



High-resolution measurements of atmospheric molecular hydrogen and its isotopic composition at the West African coast of Mauritania

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Abstract. Oceans are a net source of molecular hydrogen (H_2) to the atmosphere, where nitrogen (N_2) fixation is assumed to be the main biological production pathway followed by photochemical production from organic material. The sources can be distinguished using isotope measurements because of clearly differing isotopic signatures of the produced hydrogen.

Here we present the first ship-borne measurements of atmospheric molecular H_2 mixing ratio and isotopic composition at the West African coast of Mauritania (16–25° W, 17–24° N). This area is one of the biologically most active regions of the world's oceans with seasonal upwelling events and characterized by strongly differing hydrographical/biological properties and phytoplankton community structures. The aim of this study was to identify areas of H_2 production and distinguish H_2 sources by isotopic signatures of atmospheric H_2 . For this more than 100 air samples were taken during two cruises in February 2007 and 2008. During both cruises a transect from the Cape Verde Islands towards the Mauritanian Coast was sampled to cover differing oceanic regions such as upwelling and oligotrophic regimes. In 2007, additionally, four days were sampled at high resolution of one sample per hour to investigate a possible diurnal cycle of atmospheric H_2 .

Our results indicate the influence of local sources and suggest the Banc d'Arguin as a pool for precursors for photochemical H_2 production, whereas oceanic N_2 fixation could not be identified as a source for atmospheric H_2 during these two cruises. The variability in diurnal cycles is probably influenced by released precursors for photochemical H_2 production and also affected by a varying origin of air masses. This means for future investigations that only measuring the

mixing ratio of H_2 is insufficient to explain the variability of an atmospheric diurnal cycle and support is needed, e.g. by isotopic measurements. Nevertheless, measurements of atmospheric H_2 mixing ratios, which are easy to conduct on-line during ship cruises, could be a useful indicator of production areas of biological precursors such as volatile organic compounds (VOCs) for further investigations.

1 Introduction

Molecular hydrogen (H_2) is the second most abundant reduced compound in the atmosphere after methane (CH_4), with a global average mixing ratio of ~ 530 ppb and an atmospheric lifetime of ~ 2 yr. H_2 is not a radiatively active gas itself, but it contributes significantly to atmospheric chemistry (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002; Rahn et al., 2003; Ehhalt and Rohrer, 2009). By reaction with the hydroxyl radical ($\cdot OH$), it indirectly influences atmospheric levels and lifetimes of gases that also react with $\cdot OH$, e.g. the strong greenhouse gas CH_4 and carbon monoxide (CO) (Prather, 2003; Schultz et al., 2003; Jacobson et al., 2005; Jacobson, 2008). In the stratosphere, oxidation of H_2 is a source of water vapor. Water vapor is important for the radiative properties of the stratosphere and also forms the substrate for polar stratospheric clouds, which are key ingredients in the formation of the polar ozone holes (Tromp et al., 2003; Warwick et al., 2004; Feck et al., 2008; Jacobson et al., 2008).

H_2 is considered one of the promising future energy carriers, and the shortage, increase in cost and climate impact of fossil fuels leads to increasing interest in alternative energy

carriers. Numerous studies in the past have addressed the global atmospheric budget of H_2 . Photooxidation of CH_4 and non-methane volatile organic compounds (NM-VOC) in the atmosphere and combustion processes are the main H_2 sources, whereas soil deposition and oxidation by $\cdot OH$ 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, the range of oceanic contribution from 1% to 15% between different studies indicates high uncertainties (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 (Conrad, 1988). Regarding stoichiometry, the theoretical H_2 production is equimolar to the N_2 fixation, but due to recycling processes by uptake hydrogenases the production rate is less than the theoretical value and depends on environmental conditions and also on species (Bothe et al., 1980; Tamagnini et al., 2007; Wilson et al., 2010a). Moore et al. (2009) showed recently a strong correlation between the N_2 fixation rate and H_2 supersaturation in the equatorial Pacific surface waters. Besides N_2 fixation, also abiotic photochemical production from chromophoric dissolved organic matter (CDOM) and small organic compounds such as acetaldehyde or syringic acid has been found to be a source of hydrogen in the oceans and should be taken into account (Punshon and Moore, 2008a, and references therein).

However, the temporal and spatial contribution of these processes to the global budget is unclear because of a lack of measurements. To present knowledge, tropical and subtropical surface layers are supersaturated 2 to 3 times with respect to atmospheric H_2 concentrations and are a source of hydrogen to the atmosphere, in contrast to temperate and polar surface waters, which are undersaturated in hydrogen (Scranton et al., 1982; Herr et al., 1984, 1981; Herr, 1984; Conrad and Seiler, 1988; Seiler and Schmidt, 1974; Punshon et al., 2007). Vertical profiles display highest mixing ratios in the surface layer with 1 to 3 $nmol L^{-1}$ and a sharp decrease with depth towards undersaturation, whereas the reasons for undersaturation are not fully understood yet (e.g. Herr et al., 1981; Scranton et al., 1982; Conrad and Seiler, 1988). The H_2 production by diazotrophs has been studied intensively and several species show a high potential to produce H_2 under natural conditions (e.g. Bothe et al., 2010; Schütz et al., 2004; Wilson et al., 2010a,b; Punshon and Moore, 2008b; Scranton, 1983; Moore et al., 2009), however, the contribution of the different diazotrophs to the marine H_2 cycle is unknown. The majority of simultaneous measurements of N_2 fixation and H_2 production have been conducted on *Trichodesmium* spp. (Wilson et al., 2010a; Punshon and Moore, 2008b; Scranton et al., 1982), one of the major N_2 fixers in the oceans (Capone et al., 2005). Estimates suggest an annual new N input of at least 1.6×10^{12} mol N to the tropical North Atlantic, which means a substantial fraction of approximately 10–20% of the global N_2 fixation of 100–200 $Tg yr^{-1}$ (Capone et al., 2005;

Karl et al., 2002; Deutsch et al., 2007), and measurements on H_2 production by *Trichodesmium* indicate that a major part of the dissolved H_2 in the ocean is coming from this species, although it cannot account for the total rate of N_2 fixation (Wilson et al., 2010a; Punshon and Moore, 2008b; Montoya et al., 2007). *Trichodesmium* spp. is mostly restricted to tropical regions characterized by warm ($> 22^\circ C$) surface waters and strong vertical stability (Capone et al., 1997; Tyrrell et al., 2003; Breitbarth et al., 2007), and the eastern tropical North Atlantic is a well-known area for N_2 fixation with *Trichodesmium* spp. considered as one of the dominant species there (Voss et al., 2004; Tyrrell et al., 2003; Fernández et al., 2010; Davis and McGillicuddy jr., 2006). Besides *Trichodesmium*, several other N_2 -fixing organisms like proteobacteria and unicellular cyanobacteria are common in the tropical oceans, and some species are also 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). It is assumed, that H_2 production follows a diurnal cycle, but so far published data on dissolved H_2 are contradictory. In the oligotrophic South Atlantic, Herr et al. (1984) reported a clear diurnal cycle in the tropical South Atlantic, whereas Conrad and Seiler (1988) in the equatorial Atlantic only found a tendency towards higher H_2 mixing ratios in correlation with sunlight. Setser et al. (1982) found a dramatic increase of dissolved H_2 mixing ratios when entering warm coastal waters in the northern Pacific and a strong correlation with biological activity, which was not visible in colder open ocean waters. They found no clear daily cycle. Besides this they recalculated data from Bullister et al. (1982), who reported a daily cycle during a CEPEX container experiment. Setser et al. (1982) concluded that there was no positive evidence for a daily cycle of H_2 . However, laboratory experiments give clear evidence that H_2 production can be correlated with sunlight and depends on species, e.g. the biological production by diazotrophs (Wilson et al., 2010a) and also non-biological production by solar degradation of CDOM (Punshon and Moore, 2008a).

Additional information to the global budget and insights in production pathways could come from the analysis of the H_2 isotopic composition (δD) (definition see Sect. 2.2). The different sources produce H_2 with a very different deuterium content, and also the kinetic fractionation in the two main removal processes, soil deposition and reaction with $\cdot OH$, is different. This leads to tropospheric H_2 which is enriched in deuterium with $\delta D \sim +130\text{‰}$ (Gerst and Quay, 2001; Rhee et al., 2006a; Rice et al., 2010; Batenburg et al., 2011), whereas surface emissions from fossil fuel combustion and biomass burning have δD values of approximately -200‰ and -300‰ , respectively (Gerst and Quay, 2001; Rahn et al., 2002; Röckmann et al., 2010a; Vollmer et al., 2010). As originally proposed by Gerst and Quay (2001) from budget closure, the photochemical sources of H_2 are also enriched in deuterium with δD between $\sim +100\text{‰}$ and $+200\text{‰}$ (Rahn et al., 2003; Röckmann et al., 2003, 2010b;

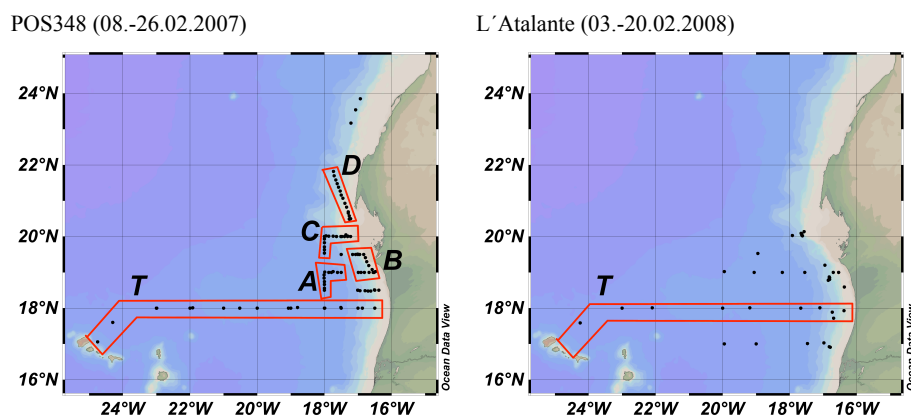


Fig. 1. Sampling positions (black dots) during POS 348 (2007, left) and *L'Atalante* (2008, right). The labels A to D indicate the four days with high sample resolution during the POS 348 cruise. Each label indicates one day of sampling: A: 20 February 2007, B: 21 February 2007, C: 22 February 2007, and D: 23 February 2007. The label T indicates the transect along 18° N (Schlitzer, 2012).

Feilberg et al., 2007; Nilsson et al., 2007, 2010; Pieterse et al., 2009). Biologically produced H_2 has the most exceptional isotopic composition with a δD below -700 ‰ (Walter et al., 2012).

The aim of this study was to examine whether the isotopic signature of atmospheric H_2 could be used to identify oceanic areas of expected biological H_2 production, which means areas of expected N_2 fixation. Based on the up-to-date knowledge described previously, we focussed on a tropical region where we could expect H_2 emissions probably produced by N_2 fixation. Assuming a release of measurable amounts of biologically produced H_2 , the combination and comparison of hydrographical and biological data together with atmospheric H_2 mixing ratios and isotopic signatures should point towards source processes and areas. We took atmospheric samples along a transect from the West African coast off Mauritania towards the open ocean in the direction of the Cape Verde Islands and also in the upwelling region off the Mauritanian coast to cover differing oceanic regions such as upwelling and oligotrophic regimes. Besides this we investigated a possible diurnal cycle of atmospheric H_2 .

2 Methods

2.1 Study area

The eastern tropical North Atlantic Ocean between Cape Verde and the Mauritanian coast (see Fig. 1) is characterized by strongly differing hydrographical and biological properties (Kock et al., 2008, and references herein). During late winter and spring, the northeast trade winds induce an intensive seasonal upwelling occurring within a narrow band along the continental margin with typical sea-surface temperatures around or below 17 °C (Mittelstaedt, 1983; Hagen, 2001). This causes strong gradients between the coastal area and the open ocean towards Cape Verde Islands re-

garding nutrient concentration and primary production (Signorini et al., 1999; Minas et al., 1982). Phytoplankton pigment measurements show that the upwelling is characterized by diatoms, whereas cyanobacteria (including *Synechococcus*, *Prochlorococcus*, and *Trichodesmium*) dominate in the oligotrophic open ocean waters west of 18 ° W (Bange, 2008; Zindler et al., 2012).

2.2 Sampling

Atmospheric samples were taken onboard the research vessels RV *Poseidon* (POS 348, 8–26 February 2007) and RV *L'Atalante* (3–20 February 2008) at the west coast of Mauritania. Both cruises covered a sampling area along the coast of Mauritania and included a transect along 18 ° N towards the Cape Verde Islands (Fig. 1). Samples were taken upwind in 1 L borosilicate glass flasks at the bridge deck regularly during the cruises. The flasks (NORMAG) are black coated to minimize photochemical reactions inside and sealed with 2 Kel-F (PCTFE) O-ring sealed valves. Storage tests indicate that glass flasks equipped with Kel-F valves are stable for H_2 (Rothe et al., 2004; Jordan and Steinberg, 2011). All flasks were previously conditioned by flushing with N_2 at 50 °C for at least 12 h. N_2 remained in the flasks 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 PM22874-86 N86ANDC). The sample air was dried with Drierite[®] ($CaSO_4$). The flasks were finally pressurized to approximately 1.7 bar, which allows duplicate measurements for the isotopic composition of an air sample. In total, 40 air samples from the *L'Atalante* and 75 air samples from the POS 348 were taken. During POS 348 four days were sampled with a high temporal and spatial resolution of one sample per hour at approximately every 30 km (Fig. 1).

2.3 Measurements

The atmospheric mixing ratio and isotopic composition of molecular H₂ were determined using the experimental setup developed by Rhee et al. (2004) and modified as described in Röckmann et al. (2010b). Briefly, the measurements consist of the following steps: (1) An air sample (typically a volume of ~500 mL at standard temperature and pressure) is exposed to a helium-cooled cold head at -240 °C, where all gaseous compounds with exception of H₂ and some noble gases are condensed; (2) The non-condensed fraction of the sample including H₂ is flushed to a preconcentration trap at -210 °C, consisting of 5 Å molecular sieve in a stainless steel tube (1/8"OD); (3) H₂ is released and focused on a capillary gas chromatographic column (filled with molecular sieve 5 Å) immersed in liquid nitrogen (-196 °C); (4) the separated H₂ is gas chromatographically purified from remaining contaminants at 50 °C; (5) the D/H ratio of molecular H₂ is determined by continuous flow isotope ratio mass spectrometry (IRMS) using a ThermoFinnigan Delta Plus XL instrument. The D/H ratio in a sample is quantified as the relative deviation from the same ratio in a standard, as δD value, and reported in per mille (‰):

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

All δD values are reported relative to Vienna Standard Mean Ocean Water (VSMOW). H₂ mixing ratios are reported as molar mixing ratios in parts per billion (ppb = nmol mol⁻¹) and linked to the MPI-2009 calibration scale for atmospheric hydrogen (Jordan and Steinberg, 2011). Pure H₂ gas was used as running gas for the mass spectrometer. As working standards we used atmospheric air from laboratory reference air bottles and synthetic air mixtures. The atmospheric reference air was collected by the Institute for Environmental Physics (IUP), University of Heidelberg. The H₂ mixing ratio was determined by IUP to be 546.2 ± 2.5 ppb and confirmed by the Max Planck Institute for Biogeochemistry to be 545.0 ± 0.5 ppb. The δD was determined to be 71.4 ± 2.0 ‰, using mixtures of synthetic isotope reference air with H₂ of known isotopic composition of -9.5 ± 0.5 ‰ and +205 ± 2 ‰, certified by Messer Griesheim, 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 given errors are random (i.e. reproducibility) errors only and do not include possible systematic errors (Batenburg et al., 2011; Walter et al., 2012). Samples were measured randomly and within less than 15 weeks after collection, and for both sample sets (2007 and 2008) the same standards were used (atmospheric reference air and synthetic isotope reference air).

To determine the overall mean reproducibility, several samples were measured twice. The average reproducibility was 6.5 ppb for H₂ mixing ratio and 2.5 ‰ for δD for the

POS 348 ($n = 19$), and respectively 7.2 ppb and 5.0 ‰ for the *L'Atalante* ($n = 7$).

Meteorological and oceanographic parameters (radiation, air and water temperatures, salinity, relative humidity) were measured using standard instrumentation, and recorded and provided by the data systems 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/>, and Ifremer, the French Research Institute for Exploration of the Sea, <http://flotte.ifremer.fr>. For each sample a backward Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) was calculated (Draxler and Rolph, 2013; <http://ready.arl.noaa.gov/HYSPLIT.php>).

3 Results and discussion

3.1 Transect along 18° N from the Cape Verde Islands toward the West African coast of Mauritania

Sea surface temperatures (SST) ranged from 16.16 °C at the Mauritanian coast to 22.74 °C near Cape Verde in 2007 and 17.70 °C and 22.10 °C in 2008, respectively, and indicate upwelling during both cruises (Mittelstaedt, 1983). During both cruises phytoplankton pigments were measured. The results show for both years that the upwelling is characterized by diatoms, whereas cyanobacteria (including *Synechococcus*, *Prochlorococcus*, and *Trichodesmium*) dominate in the oligotrophic open ocean waters west of 18° W (Bange, 2008; Zindler et al., 2012).

Figure 2 shows the H₂ mixing ratio (Fig. 2a) and the isotopic composition δD (Fig. 2b) along the 18° N transect between Cape Verde Islands and the west coast of Mauritania during the two cruises. In this and all subsequent figures, green symbols indicate the cruise with RV *Poseidon* in February 2007 and red symbols the cruise with RV *L'Atalante* in February 2008. The mean H₂ mixing ratio in 2008 was 549 ± 7 ppb, but without a clear difference between the open ocean and upwelling area. In 2007 the H₂ mixing ratio was 507 ± 6.5 ppb near the coast of Mauritania and changed significantly towards the open ocean by an increase of about 20 ppb. δD shows values between +110 ‰ and +130 ‰ with generally slightly higher values in 2007. However, during both cruises no significant depletion in the isotopic ratio towards the open ocean was found, neither in 2007 nor in 2008. There is actually a tendency of increasing δD values towards the open ocean during both cruises, but these variations are within the range of measurement uncertainties. Monthly measurements of H₂ mixing ratio and δD as part of the EUROHYDROS project (Batenburg et al., 2011) from the Cape Verde observation tower (24°87' W, 16°85' N) reveal an atmospheric H₂ background close to our results near this position (Fig. 2).

To interpret the H₂ concentration gradient in 2007, different scenarios are conceivable. We can assume either (I) an

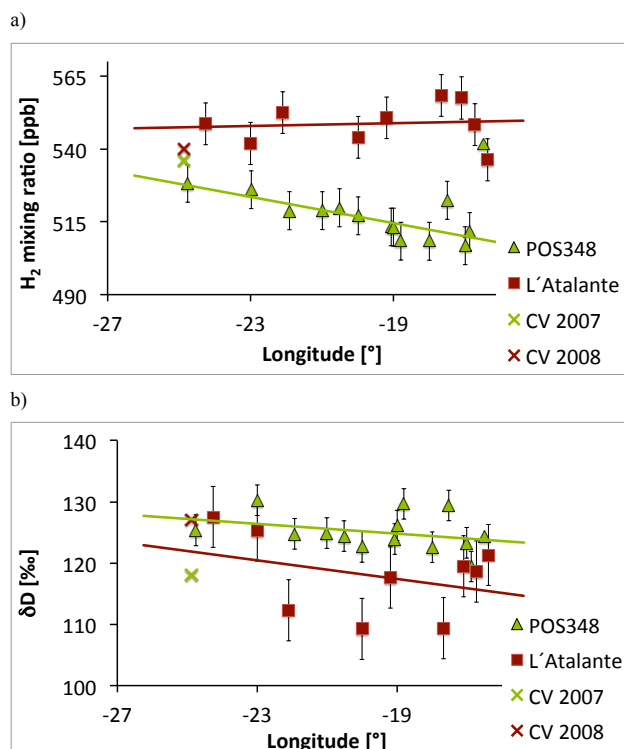


Fig. 2. H₂ mixing ratio (ppb) and δD (‰) along the 18° N transect between the Cape Verde Islands and the West African coast in 2007 (green labeled) and 2008 (red labeled). The error bars indicate the average reproducibility. The crosses (CV 2007 and CV 2008) indicate the monthly measurement results from the Cape Verde observation tower (24°87'W, 16°85'N) closest to the sampling period (29 March 2007, and 8 February 2008). The Cape Verde measurements were part of the EUROHYDROS project (Batenburg et al., 2011). (a) H₂ mixing ratio (ppb): RV *Poseidon* (2007): $-2.25x + 472$, $n = 13$, $r = 0.79$; RV *L'Atalante* (2008): $0.24x + 553$, $n = 9$, $r = 0.10$. (b) Isotopic composition δD (‰): RV *Poseidon* (2007): $-0.40x + 117$, $n = 13$, $r = 0.31$; RV *L'Atalante* (2008): $-0.76x + 103$, $n = 9$, $r = -0.35$.

increase towards the Cape Verde in 2007 caused by sources, (II) a decrease in mixing ratio towards the coast caused by sinks, or (III) an increase/decrease due to mixing of air masses, or a combination of them.

Previous studies showed that biologically produced H₂ released from aquatic systems is extremely depleted with δD values below -700 ‰ independent of species and probably from uptake/recycling within the system (Walter et al., 2012). This means that biologically produced and emitted H₂ is expected to be approximately 800‰ depleted relative to the ambient H₂ reservoir, and therefore, an increase of 1% in the H₂ mixing ratio would result in a 8‰ lower δD value. In 2007, the mixing ratio increased by 3% towards the open ocean, and if this amount were produced via N₂ fixation, a significant decrease of the isotopic signal of approximately 24‰ would be expected. An isotopic fractionation during

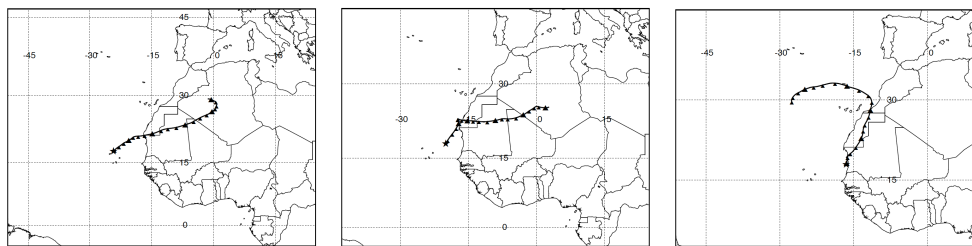
the release to the atmosphere is possible and probable, but would change this result by less than 2‰ (Knox et al., 1992; Muccitelli and Wen, 1978; Vignais, 2005) and is therefore negligible for the overall picture. Thus, a significant contribution due to N₂ fixation can be excluded.

Punshon and Moore (2008) showed that photochemical production is possible, and gave a H₂ formation rate of 37 pmol H₂ L⁻¹ h⁻¹ in coastal waters, which is 4 to 5 times lower than in lake water. The formation rates are positively correlated with CDOM concentrations and the products of its photo-degradation. Given that CDOM concentrations in the oligotrophic ocean may be an order of magnitude lower than in coastal regions (Punshon and Moore, 2008; Siegel et al., 2002), production in the open ocean should be much lower. No correlation between the mixing ratio and the radiation was found.

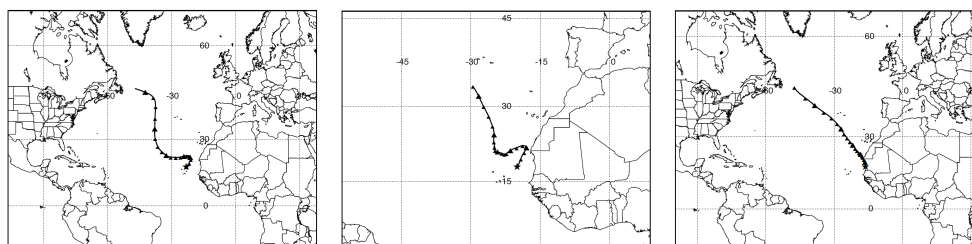
The isotopic signature of photochemically produced H₂ is expected to be between $\sim +100$ ‰ and $+200$ ‰ (Rahn et al., 2003; Röckmann et al., 2003, 2010b; Rhee et al., 2006a, b; Feilberg et al., 2007; Nilsson et al., 2007, 2010; Pieterse et al., 2009), and a Keeling plot analysis of our results reveals a source signature slightly above this range ($+218$ ‰), although with high uncertainties. We therefore cannot exclude a contribution of photochemically produced H₂; however, due to the low expected formation rates and the fact that H₂ increases towards the open ocean, a strong photochemical contribution to the atmospheric H₂ mixing ratio along this transect seems unlikely.

H₂ removal could be explained by two sink processes: the reaction with $\cdot\text{OH}$ and dry deposition to the soil. The oxidation of H₂ by $\cdot\text{OH}$ is slow and cannot explain a fast regional decrease of 20 ppb. Dry deposition to the soil is the most important sink for atmospheric H₂, and it is reasonable to assume that contact with the land surface led to a significant decrease in H₂ mixing ratio (Smith-Downey et al., 2008; Rhee et al., 2006b; Ehhalt and Röhrer, 2009). Figure 3 shows 120 h backward trajectories for the most eastern and the most western position sampled during these 18° N transects, and one in between. The trajectories were performed using the NOAA HYSPLIT model (<http://www.arl.noaa.gov/ready/hysplit4.html>), and the ones shown here are representative for the whole transect. The air mass back trajectories revealed clear differences between the two cruises regarding the origin of wind: in 2008 wind came exclusively from the oceanic sector for at least three to four days before sampling, ranging from 324° to 33° and with a mean wind speed of 15.3 ± 4.2 m s⁻¹. In contrast, in 2007 the wind came mainly from the northeast over land, crossing Morocco and Mauritania, in some cases also Algeria, in a range of 341° to 65° and with a mean wind speed of 9.9 ± 2.3 m s⁻¹. Based on this we conclude that the lower concentrations measured 2007 near the Mauritanian coast are likely a result of soil deposition. During the subsequent transport over the ocean toward the Cape Verde Islands, the H₂ mixing ratio increases due to mixing with air that had less contact with the land surface

a) Backward trajectories 2007



b) Backward trajectories 2008



http://ready.arl.noaa.gov/HYSPLIT_traj.php

Fig. 3. Backward trajectories (HYSPLIT), 120 h for representative sampling locations along the 18° N transect: (a) POS 348 (2007) and (b) *L'Atalante* (2008).

and show H₂ background mixing ratios. Thus, the mixing ratio gradient between the Cape Verde Islands and the west coast of Mauritania is likely a result of dry deposition during transport over land and mixing with H₂ enriched ambient air masses during transport over sea. The isotopic ratio measurements support this scenario. The fractionation factor for soil uptake is small, $\alpha = 0.94$ (Gerst and Quay, 2001), and the expected δD enrichment for the observed change in mixing ratio is only 2 to 3 ‰. These values are within the range of measurement uncertainty and can explain why no clear δD gradient was found. A Rayleigh analysis of our data gives an $\alpha = 0.88 \pm 0.03$ ($n = 12$, $r = 0.39$).

In 2008, mixing ratios are generally higher compared to 2007, close to background concentrations, and no trend neither in signature nor mixing ratio was observed. The wind came from the Atlantic for at least 3 to 4 days before sampling, without transport of air over land. Therefore we conclude that the results from 2008 represent remote oceanic conditions for H₂ without a soil sink signal such as during the POS 348 cruise in 2007.

3.2 Spatial and temporal high-resolution sampling at the Mauritanian coast

During all days the general weather conditions were stable without significant differences between the days (Table 1). All days were sunny and cloudless with maximum global radiation of 844 to 892 W m⁻². The wind blew stable from NNW (341°) to NE (65°) directions with wind speeds between 6 and 15 m s⁻¹. In the morning wind came more from eastern directions, shifting to the north during the

day. HYSPLIT trajectories reveal a common origin of the air masses for the previous 24 h without significant intrusions from higher altitudes (tested height of air masses 20 m, 500 m and 1000 m). The mean atmospheric mixed layer depth was approximately 500 m, with a range between 300 and 800 m.

To investigate a possible diurnal cycle, atmospheric H₂ mixing ratios from the high resolution sampling periods are compared to radiation in Fig. 4. Similar to previous published data on diurnal cycles of dissolved H₂, our results for the four days do not show a consistent picture. During the four high-resolution sampled days in 2007, the atmospheric H₂ mixing ratio showed a range of 473 ppb to 563 ppb, and δD ranged from 107 ‰ to 135 ‰ (Table 1).

All days started with a mean background mixing ratio between 500 and 520 ppb. The first two days (Fig. 4a, b) show a clear positive correlation between the two parameters. While the increase in H₂ mixing ratio was moderate (about 17 ppb) during the first day, the increase during the second day was surprisingly high (about 61 ppb). For both days, no clear trend in δD was detectable. The positive correlation between mixing ratio and radiation was not observed for the third and fourth day (Fig. 4c, d). Here we found no clear correlation with slightly decreasing mixing ratios of 9 ppb on 22 February (Fig. 4c) and a negative correlation with a decrease of H₂ mixing ratio of 44 ppb on 23 February (Fig. 4d), respectively. This negative correlation is parallel shifted in the evening to higher mixing ratios. On day 4, an increase in δD of 25 ‰ from 107 ‰ (07:24 UTC) to 132 ‰ (15:04 UTC) was observed, positively correlated with radiation.

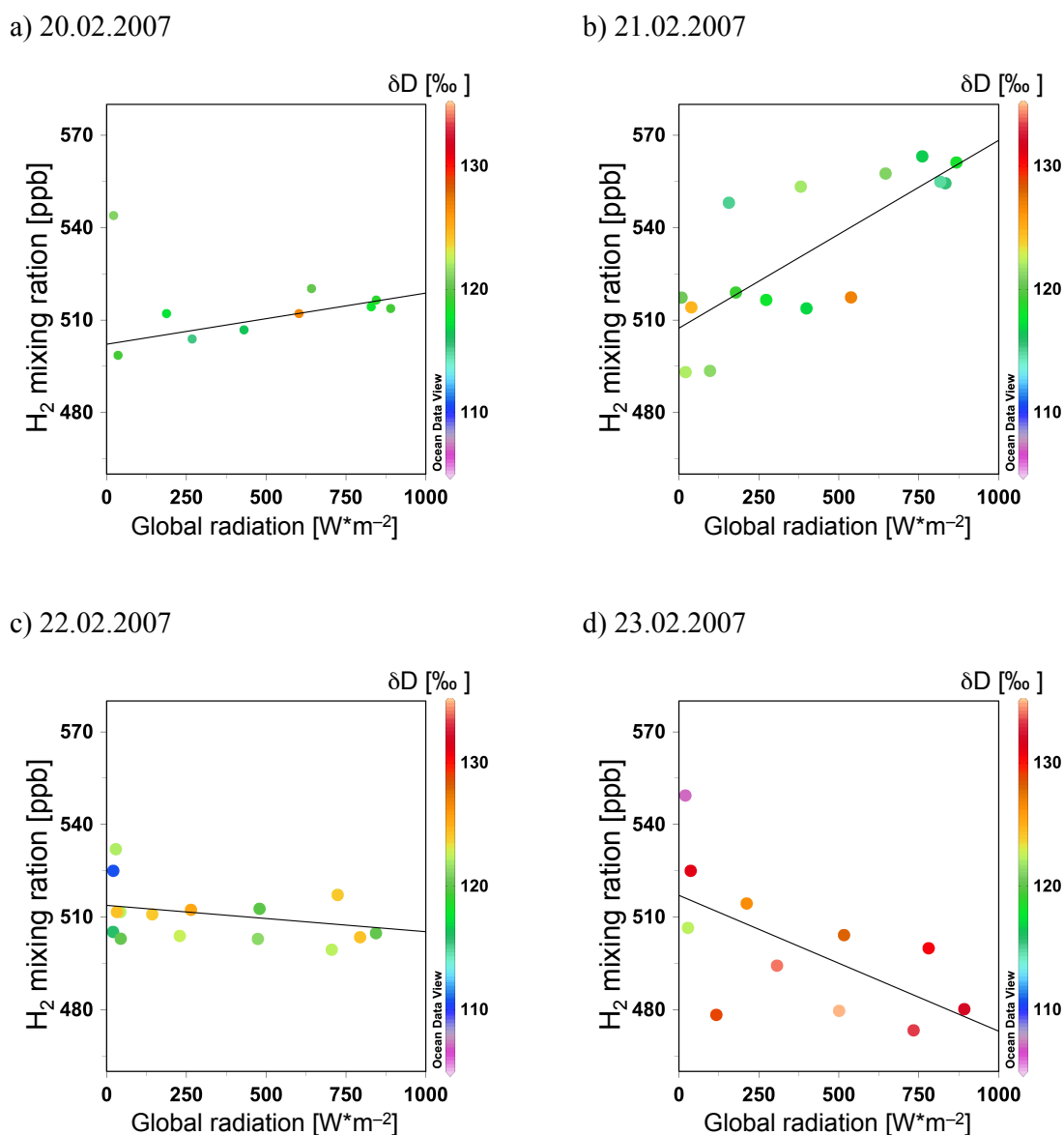


Fig. 4. Correlation between H_2 mixing ratio (ppb) and radiation (W m^{-2}) with color-coded δD (‰) during the four high-resolution sampled days 2007. (a): 20 February 2007, excluding 1 outlier (07:31 UTC), $y = 0.0167x + 502.14$, $r = 0.771$, $n = 9$; (b): 21 February 2007, $y = 0.061x + 507.38$, $r = 0.784$, $n = 15$; (c): 22 February 2007, $y = -0.009x + 513.79$, $r = -0.311$, $n = 16$; and (d): 23 February 2007, $y = -0.044x + 517.04$, $r = -0.618$, $n = 11$ (Schlitzer, 2012).

Table 1. Sampling location and weather conditions during the four high-resolution sampled days (POS 348, 2007).

Date	Location	Sampling time (UTC)	n	Range H_2 [ppb]	Range δD [‰]	Humidity (%)	Radiation [W m^{-2}]	Salinity	SST ($^{\circ}\text{C}$)	Wind direction ($^{\circ}\text{N}$)	Wind speed (m s^{-1})
20 Feb 2007	18.0° W, 18.5° N–17.5° W, 19.0° N	07:38–21:15	10	499–544	115–127	69–80	890	35.83–36.00	18.8–20.0	349–36	9.3–15.3
21 Feb 2007	17.0° W, 19.0° N–17.2° W, 19.5° N	06:31–20:30	15	493–563	115–127	45–82	868	35.56–35.89	16.2–18.3	341–60	6.1–12.3
22 Feb 2007	18.0° W, 19.5° N–17.2° W, 20.0° N	07:03–22:24	16	499–532	110–125	66–81	844	35.57–36.12	17.2–18.6	344–35	7.0–12.0
23 Feb 2007	17.3° W, 20.4° N–17.7° W, 21.8° N	07:24–21:10	11	473–549	107–135	68–82	892	36.04–36.35	17.4–18.2	1–44	6.4–13.4

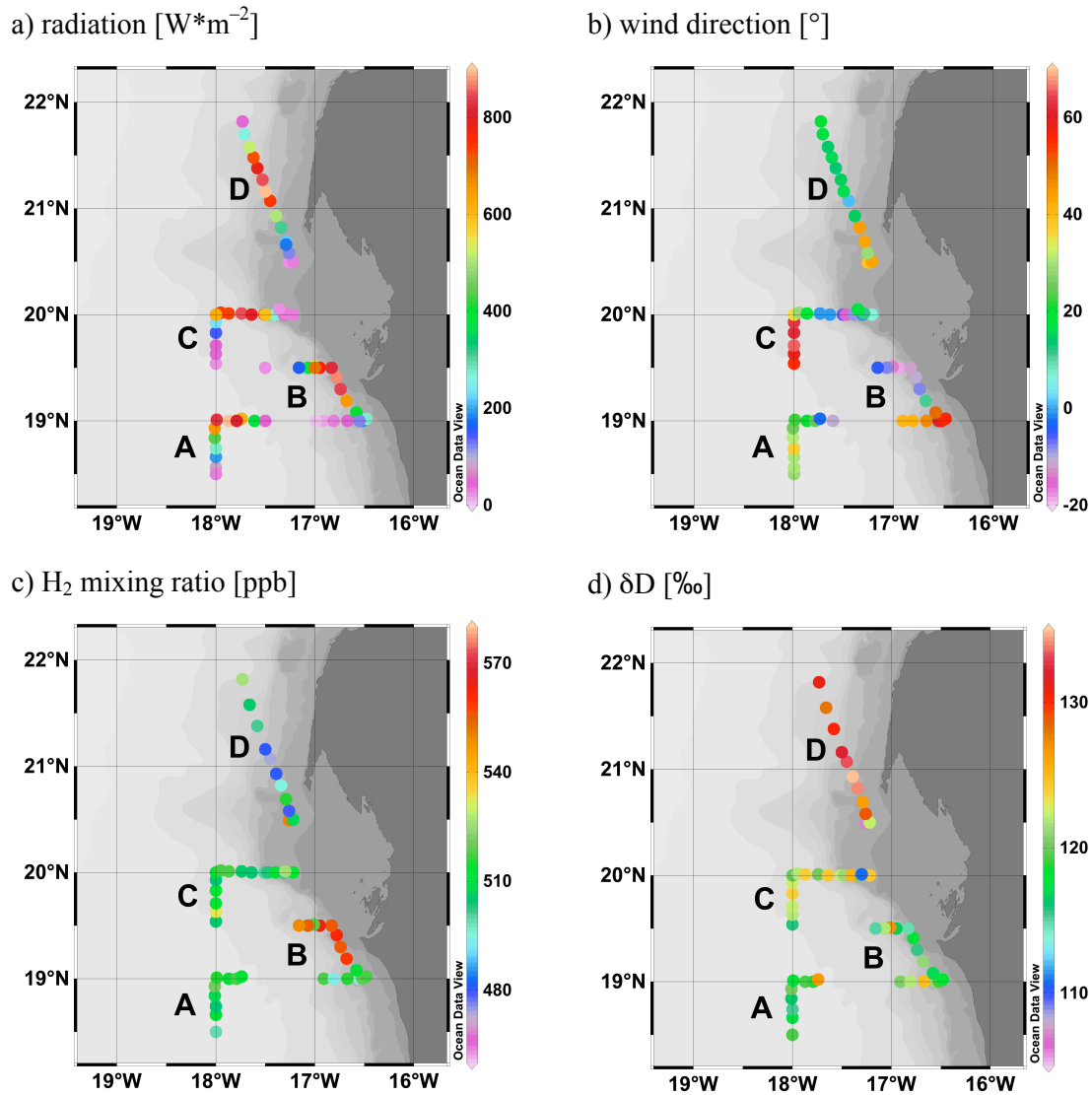


Fig. 5. Sampling positions with color-coded results for (a) radiation (W m^{-2}), (b) wind direction ($^{\circ}$), (c) H_2 mixing ratio (ppb), and (d) δD (‰). The labels in each subfigure A to D indicate the days of high-resolution sampling: A: 20 February 2007, B: 21 February 2007, C: 22 February 2007, and D: 23 February 2007. Note: the wind direction is given in a range from -180° to 180° to give a better resolution (0° means wind coming from northern directions; Schlitzer, 2012).

Intrusion of air masses from a higher altitude and contamination by biomass burning or anthropogenic sources are conceivable sources for enhanced H_2 mixing ratios during the first two days, but both are unlikely in this case due to the following reasons:

- The weather conditions were stable for all days, with no intrusion from higher altitudes. In addition, typical vertical variability in the mixing ratio is not sufficient to explain such high variations in mixing ratio found here (Schmidt, 1978; Hauglustaine and Ehnhalt, 2002; Pieterse et al., 2011).
- The wind during sampling and the days before came from northern directions; biomass burning is expected to occur further south. Due to similar wind directions and velocities, this signature would probably be visible during all days. This applies also for anthropogenic sources.
- The isotope values do not support the possibility of enhanced mixing ratios due to biomass burning or anthropogenic sources. Both sources show distinctly depleted δD values of approximately -200 to -300 ‰ (Gerst and Quay, 2001). A contribution of more than 60 ppb from these sources to the observed H_2 mixing ratio would result in a significant decrease of δD of approximately 40–50‰.



Fig. 6. MODIS picture of the west Mauritanian coast, 2006. Note: the circled area indicates the Banc d'Arguin (<http://earthobservatory.nasa.gov/IOTD/view.php?id=7240>).

For these reasons we exclude biomass burning and fossil fuel combustion as major contributors to explain the increase in H_2 mixing ratio during the first two days. The hypothesis of H_2 release as a byproduct of nitrogen fixation is also not supported by our data as well. Biologically produced hydrogen with a δD value of less than -700‰ (Walter et al., 2012) would result in an even more depleted signal than for biomass burning and fossil fuel combustion.

The strongest diurnal variation is observed on the second day. Detailed analysis of the variations of mixing ratios and δD with wind direction (see Fig. 5) shows that the second day is split in two periods by the small, typical daily shifts in wind direction: after noon the wind came more from N to NNW directions and the data show higher H_2 mixing ratios ($556\text{ ppb} \pm 5$, $n = 7$) and slightly lower δD ($117\text{‰} \pm 3$, $n = 7$), while wind from NE in the morning is associated with lower mixing ratios ($511\text{ ppb} \pm 11$, $n = 8$) and higher δD ($121\text{‰} \pm 3$, $n = 8$). Wind from NE directly came from the African continent, while wind from the more northern directions crossed the Banc d'Arguin.

The Banc d'Arguin (see circled area in Fig. 6), a national park and UNESCO World Heritage Site, is a large-scale negative estuary with no or scant river discharge and increasing water densities towards the land. The park covers an area of over $10\,000\text{ km}^2$ of shallow water and tidal flats between the Sahara and the upwelling system off the

Mauritanian coast. Its eutrophic ecosystem is highly productive and dominated by a detritus-based benthic food web in which seagrasses (*Zostera noltii*, *Cymodocea nodosa*, *Halodule wrightii*) are the principal primary producers, followed by several species of seaweeds. A mangrove swamp (3.100 ha) is a relict of a previous humid geological period (Monod, 1977; Schaffmeister et al., 2006; Dahdouh-Guebas and Koedam, 2001; Wolff et al., 1993; Sevrin-Reyssac, 1993).

Punshon and Moore (2008a) showed that H_2 could be produced non-biologically by photochemical reactions, potentially from low-molecular-weight molecules associated with chromophoric dissolved organic matter (CDOM), e.g. syringic acid or to a minor extent acetaldehyde. Syringic acid is one of the most common monophenols to be released during the degradation of lignin (Thoss et al., 2002), which is one of the major constituents of seagrasses and trees such as mangroves (Bourgues et al., 1996; Torbatinejad et al., 2007; Klap et al., 2000),

The largest source of atmospheric acetaldehyde is thought to be photochemical degradation of volatile organic compounds (VOCs), e.g. isoprene (Millet et al., 2010). Both isoprene and acetaldehyde are emitted from the ocean, e.g. from seaweeds (Broadgate et al., 2004), correlating with light and phytoplankton abundance (Sinha et al., 2007; Zepp et al., 1998). The lifetime of acetaldehyde is approximately one day, and diurnal cycles are known for several low-molecular-weight carbonyl compounds, not only acetaldehyde but also formaldehyde (Singh et al., 2004; Zhou and Mopper, 1997). Until now the global budget of these reactive trace gases is highly uncertain and no information about the isotopic composition of photochemically produced H_2 from non-methane hydrocarbons (NMHC) exist, although a contribution of $\sim 20\%$ to the total photochemical production is estimated (see Ehhalt and Rohrer, 2009; Pieterse et al., 2011, and references herein). For global models a δD of $+162\text{‰}$ is assumed (Rice et al., 2010), and recently Pieterse et al. (2011) calculated a δD value of $+116\text{‰}$. Keeling plot analyses of the first two days give a mean source signature of 98‰ , within a range of 82‰ to 265‰ , depending on spatial or temporal clustering of the data. These data clearly exclude biological sources as the main contributors to the observed results and support the hypothesis of photochemical production. The data suggest that large amounts of precursors for photochemical production of H_2 may be emitted from the Banc d'Arguin and that the subsequent photochemical production may cause the observed H_2 increase during the second day. As the wind direction changes in a similar way, this could also explain the results of the first and third day.

The same pattern as of the second day was also found for dissolved and atmospheric CH_4 (Kock et al., 2008, and additional unpublished data). Although in this study the water column was supersaturated with CH_4 , the emissions from surface waters were not considered sufficient to explain the

full increase in mixing ratios. Therefore, the authors also assumed a possible contribution from the Banc d'Arguin.

During the fourth day we observed a decrease in mixing ratio of 44 ppb (Fig. 4d), which is negatively correlated with radiation and parallel shifted to higher mixing ratios in the evening. The δD values increased in the mean by about 13 ‰, positively correlated with radiation. As argued above, the oxidation of H_2 by $\cdot OH$ is slow and cannot explain the decrease of 44 ppb during the day. A decrease in mixing ratio of 44 ppb mainly due to soil deposition would result in an increase of isotopic ratios of approximately 9 ‰, which fits with our results. The HYSPLIT model reveals stable wind from on-shore, with a shallow mixed layer depth and no intrusions of air masses from higher altitudes. During the day the wind shifts slightly towards the open ocean. This results in a shorter transport time over land and might explain the slight shift of correlation towards higher mixing ratios and lower delta values because of less deposition. A Rayleigh analysis gives an $\alpha = 0.89$ ($n = 11$, $r = -0.77$) and supports this hypothesis.

Therefore we suggest that the decrease in mixing ratio combined with the slight increase of isotopic signature is probably related to the soil sink and mixing with remote air, comparable to the results of the 18° N transect.

4 Conclusions

The aim of this study was to identify areas of H_2 production and distinguish H_2 sources by isotopic signatures of atmospheric H_2 . Besides this, a diurnal cycle of atmospheric H_2 was investigated. A biological source of atmospheric H_2 such as N_2 fixation could not be identified by isotopic measurements, although Cyanobacteria (including *Trichodesmium*) have been shown to be one of the dominant species in the region outside the upwelling area. The data indicate that probably photochemical sources in biologically active areas such as the Banc d'Arguin play an important role, and suggest that these areas may release significant amounts of precursors, which are then photochemically degraded and produce H_2 .

The variability in diurnal cycles is probably influenced by released precursors for photochemical H_2 production and also affected by a varying origin of air masses. This means for further investigations that only measuring the mixing ratio of H_2 is insufficient to explain the variability of an atmospheric diurnal cycle and support is needed, for example, by isotopic measurements. However, measurements of H_2 mixing ratios, which are easy to conduct online during ship cruises, could be a useful indicator of production areas of biological precursors such as volatile organic compounds for further investigations. Considering the size and the importance of the oceans for trace gases, the ocean's influence is poorly understood.

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