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

S. Walter[1], **A. Kock**[2], **and T. Röckmann**[1]

[1]Institute for Marine and Atmospheric Research (IMAU), Utrecht University, The Netherlands
[2]Marine Biogeochemistry, GEOMAR/Helmholtz-Centre for Ocean Research, Kiel, Germany

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Correspondence to: S. Walter (s.walter@uu.nl)

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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 besides 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. Besides this a diurnal cycle of atmospheric H_2 was investigated. For this more than 100 air samples were taken during two cruises in February 2007 and 2008, respectively. During both cruises a transect from the Cape Verde Island towards the Mauritanian Coast was sampled. In 2007 additionally four days were sampled with a high resolution of one sample per hour.

Our results clearly indicate the influence of local sources and suggest the Banc d'Arguin as a pool for precursors for photochemical H_2 production, whereas N_2 fixation could not be identified as a H_2 source during these two cruises. With our experimental setup we could demonstrate that variability in diurnal cycles is probably influenced and biased by released precursors for photochemical H_2 production and the origin of air masses. This means for further investigations that just measuring the mixing ratio of H_2 is insufficient to explain the variability of a diurnal cycle and support is needed, e.g. by isotopic measurements. However, measurements of H_2 mixing ratios, which are easy to conduct online during ship cruises could be a helpful tool to easily identify production areas of biological precursors such as VOC´s 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 radiative 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) and by reaction with the hydroxyl radical (•OH), it indirectly influences atmospheric levels and lifetime of gases that also react with •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, which 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 as 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, but still none of the individual source or sink strengths is constrained to better than ±25 % (Ehhalt and Rohrer, 2009). Additional constraints could come from the analysis of the H_2 isotopic composition (δD, definition see Sect. 2.2), because the different sources produce H_2 with a very different deuterium content. Also the kinetic fractionation in the two main removal processes, soil deposition and reaction with •OH, is different.

Tropospheric H_2 is enriched in Deuterium with δD ~ +130 ‰, (Gerst and Quay, 2001; Rhee et al., 2006; 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 ~ +100 ‰ and +200 ‰, (Rahn et al., 2003; Röckmann et al., 2003, 2010b; 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). Due to this very depleted isotopic ratio even small amounts of biologically produced H_2 can be detected.

Photooxidation of CH_4 and non-methane volatile organic compounds (NM-VOC) in the atmosphere and combustion processes are the main H_2 sources, but oceans also contribute significantly to the global H_2 budget (Novelli et al., 1999; Hauglustaine and Ehalt, 2002; Ehalt and Rohrer, 2009). Oceanic H_2 production is assumed to be mainly biological as a byproduct of nitrogen (N_2) fixation (N_2+ 8 H^++ 8 e^-+ 16 ATP → 2 NH_3+ H_2+16 ADP + 16 P_i) (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 a source of hydrogen to the atmosphere, in contrast to temperate and polar surface waters, which are undersaturated with hydrogen (Scranton et al., 1982; Herr et al., 1981, 1984; 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 up to undersaturation (e.g. Conrad and Seiler, 1988; Moore et al., 2009). 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 and 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 °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* sp. considered as one of the dominant species here (Voss et al., 2004; Tyrell et al., 2003; Fernandéz 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).

The aim of this study was to examine whether oceanic areas of expected biological H_2 production, that means areas of N_2 fixation, could be identified by an isotopic depletion of atmospheric H_2 due to the emission of biologically produced H_2. To investigate this, we sampled in 2007 and 2008 the upwelling region at the West African coast of Mauritania as well as a transect towards the open ocean in the direction of the Cape Verde Islands. The eastern tropical North Atlantic Ocean between Cape Verde and the Mauritanian coast (see Fig. 1) is characterized by strongly differing hydrographic 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 regarding nutrient concentration and primary production (Signorini et al., 1999; Minas et al., 1982). Zindler et al. (2012) demonstrated for 2008 that the major phytoplankton group in the upwelling area were diatoms, whereas cyanobacteria (including *Synechococcus*, *Prochlorococcus*, and *Trichodesmium*) are dominating in the oligotrophic open ocean waters west of 18° W. The idea was to investigate if this gradient could cause an increase of N_2 fixation towards the open ocean visible by an increase of atmospheric H_2 mixing ratio and a resulting depletion of isotopic ratios. Besides this we investigated a possible diurnal cycle of H_2 production in the atmosphere. So far published data on dissolved H_2 are contradictory. In the oligotrophic South Atlantic Herr et al. (1984) reported a clear dial 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 and concluded that there was no positive evidence for a daily cycle of H_2. However, laboratory experiments give clear evidence that H_2 production is correlated with sunlight and depending 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). Due to the differing isotopic signature of H_2 produced by these two processes, they should be clearly distinguishable with isotope measurements.

2 Methods

2.1 Sampling

Atmospheric and water samples were taken onboard the research vessels FS Poseidon (POS 348, 08.02.2007–26.02.2007) and RV L'Atalante (03.02.2008–20.02.2008) 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 1L 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 (Jordan and Steinberg, 2011). All flasks were 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).

2.2 Measurements

The mixing ratio and isotopic composition of molecular H_2 was determined using the experimental setup developed by Rhee et al. (2004) and modified as described in Röckmann et al. (2010b). The measurements consist briefly 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 H_2 and some noble gases are condensed; (2) the non-condensed fraction of the sample including H_2 is flushed to a preconcentration trap at −210 °C, consisting of 5Å molecular sieve in a stainless steel tube (1/8″); (3) H_2 is released and focused on a capillary gas chromatographic column (filled with molecular sieve 5Å) immersed in liquid nitrogen (−196 °C); (4) the separated H_2 is gas chromatographically purified from remaining contaminants at 50 °C; (5) the D/H ratio of molecular H_2 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 (‰):

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

All δD values are reported relative to Vienna Standard Mean Ocean Water (VSMOW). H_2 mixing ratios are reported as molar mixing ratios in parts per billion (ppb = nmole mole^{-1}) and linked to the MPI2009 calibration scale for atmospheric hydrogen (Jordan and Steinberg, 2011). Pure H_2 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 H_2 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 H_2 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 H_2 mixing ratio and 2.5 ‰ for δD for the POS 348 ($n = 19$), respectively 7.2 ppb and 5.0 ‰ for the L'Atalante ($n = 7$).

Meteorological and oceanographically 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/) and the Ifremer, French Research Institute for Exploration of the Sea (http://flotte.ifremer.fr). For each sample a backward "Hybrid Single Particle Lagrangian Integrated Trajectory" (HYSPLIT) was calculated (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

Figure 2 shows the H_2 mixing ratio (Fig. 2a) and isotopic composition δD (Fig. 2b) along the 18° N transect between Cape Verde Island and the west coast of Mauritania during the two cruises. In this and all subsequent figures, green symbols indicate the cruise with FS Poseidon in February 2007 and red symbols the cruise with FS L'Atalante in February 2008.

The H_2 mixing ratios in 2008 are significantly higher than in 2007. The mean mixing ratio in 2008 was at approximately 545 ppb, but without a clear difference between the open ocean and upwelling area. In 2007 the H_2 mixing ratio was 507 ppb near the coast of Mauritania and increased significantly towards the open ocean by about 20 ppb. The values are in line with the monitoring data presented by Batenburg et al. (2011) and results of measurements during a cruise along a meridional Atlantic transect in April/May 2008 (Walter et al., unpublished data). δD shows values between +110 and +130 ‰ with generally slightly higher values in 2007. Zindler et al. (2012) demonstrated for 2008 that the major phytoplankton group in the upwelling area were diatoms, whereas cyanobacteria (including Synechococcus, Prochlorococcus, and Trichodesmium) are dominating in the oligotrophic open ocean waters west of 18° W. 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. 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), whereas the upwelling signal during 2008 was weaker than in 2007. Biologically produced H_2 is extremely depleted with δD below −700 ‰ (Walter et al., 2012), which is also expected for H_2 produced by diazotrophs in the ocean and released to the atmosphere. Thus, emitted H_2 is approximately 800 ‰ depleted relative to the ambient reservoir and therefore, an increase of 1 % in the H_2 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 N_2 fixation, a significant decrease of the isotopic signal of approximately 24 ‰ would be expected. This is clearly not the case (see Fig. 2), thus a significant hydrogen production due to N_2 fixation can be excluded and the difference in mixing ratio must have other causes.

Air mass back trajectories revealed clear differences between the two cruises regarding the origin of wind (HYSPLIT, http://www.arl.noaa.gov/ready/): In 2008 wind came exclusively from the oceanic site for at least three to four days before sampling, ranging from 324° to 33° and with a mean wind speed of $15.3 \pm 4.2\,\mathrm{m\,s^{-1}}$. Contrasting this in 2007 the wind came mainly from the north east overland crossing Morocco and Mauritania, in some cases also Algeria in a range of 341° to 65° and with a mean wind speed of $9.9 \pm 2.3\,\mathrm{m\,s^{-1}}$. Figure 3 shows 2-day 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). The trajectories shown here are representative for the whole transect.

Dry deposition to the soil is the most important sink for H_2 and it is reasonable to assume that contact with the land surface led to a significant decrease in H_2 mixing ratio (Smith-Downey et al., 2008; Rhee et al., 2006; Ehhalt and Rohrer, 2009). In 2007 the wind came mainly overland from the northeast sector, the direction of the African continent. During the subsequent transport over the ocean toward the Cape Verde Islands the H_2 mixing ratio is increasing due to mixing with air that has not been in contact with the land surface. Thus the mixing ratio gradient between the Cape Verde Island and the west coast of Mauritania is likely a result of dry deposition during transport over land and mixing with H_2 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 explain why no clear δD gradient was found.

In 2008, the wind came from the Atlantic for at least 3 to 4 days before sampling, without transport of air over land. Mixing ratios are generally higher, compared to 2007 and no trend neither in signature nor mixing ratio was observed. Therefore a soil sink signal such as during the POS 348 is not detectable and the results represent remote oceanic conditions for H_2.

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

To investigate a possible diurnal cycle H_2 mixing ratios are compared to radiation in Fig. 4. Similar to previous published data, our results for the four days do not show a consistent picture. During the four high-resolution sampled days in 2007 the H_2 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 and b) show a clear positive correlation between the two parameters. While the increase in H_2 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 valid for the third and fourth day (Fig. 4c and d). Here we found no clear correlation with slightly decreasing mixing ratios of 9 ppb (Fig. 4c) and a negative correlation with a decrease of H_2 mixing ratio of 44 ppb (Fig. 4d), respectively. This negative correlation is parallel shifted in the evening to higher mixing ratios. On day 4, enrichment in δ D of 25 ‰ from 107 ‰ (07:24 UTC) to 132 ‰ (15:04 UTC) was observed, positively correlated with radiation.

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 $\mathrm{W\,m^2}$. The wind blew stable from NNW (341°) to NE (65°) directions with wind speeds between 6 and 15 $\mathrm{m\,s^{-1}}$. 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 last 24 h without significant intrusions from higher altitudes (tested height of air masses 20 m, 500 m and 1000 m). The mean mixed layer depth was approximately 500 m, with a range between 300 and 800 m.

Intrusion of air masses from a higher altitude and contamination by biomass burning or anthropogenic source 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. Even than the altitudinal variation in the mixing ratio is not sufficient to explain such high variations in mixing ratio found here (Schmidt, 1978; Hauglustaine and Ehhalt, 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 visible during all days. This applies also for anthropogenic sources.

- The isotopic values are not supporting the possibility of enhanced mixing ratios due to biomass burning or anthropogenic sources. Both sources show distinctly depleted isotopic ratios of approximately −200 – −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 ‰.

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. Biologically produced hydrogen has a δD value of less than −700 ‰ (Walter et al., 2012) and this would result in an even more depleted signal than expected for a contribution of biomass burning and fossil fuel combustion.

Comparing the mixing ratios with δD and the wind direction (see Fig. 5), the second day is clearly split in two periods by wind direction: after noon the wind came more from N to NNW directions and the data show higher H_2 mixing ratios (556 ppb ± 5, $n = 7$) and slightly lower δD (117 ‰ ± 3, $n = 7$), while wind from NO in the morning is associated with lower mixing ratios (511 ppb ± 11, $n = 8$) and higher δD (121 ‰ ± 3, $n = 8$). Wind from NO 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, is a large-scale negative estuary with an area of over 10 000 km^2 of shallow water and tidal flats between the Sahara and the upwelling system off the Mauritanian coast. It's eutrophic ecosystem is highly productive and dominated by a detritus-based benthic foodweb in which seagrasses (*Zostera noltii, Cymodocea nodosa, Halodule wrightii*) are the principal primary producers, followed by several species of seaweeds. A mangrove swamp (3100 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 amount acetaldehyde. Syringic acid is one of the most common mono-phenols 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 for formaldehyde (Singh et al., 2004; Zhou and Mopper, 1997). Up to 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 ~ 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 ‰ is assumed (Rice et al., 2010), and recently Pieterse et al. (2011) calculated a δD value of +116 ‰. These values fit our results very well and we suggest the Banc d'Arguin to emit large amounts of precursors for photochemical production of H_2. We suggest that this region could be a strong local source that causes the observed H_2 increase during the second day. As the wind direction change in a similar way, this could also explain the results of the first and third day.

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 about 13 ‰, positively correlated with radiation. A decrease in the H_2 mixing ratio could be explained by two sink processes: the reaction with •OH and dry soil deposition. The oxidation of H_2 by •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 in the evening. 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.

Therefore we suggest that the decrease in mixing ratio combined with the slight increase of isotopic signature is probably related to the soil sink, 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 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. We could demonstrate that probably photochemical sources in biologically active areas such as the Banc d'Arguin play an important role, and suggest these areas to release significant amounts of precursors, which are photochemically degraded and produce H_2. Our results clearly indicate the influence of local sources and suggest the Banc d'Arguin as a pool for precursors for photochemical H_2 production, whereas N_2 fixation could not be identified as a H_2 source during these two cruises. With our experimental setup we could demonstrate that variability in diurnal cycles is probably influenced and biased by locally released precursors for photochemical H_2 production and the origin of air masses. This means for further investigations that just measuring the mixing ratio of H_2 is insufficient to explain the variability of a diurnal cycle and support is needed, e.g. by isotopic measurements. However, measurements of H_2 mixing ratios, which are easy to conduct online during ship cruises could be a helpful tool to easily identify production areas of biological precursors such as VOC's. Considering the size and the importance of the oceans for trace gases, the ocean's influence is poorly understood.

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Table 1. Sampling location and weather conditions during the four high-resolution sampled days.

Date	Location	sampling time (UTC)	*n*	Range H_2 [ppb]	Range δD [‰]	Humidity (%)	Radiation [W m^{-2}]	salinity	SST (°C)	Wind direction (° N)	Wind speed (m s^{-1})
20.02.2007	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
21.02.2007	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
22.02.2007	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
23.02.2007	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

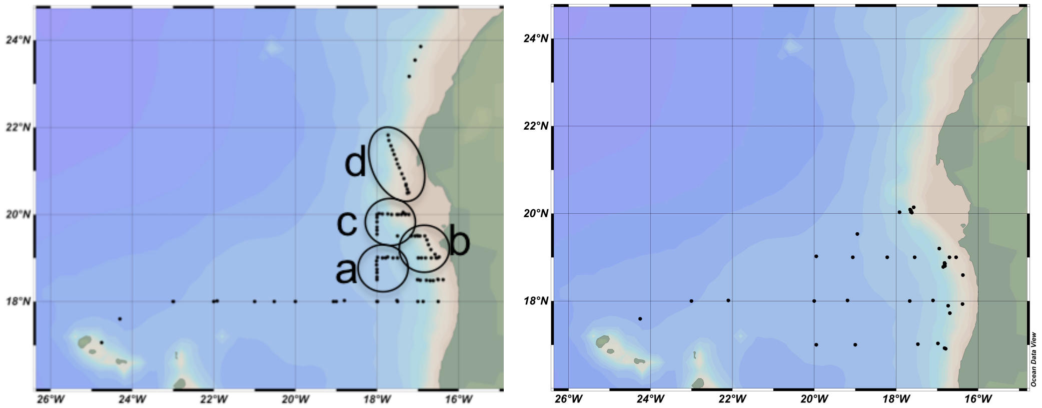

Fig. 1. Sampling positions during POS 348 (2007, left) and L'Atalante (2008, right). The labels **(a)** to **(d)** indicate the four days with high sample resolution during the POS348 cruise. Each label indicate one day of sampling: **(a)** 20 February 2007, **(b)** 21 February 2007, **(c)** 22 February 2007, and **(d)** 23 February 2007 (Schlitzer, 2012).

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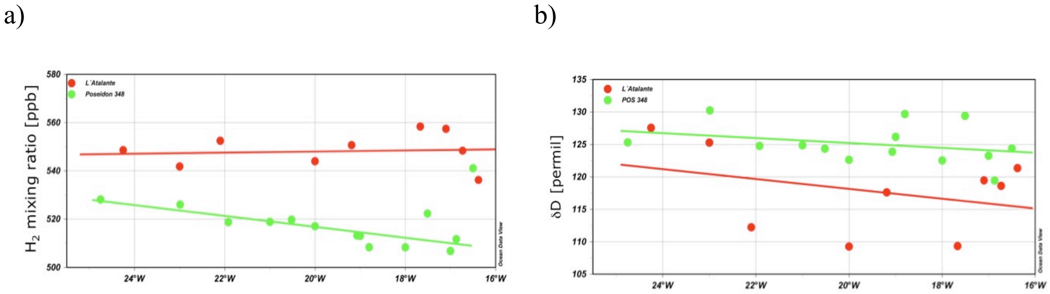


Fig. 2. H_2 mixing ratio [ppb] and δD [‰] along the 18° N transect between the Cape Verde islands and the West African Coast in 2007 (green labeled) and 2008 (red labeled). **(a)** H_2 mixing ratio [ppb] FS Poseidon (2007): $-2.25 \times +1283$, $n = 13$, $r = 0.79$; FS L'Atalante (2008): $0.24 \times +468$, $n = 9$, $r = 0.10$; **(b)** Isotopic composition δD [‰] FS Poseidon (2007): $-0.40 \times +261$, $n = 13$, $r = 0.31$; FS L'Atalante (2008): $-0.76 \times +376$, $n = 9$, $r = -0.34$ (Schlitzer, 2012).

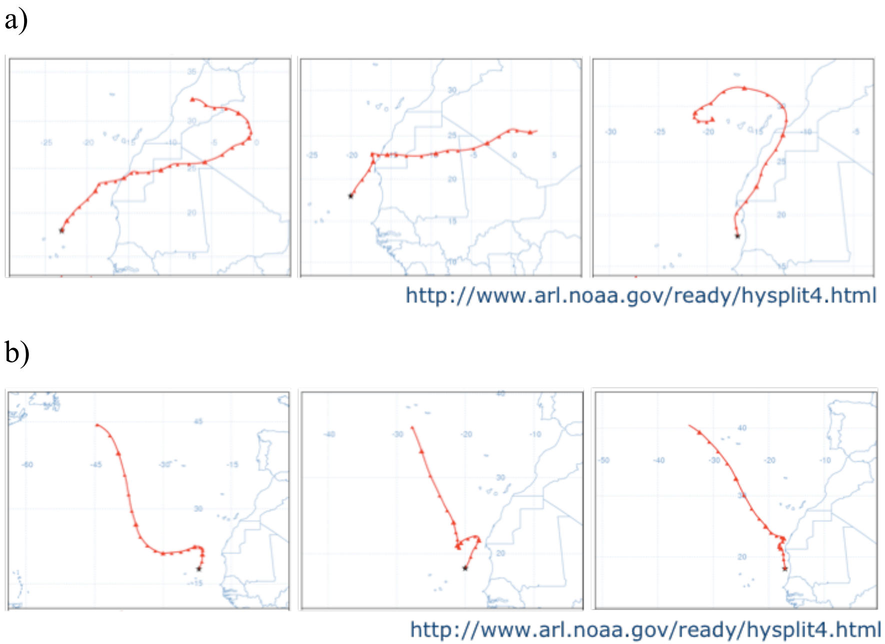


Fig. 3. Representative 2-day backward trajectories (HYSPLIT) for selected sampling locations along the 18° N transect: **(a)** POS 348 (2007) and **(b)** L'Atalante (2008).

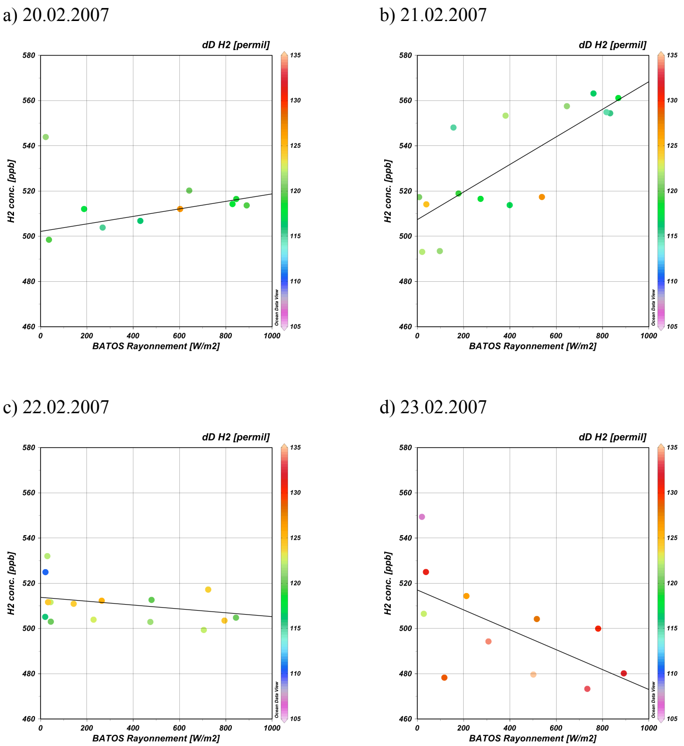
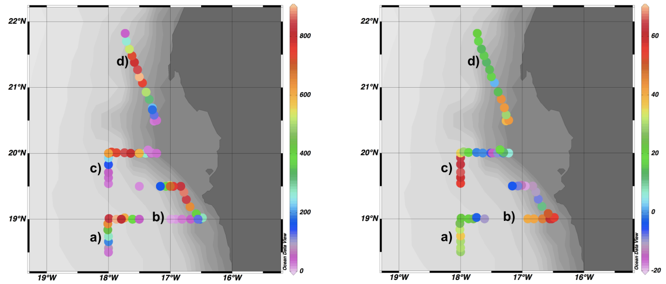
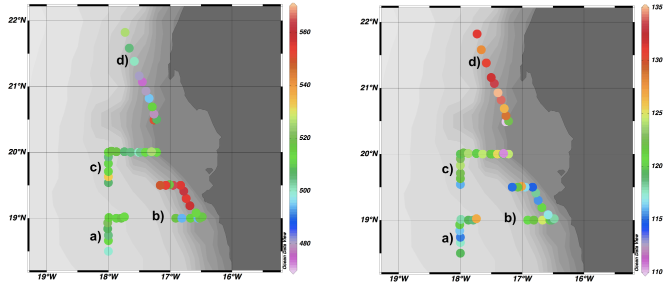


Fig. 4. Correlation between H_2 mixing ratio [ppb] and radiation [W m^2] with color-coded δD [‰] during the four high-resolution sampled days 2007 **(a)** 20 February 2007, exc. 1 outlier (07:31 UTC), $y = 0.0167 \times +502.14$, $R^2 = 0.594$, $n = 9$; **(b)** 21 February 2007, $y = 0.061 \times +507.38$, $R^2 = 0.615$, $n = 15$, **(c)** 22 February 2007, $y = -0.009 \times +513.79$, $R^2 = 0.097$, $n = 16$; **(d)** 23 February 2007, $y = -0.044 \times +517.04$, $R^2 = 0.382$, $n = 11$ (Schlitzer, 2012).


a) radiation [W/m^2]

b) wind direction [°]


c) H$_2$ mixing ratio [ppb]

d) δD [‰]

Fig. 5. Sampling positions with color-coded results for **(a)** radiation [W m^2], **(b)** wind direction [°], **(c)** H_2 mixing ratio [ppb], and **(d)** δD [‰]. The labels in each subfigure **(a)** to **(d)** indicate the days of 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).

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).

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