_h V_h}{\eta V_w}$$

(3)

The concentration in the headspace, $c_h$, was not measured directly, but can be derived from the measured H$_2$ mole frac-
tion in the sampling flask. The sampling procedure following gas extraction under vacuum can be broken into three steps (see Methods section):

1. expansion of the headspace into the gas transfer system
2. addition of makeup gas
3. expansion of the headspace / makeup gas mixture into a sample flask.

As shown in the Appendix, the original concentration of \( \text{H}_2 \) in seawater (in nmol L\(^{-1}\)) can be calculated using the following equation

\[
\eta_{w0} = \frac{y_f \left(1 + \frac{V_m}{V_h}\right) \rho_{\text{num}} - \rho_{\text{H}_2}\text{O}}{V_w RT} - \gamma_n \left(1 + \frac{V_m}{V_h}\right) \rho_{\text{num}} - \rho_n,
\]

(4)

where \( y_f \) is the dry mole fraction of the air in the flask and \( \gamma_n \) the mole fraction of the makeup gas = (543.9 \pm 0.3) ppb.

The extraction efficiency, \( \eta \), can be calculated from the following mass balance

\[
V_w c_{w0} = V_h c_h + \alpha V_w c_h.
\]

(5)

Assuming that headspace gas phase and water phase are in equilibrium, the ratio of the \( \text{H}_2 \) concentration in water and in the headspace is given by the Ostwald coefficient (Battino, 1984) (where the concentrations refer to in situ temperature):

\[
\alpha = \frac{c_w}{c_h}.
\]

(6)

This gives for the extraction efficiency as defined in Eq. (2)

\[
\eta = \left(1 + \alpha \frac{V_m}{V_h}\right)^{-1}.
\]

(7)

In the present case, \( \alpha = \alpha(\text{H}_2) \) was equal to 0.0163 \( \pm \) 0.0001, which gives \( \eta = 92.12 \) (\( \pm \) 0.013) % for \( V_a/V_h = 8.4/1.6 = 5.25 \).

Two alternative scenarios were considered to derive the \( \delta \)D of the dissolved \( \text{H}_2 \), with scenario 1 assuming equilibrium isotopic fractionation between headspace and water, and scenario 2 assuming kinetic isotopic fractionation during extraction from Niskin bottle to glass vessel.

Scenario 1 : \( \delta_{w0} = \delta_h + \xi (1 - \eta) (1 + \delta_h) \)

(8)

The equilibrium isotopic fractionation between dissolved phase and gas phase is \( \xi = (37 \pm 1) \% \) at 20°C (Knox et al., 1992).

Scenario 2 : \( \delta_{w0} = \frac{(1 + \delta_h) \eta}{1 - (1 - \eta)^{1+\varepsilon_k}} - 1 \)

\[
\approx \delta_h + \varepsilon_k (1 - \eta) \left(1 + \delta_h\right) \frac{\ln(1 - \eta)}{\eta}
\]

(9)

The kinetic isotope fractionation during gas evasion is \( \varepsilon_k = (-18 \pm 2) \% \) at 20°C (Knox et al., 1992). The approximation is not used and only shown to illustrate the small difference between \( \delta_{w0} \) and \( \delta_h \) when \( \eta \approx 1 \).

The temperature dependences of \( \xi \) and \( \varepsilon_k \) are unknown and were neglected here.

The air saturation equilibrium concentration, \( c_{\text{sat}}(\text{H}_2) \), was determined using the parameterization of Wiesenburg and Guinasso (1979). The \( \text{H}_2 \) saturation anomaly, \( \Delta(\text{H}_2) \), was calculated as the difference between the measured \( \text{H}_2 \) concentration, \( c(\text{H}_2) \), and \( c_{\text{sat}}(\text{H}_2) \):

\[
\Delta(\text{H}_2) = c(\text{H}_2) - c_{\text{sat}}(\text{H}_2).
\]

(10)

Meteorological and oceanographic parameters (radiation, air and water temperatures, salinity, relative humidity) were measured using standard instrumentation and recorded and provided by the data system of the ships. More information about devices and sensor documentation can be found on the website of the Alfred Wegener Institute http://dship.awi.de. Backward trajectories were calculated using the backward “Hybrid Single Particle Lagrangian Integrated Trajectory” (HYSPLIT, Schlitzer, 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

We performed simulations of \( \text{H}_2 \) 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-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, \( \text{HH} \) and HD are treated separately and have different reaction rates).

The \( \text{H}_2 \) sources and isotopic signatures are given as input; these and also the \( \text{H}_2 \) soil deposition velocities are identical to Pieterse 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

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 \( \text{H}_2 \) source of 5 Tg a\(^{-1}\) as given from global budget calculations (see Ehnhalt and Rohrer, 2009, and references therein, Pieterse et al., 2013). The spatial and temporal variability of oceanic \( \text{H}_2 \) emissions caused by \( \text{N}_2 \) fixation are adopted from the spa-
and temporal distribution of oceanic CO (Erickson and Taylor, 1992).

3 Results and discussion

3.1 Atmospheric H₂ transects

Our data set includes data of two hemispheres and two seasons between 2008 and 2010 (see Table 2, Fig. 4). The mean mole fraction of H₂ ranged between (532.0 ± 10.7) and (548.5 ± 6.8) ppb. In spring, the mean values were almost equal between the hemispheres with approximately 1 to 2 ppb difference, but they differed significantly in autumn. In this season, the mean values in the Northern Hemisphere (NH) were approximately 16 ppb or 3 % lower compared to the Southern Hemisphere (SH), with a distinct transect pattern. In the NH, the mole fraction during this season ranged between (140.5 ± 21.1) and (145.4 ± 5.3) ‰. In contrast, D values differed significantly between the hemispheres in both seasons. In the Southern Hemisphere, absolute δD values were always between 9 and 27 ‰ higher than in the NH, and higher microbial activity in the summer, the mole fraction during this season was always between 9 and 27 ‰ higher than in the Northern Hemisphere (NH), with a distinct transect pattern. In the NH, mole fractions and isotopic composition δD 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 δD values between the hemispheres. In winter, molecular hydrogen is accumulating in the NH, and the main source is fossil fuel combustion with a depleted isotopic composition. The NH isotopic signature is caused by mainly emissions and chemical loss with an isotope delta of approximately −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 δD gradient, with isotopically lighter H₂ 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 H₂ seasonal cycle in the NH is much weaker compared to the NH. The SH isotopic H₂ signature is caused by mainly emissions and chemical loss with an isotope delta of approximately +190 ‰, which explains the generally higher δD values. The Intertropical Convergence Zone (ITCZ) separates the two hemispheres and is clearly visible, not only in the H₂ distribution, but also in the CO distribution.

Simulations of H₂ 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 H₂ 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 emiss-
Figure 4. $\delta D (\text{H}_2) \text{‰}$ (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.
Spatial and temporal high-resolution transects during ANT-XXV/5

In April 2009 the sampling resolution was increased to approximately one sample per 2 h for five selected sections of the transect during ANT-XXV/5 (Fig. 4, Table 3): three in the Southern Hemisphere, one crossing the equator and one in the Northern Hemisphere. These transects were chosen based on previously published data (Herr et al., 1984; Conrad and Seiler, 1988) and with the aim to get an indication of small-scale sources or diurnal cycles of atmospheric \( \text{H}_2 \) for further investigations.

All transects showed neither a diurnal cycle nor a correlation with radiation and a range of \( \delta \text{D} \) values within or only slightly outside a 2σ range around the mean, except for the one between 23.5 to 15.7°S (Fig. 6a). Here the highest \( \text{H}_2 \) mole fractions of \( 631.9 \pm 3.2 \) ppb, combined with the lowest \( \delta \text{D} \) values of \( 20.9 \pm 5.0 \) ‰, were found around 16°S. Due to the limited spatial resolution and therefore low number of 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 2010 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 \( \text{H}_2 \) mole fractions and \( \delta \text{D} \) values. These findings indicate a strong but local source, and the low \( \delta \text{D} \) 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 \( \text{H}_2 \) mole fractions in surface waters was reported previously in correlation to high \( \text{N}_2 \) fixation rates (Moore et al., 2009, 2014). Although reported for other oceanic regions, the \( \text{H}_2 \) mole fractions and \( \delta \text{D} \) values here neither show a diurnal cycle (Herr et al., 1984), nor are they 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 \( \text{H}_2 \) 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 \( \text{H}_2 \) cy-
Figure 5. Comparison of measurement results of H\textsubscript{2} and CO mole fractions and δD with TM5 model results (given in red). Data are shown against latitude. The blue markers show results of flask samples, and 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.

3.3 Dissolved H\textsubscript{2}

A new method has been presented to extract H\textsubscript{2} from surface waters for isotopic determination. Before discussing the
measurement results, we will give an overview of the possible main errors and their effects. To show the effect of the errors on the measurements, we will present error factors, thus how much the final data differ by shifting the respective parameter by 1 % and also the absolute assumed error.

For the extraction method several error sources could be identified: the determination of pressure, especially in the sampling vessel before adding the make-up gas and during extraction, the temperature of air and water, respectively the difference between them when the sample is extracted from the headspace, and the volume of the set-up and the sample. The determination of pressure in the sampling vessel would be one issue of further improvement, because the error caused by pressure deviations for the total pressure after adding the make-up gas is about a factor of 0.7 for concentrations and 0.2 for the isotopic values. The error based on temperature of air, water and sample is negligible due to high-precision measurements and the short handling time between water sampling and headspace extraction. The error for the volume parameter for the set-up is negligible due to the high volume, the precise determination of the glass vessel volume by weighing, and the calculation of the tubing volume. The main error source is the water volume of the sample, which counts by a factor of 5.9 for the concentration, but with negligible effect on the isotopic values. Although the relative error factor is quite high, the absolute value is assumed to be around 0.5 % due to the sample size, which has also been weighed at the home lab. The H₂ measurement procedure is the same as for atmospheric samples and possible errors are described in the respective sessions or related literature. However, the error caused by the determination of the dry mole fraction itself seems to have the main input by a factor of 5.3 for concentration and 4.6 for the isotopic values of dissolved H₂. Errors of the determination of the isotopic value are much less significant and count by a factor of 0.2.

Taking measurement and handling errors during the extraction as well as errors in the determination of the dry mole fraction into account, we assume a robust overall uncertainty of ±6.9 % for the dissolved H₂ mole fractions and ±4.7 % for the isotopic values by calculating the root of the sum of the squared uncertainties.

As shown in Table 4 we also tested the effect of equilibrium isotopic fractionation and kinetic isotopic fractionation. The effect is less than 0.2 %.

Therefore, recommendations for the extraction method are to additionally measure parameters such as the initial pressure in the glass vessel and to ensure a precise determination of the sample volume. Besides this we recommend high-precision IRMS measurements and to consider multiple sampling for better statistics on the data.

### 3.3.1 H₂ 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 analyze the H₂ mole fraction and the isotopic composition (see Table 4).

Although our setup was a prototype with possibilities for improvement, the mole fractions are in line with previously published data. The H₂ excess, \( \Delta(H_2) \), exceeds 5 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 Mauritania (Fig. 7a, Table 4).

Herr et al. (1984) reported patchy enhanced H₂ concentrations in the surface water with up to 5-fold supersaturation in the subtropical south Atlantic (18–31° and 29–42° W). This is comparable to what Conrad and Seiler (1988) found in the

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**Figure 6.** (a) H₂ 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.
southern Atlantic, on a similar cruise track as the RV Polarstern. Around the equator they measured H₂ surface water concentrations up to 12-fold supersaturation. In the southern Pacific, Moore et al. (2009) combined H₂ surface water measurements with N₂ fixation measurements. They reported a strong correlation between these parameters, a patchy distribution and a steep maximum of H₂ concentrations up to 12.6 nmol L⁻¹ around 14° S.

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 sub tropics. However, our saturations are lower than the ones given by them, especially in the Northern Hemisphere. Such differences

Table 4. Overview of headspace sample results from the ANT-XXVI/4 cruise (2010) and the L’Atalante-ATA-3 (2008). χ₀ is the measured mole fraction of the headspace in parts per billion (ppb = mole mole⁻¹). δ₀ is the corresponding atmospheric mole fraction in ppb, δD₀ and δD₀ is the measured isotopic composition in permil (%). The H₂ equilibrium concentration c₀(H₂) was determined by using the equations from Wiesenburg and Guinasso (1979), the initial dissolved H₂ concentration c₀ is calculated as given in Supplement 1, and the excess ΔH₂ is the difference between them. δw₀ SC1 and δw₀ SC2 show the two scenarios to derive the initial isotope delta of dissolved H₂. S(H₂) is the saturation of H₂ in the surface water. The calculated extraction efficiency was 92.12 (±0.013)% . The calculations are given in the Supplement in more detail.

<table>
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<tr>
<th>Date/Time (UTC)</th>
<th>Sampling position</th>
<th>χ₀</th>
<th>δD₀</th>
<th>δD₀</th>
<th>c₀(H₂)</th>
<th>c₀(SC1)</th>
<th>c₀(SC2)</th>
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Figure 7. (a) H$_2$ saturation in the surface water (color coded) along the RV Polarstern cruise track of ANT-XXVI/4 and the RV L’Atalante cruise ATA-3, with maxima around the Cape Verde islands and 10–15°S. Note: each sample is represented by a single dot. (b) Comparing the δD (H$_2$) at different water temperatures, the respective H$_2$ saturation are color coded, sample dots marked with a diamond belong to the RV L’Atalante cruise, sample dots without to the ANT-XXVI/4 cruise; y = −35.2x + 360.9, $R^2 = 0.66$, $n = 22$. (c) Distribution of δD (H$_2$) (color coded) in correlation between water temperature and salinity. (d) Correlation between water temperature and H$_2$ saturation, the δD (H$_2$) is color-coded, the exceptional high saturation has been excluded from the correlation calculation, $y = 0.26x - 2.79$, $R^2 = 0.22$, $n = 21$.

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 92.12 (±0.013)% (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$_2$ 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 H₂

Additional information about H₂ sources comes from the analysis of the H₂ isotopic composition. In the literature, only one experimental value of dissolved marine δD exists, δD = −628 ‰ (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 ‰, as expected for thermodynamic isotope equilibrium between H₂ and H₂O based on the calculations of Bottinga (1969). The results presented here are the first well-documented experimental results for isotope analysis of dissolved H₂ in seawater.

From the measurement of the isotopic composition of H₂ in the headspace we calculate the isotopic composition of H₂ that was originally dissolved in the sea water as described in Sect. 2.4.3 and in the Appendix, using two different assumptions for fractionation between dissolved H₂ and H₂ in the gas phase. The results shown in Table 4 reveal δD values for the dissolved H₂ that vary within a wide range of −112 to −719 ‰ for both fractionation scenarios. Interestingly, δD shows two distinct groups of samples that can be separated by the water temperature (Fig. 7b). In water masses with a temperature above 21 °C the δD values are (−629 ± 54) ‰ (n = 14), in water masses with a temperature of 20 °C or below δD values are (−249 ± 88) ‰ (n = 8). There is no correlation of δD with salinity (Fig. 7c), but the high temperature (and low δD) waters show also a generally higher saturation than the low temperature (high δD) waters (Fig. 7d).

The very depleted isotope signature of the H₂ in the warmer water masses is consistent with the values expected for biological production. The slight enrichment compared to the value of ≈−700 ‰ that is expected for biologically produced H₂ in equilibrium with ocean water (Bottinga, 1969; Walter et al., 2012) may be caused by a partial consumption within the water, which would enrich the remaining fraction. The relatively smooth distribution of the isotopic composition of H₂ in the atmosphere strongly indicates that the contribution from atmospheric variability cannot be a main contributor of the isotope variations observed in dissolved H₂, even within the group of the depleted samples.

To our knowledge this is the first time that oceanic production of H₂ has been directly attributed to biological processes by using isotope techniques. For the samples collected from warm surface waters, our results verify the general assumption of a biological production process as a main source of oceanic H₂ to the atmosphere rather than photochemical or other sources (Herr et al., 1981; Conrad, 1988; Punshon and Moore, 2008; Moore et al., 2009). The dominance of biological formation at higher temperatures is qualitatively consistent with the general understanding of the temperature dependence of N₂ fixation rates for N₂ fixers such as e.g., Trichodesmium sp., which exhibit highest N₂ fixation rates within a temperature range between 24 to 30 °C (Breitbarth et al., 2007; Stal, 2009). In fact, the saturations also show a correlation with temperature, but less clear than for δD (Fig. 7d), presumably due to simultaneous uptake and consumption processes in a complex microbial community.

However, this clear attribution is only valid in water masses with higher temperatures and the unexpectedly high δD values in cooler waters indicate the influence of other processes. The isotopic enrichment that is expected for removal of H₂ (Chen et al., 2015; Rahn et al., 2003; Constant et al., 2016) is highly unlikely to cause a shift of almost 400 ‰ in δD 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 H₂ (Chen et al., 2015). We suggest that a source of H₂ must exist in these surface waters, which produces H₂ 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 abiogenic photochemical H₂ 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 H₂ with high δD values. It is thus possible that abiogenic photochemical production in the surface water might be an alternative source of H₂ excess, which is not isotopically equilibrated with water, especially in regions with high radiation and biological activity, and less N₂ 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 H₂ 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 H₂ measurements, Moore et al. (2014) suggested a substantial underestimation of oceanic N₂ fixation, especially due to high H₂ supersaturations measured in the Southern Hemisphere. By using direct measurements of N₂ fixation rates, a systematic underestimation by approximately 60 % was also proposed by Großkopf et al. (2012) who suggested a global marine N₂ fixation rate of (177 ± 8) Tg N a⁻¹. In order to identify a possible significant mismatch between N₂ fixation rates and total marine H₂ 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 H₂ source of 5 Tg a⁻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 H₂ sea-to-air fluxes mostly in the range of (10 ± 5) mmol, m⁻² 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 Tg N a⁻¹ and an additional 20 Tg N a⁻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 H₂ concentrations and δD and the model results from the TM5 model indicate that the oceanic emissions of H₂ to the atmosphere are actually well represented in current atmospheric models (Pieterse et al., 2013 and references herein). The proposed underestimate of oceanic N₂ fixation and a possible additional H₂ release during this process seems already be incorporated in the current atmospheric budgets of H₂. Thus, supposing that both an assumed total oceanic H₂ source of 5 Tg a⁻¹ to the atmosphere and a total global nitrogen fixation rate of approximately 177 Tg N a⁻¹ are correct, our calculations clearly support the suggestion of Großkopf et al. (2012) that N₂ fixers other than *Trichodesmium* have been severely underestimated in the global picture and that the oceanic release ratio of H₂ to fixed N₂ clearly needs more attention. Besides *Trichodesmium*, several other N₂-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-N₂-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 H₂ has been assumed to be produced mainly biologically in the oceans, direct evidence was lacking. Our results verify a biological production as a main source of H₂ 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 δD values in colder temperate water masses indicate the significant influence of processes other than then biological production, and additional information, e.g., by isotopic composition is needed to distinguish and verify possible sources and supersaturations of dissolved oceanic H₂. Especially the investigation of the isotopic composition of possible production pathways such as abiotic photochemical H₂ production needs further attention and should be an upcoming issue.

The pattern of mole fractions and isotopic composition of H₂ along a north–south Atlantic transect clearly depends on season and hemisphere and is consistent with previous published data and models. A possible significant underestimation of N₂ fixation as assumed by several authors could – providing a net H₂ release rate – go along with higher H₂ 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 H₂ budget is reasonable and in general reproduced well; therefore, a proposed underestimation in the oceanic N₂ fixation seems already to be corrected (from atmospheric considerations) in the current atmospheric budgets of H₂. 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 H₂ the composition of N₂ fixer communities and the release ratio of H₂ to N₂ fixed needs more investigation to understand the general processes and distributions of oceanic H₂ in more detail.

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