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hydrogen cycle**

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# The overwhelming role of soils in the global atmospheric hydrogen cycle

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## Abstract

The removal of molecular hydrogen ( $H_2$ ) from the atmosphere is dominated by the up-  
take in soils. Notwithstanding, estimates of the magnitude of this important process on  
a global scale are highly uncertain. The CARIBIC aircraft observations of the seasonal  
variations of  $H_2$  and its D/H isotopic ratio in the northern hemisphere allow an inde-  
pendent, better constrained estimate. We derive that 82% of the annual turnover of  
tropospheric  $H_2$  is due to soil uptake, equaling  $88 (\pm 11) \text{ Tg a}^{-1}$ , of which the northern  
hemisphere alone accounts for  $62 (\pm 10) \text{ Tg a}^{-1}$ . Our calculations further show that  
tropospheric  $H_2$  has a lifetime of only  $1.4 (\pm 0.2)$  years – significantly shorter than the  
recent estimate of  $\sim 2$  years – which is expected to decrease in the future. In addition,  
our independent top-down approach, confined by the global and hemispheric sinks of  
 $H_2$ , indicates  $64 (\pm 12) \text{ Tg a}^{-1}$  emissions from various sources of volatile organic com-  
pounds by photochemical oxidation in the atmosphere. This estimate is as much as up  
to 60% larger than the previous estimates. This large airborne production of  $H_2$  helps  
to explain the fairly homogeneous distribution of  $H_2$  in the troposphere.

## 1. Introduction

Hydrogen ( $H_2$ ) gas is considered to be a promising future energy carrier (Ogden, 1999;  
Turner, 2004) and pilot scale implementation is already taking place. Of concern is  
the potential global environmental impact accompanying a large scale use of  $H_2$ , and  
clearly this has to be thoroughly assessed at an early stage. Recent modeling studies  
(Schultz et al., 2003; Tromp et al., 2003; Warwick et al., 2004) presume that major  
changes in the atmospheric  $H_2$  budget may occur when hydrogen gas is used on a  
large scale because of unavoidable leakage into the atmosphere. These studies pro-  
vide scenarios for the consequent impact on the chemistry of the atmosphere and  
ultimately global climate.

However, present knowledge of the atmospheric  $H_2$  budget is rather qualitative given

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the large uncertainties in most of the source and sink strength determinations (Table 1). Particularly the estimation of the soil sink, which dominates the budget, is most uncertain being based on a “bottom-up” approach. Such approach basically uses the up-scaling from local measurements to the global scale, which is prone to large errors. Furthermore, all previous estimates depend on the  $H_2$  deposition velocity applied and the effective soil area. The deposition velocities are widely spread from 0.003 to  $0.14 \text{ cm s}^{-1}$  (Conrad and Seiler, 1980; Conrad and Seiler, 1985; Liebl and Seiler, 1976; Schmidt et al., 1980) (equivalent to approximately  $4.2\text{--}200 \text{ Tg a}^{-1}$  providing the effective soil surface area of  $1.04 \times 10^8 \text{ km}^2$ ; Table 4). These values have been used for the estimation of global soil sinks in numerous literature (Novelli et al., 1999, and references therein).

In contrast, we apply an independent “top-down” approach and include not only the atmospheric  $H_2$  mixing ratio, but also the stable isotope composition. Isotope analysis is extraordinarily useful for investigating the atmospheric  $H_2$  cycle, since the two sink processes, uptake by soils and photochemical oxidation by OH, are both accompanied by substantial kinetic isotope effect, but wide difference in its individual magnitudes. Moreover, nearly all of the 5 identified sources of  $H_2$  have a strongly differing isotopic composition (Table 1). The D/H isotope ratio is commonly expressed as  $\delta D$  which is defined as  $\delta D = (R_{\text{SPL}}/R_{\text{SMOW}} - 1) \times 1000$  (‰), where  $R_{\text{SPL}}$  is the D/H ratio of sample and  $R_{\text{SMOW}}$  is that of Standard Mean Ocean Water (SMOW) ( $=0.015576 \pm 0.000006$ ; Hagemann et al., 1970).

The previous measurements of the  $\delta D$  value of atmospheric  $H_2$  were limited to the planetary boundary layer in contact with soils (e.g. Friedman and Scholz, 1974; Gerst and Quay, 2000). Since the soil surface destroys a major portion of atmospheric  $H_2$ , this may lead to a large variability in  $\delta D$  values. In addition, other local sources may prevent the observation from being the representative in synoptic scale of space. We analyzed the free tropospheric air samples collected by the CARIBIC project (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container) (Brenninkmeijer et al., 1999). Being above the planetary boundary layer, the

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free troposphere represents “background” chemical composition of the troposphere. In addition, as indicated by the large vertical eddy diffusivity, the atmospheric mixing in the free troposphere is rapid so as to reduce a potential local bias. This provides us an unprecedented opportunity to apply the aircraft observations to the global atmospheric H<sub>2</sub> cycle in the troposphere.

## 2. Methods

Air samples were collected over Europe and Africa at altitudes of 9 to 12 km using the CARIBIC Boeing 767. Two flights were carried out from Windhoek, Namibia, in May and July, and one flight from Cape Town, South Africa, in December, to Munich, Germany, all in 2000. The flight tracks cover ~30° S to ~50° N along the longitude ~10° E (Table 2). Twelve air samples were regularly collected along the flight track in 21 L tanks at a final pressure of 17 bar taking ~20 min (~300 km distance) per sample. Upon return of the aircraft aliquots were transferred into 2.5 L electro-polished stainless steel canisters at 5 bar, archived in a freezer at –25°C, and later used to determine the  $\delta D$  values and mixing ratios of H<sub>2</sub> using a continuous-flow isotope ratio mass spectrometry (CF-IRMS) following the procedure described in detail by Rhee et al. (2004).

## 3. Results

Figure 1 shows the H<sub>2</sub> mixing ratios and  $\delta D$  values along the 3 flight tracks together with in situ measurements of the ultra-fine particle number concentrations for the size of 4–12 nm (N<sub>4–12</sub>) (Heintzenberg et al., 2003), and the CO and O<sub>3</sub> mixing ratios (Zahn et al., 2002). These in situ observations are utilized to define three characteristic regions. Large N<sub>4–12</sub> indicates the uplifting of air parcels from the boundary layer by deep convection near the intertropical convergence zone (ITCZ) (Heintzenberg et al., 2003). Simultaneous enhancement of CO confirms the occurrence of uplift of polluted

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boundary layer air to the cruising altitude. This region is defined as the equatorial tropics. The adjacent regions to the south and north are classified as representative for the southern hemisphere (SH) and the northern hemisphere (NH), respectively. Whereas the SH sections for each of the 3 flights lie entirely in the troposphere, the NH sections extend to near the tropopause or into the lowermost stratosphere where  $O_3$  mixing ratios are strongly elevated. These data are excluded from the present analysis as we focus on the  $H_2$  cycle in the troposphere.

Following the partitioning of the flight tracks based on the in situ observations, we estimate the mean  $H_2$  mixing ratios and  $\delta D$  in the SH and NH sections of each flight. For this calculation we exclude one sample collected at  $46^\circ N$  in May, and one at  $31^\circ N$  in December. These two samples do not represent free tropospheric air masses, as they had resided at the surface prior to sampling. This is evidenced by the increase of  $N_{4-12}$  and the respective 5-day backward trajectories (see the web site [http://www.knmi.nl/samenw/campaign\\_support/CARIBIC/](http://www.knmi.nl/samenw/campaign_support/CARIBIC/), together with other meteorological graphs for the flights). The  $H_2$  mixing ratios for the NH and SH (Fig. 2a and b) show almost the same seasonal cycle as observed at Mauna Loa (MLO) and Cape Grim (CGO) by the National Oceanic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) from 1989 to 1998 (Novelli et al., 1999). The observations at these two stations represent the background  $H_2$  variations in both hemispheres without local influences. The agreement in both phase and magnitude of the seasonal cycle of  $H_2$  mixing ratios confirm spatial homogeneity of  $H_2$  in remote areas of the two hemispheres.

The phase of the seasonal cycle of  $\delta D$  with respect to that for  $H_2$  shows a strong contrast between the two hemispheres (Fig. 2c and d). In the NH,  $\delta D$  and  $H_2$  vary out of phase, while in the SH they are almost in phase. Moreover, although the amplitude of the  $H_2$  cycle in the NH is more than twice as large as that in the SH, the amplitudes of the  $\delta D$  cycles are the same. In addition, while the annual mean  $H_2$  mixing ratios in both hemispheres are the same, the annual mean  $\delta D$  value in the SH is 8‰ higher (Table 3). These properties of the seasonal cycles of  $H_2$  and  $\delta D$  imply differences in

the processes that control H<sub>2</sub> in each hemisphere.

## 4. Discussion

### 4.1. Northern hemispheric H<sub>2</sub> cycle

The spring time peak in the H<sub>2</sub> mixing ratio and corresponding lowest  $\delta D$  value in the NH can be ascribed to the winter time accumulation of H<sub>2</sub> emitted from sources with low  $\delta D$  values, while in fall these two parameters undergo opposite changes due to the strong uptake by soil during summer and the associated isotopic fractionation which renders the remaining H<sub>2</sub> isotopically heavier. It has been long recognized that soil provides the most significant sink of atmospheric H<sub>2</sub> (Liebl and Seiler, 1976). Long-term monitoring of H<sub>2</sub> at different latitudes has revealed that the seasonal amplitude of H<sub>2</sub> increases with latitude in the NH (Novelli et al., 1999) likely due to increase of the fraction of land area. Several factors such as soil temperature, humidity, and the organic carbon content are likely to influence the uptake rate (Conrad and Seiler, 1985). However, it is unclear how significantly these factors contribute to the soil uptake rate on a global scale and which factor controls the seasonal variation of soil uptake as none of the literature clearly shows a correlation between a given parameter and soil deposition velocity of H<sub>2</sub>. Probably a complex non-linear combination of factors that control H<sub>2</sub> uptake by soil in a local environment (e.g. Yonemura et al., 2000a) makes it difficult to find a major driving force on the global scale.

Long-term satellite observations show a large annual oscillation of the snow-cover extent by as much as ~40% of the NH land area (Armstrong and Brodzik, 2001) (see Fig. 2a). A snow-cover on the soil surface hinders contact with air and retards diffusion of H<sub>2</sub> into soil voids where H<sub>2</sub> removal takes place (Yonemura et al., 2000b). Microbial or enzymatic activity of H<sub>2</sub> consumption also decreases with soil temperature. Furthermore, the phase of seasonal variation of snow-cover extent corresponds precisely to the NH H<sub>2</sub> cycle: the fastest removal rate of H<sub>2</sub> in late July coincides with the lowest

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snow-cover extent, and vice versa. Therefore, we hypothesize that the large seasonal cycle of the snow-cover extent dominates the seasonality of NH<sub>2</sub>.

#### 4.2. Soil uptake rate of atmospheric H<sub>2</sub>

When the isotopic compositions of the sources are invariable, the relative change in the  $\delta D$  value compared to that in the H<sub>2</sub> mixing ratio depends solely on sink processes at equilibrium state of the isotopic ratio between source and sink processes in a reservoir, and is represented by isotopic fractionation factor (Lassey et al., 2000). One can calculate the isotopic fractionation factor at the isotopic equilibrium by virtue of the Rayleigh distillation model (Allan et al., 2001; Bergamaschi et al., 2000) and verify the isotopic equilibrium based on the relation  $\alpha = \frac{R_Q}{R_r}$ , where  $R_Q$  is the isotopic ratio of the combined sources and  $R_r$  is that for the reservoir. Atmospheric H<sub>2</sub> is destroyed not only by soil uptake, but the oxidation of H<sub>2</sub> by the OH radical also contributes to the removal of H<sub>2</sub>. This process induces a strong isotopic fractionation (Talukdar et al., 1996), thus efficiently increasing  $\delta D$  of the atmospheric H<sub>2</sub> reservoir. These two loss processes and their associated isotopic fractionation provide a key to derive the magnitude of the H<sub>2</sub> uptake by soil. The apparent isotopic fractionation factor of 0.90 ( $\pm 0.02$ ), which reflects the combined sink processes, is derived by applying the Rayleigh distillation model (Rayleigh, 1902):

$$\alpha_{\text{app}} = 1 + \frac{\ln \frac{(\delta D_{mx} \times 10^{-3} + 1)}{(\delta D_{mn} \times 10^{-3} + 1)}}{\ln \frac{[H_2]_{mn}}{[H_2]_{mx}}} \quad (1)$$

where indices of  $mn$  and  $mx$  indicate the minimum and maximum values for annual cycle of  $\delta D$  and H<sub>2</sub> shown in Fig. 2c. The uncertainty of  $\alpha_{\text{app}}$  is derived by error propagation in Eq. (1) using the uncertainties of the sinusoidal fittings for  $\delta D$  and H<sub>2</sub> (Table 3). A boot strap method (Press et al., 1992) is applied to estimate uncertainties

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of the fitting parameters within the errors of data. One thousand results that fit the annual sinusoidal cycle were collected to estimate uncertainty.

The calculated value implies that the NH soil sink accounts for  $87(\pm 7)\%$  of the total NH sink since the fraction of soil uptake ( $g$ ) can be derived by  $\alpha_{\text{app}} = g \times \alpha_{\text{sl}} + (1-g) \times \alpha_{\text{OH}}$ , where the isotopic fractionation factor for the photochemical oxidation with OH ( $\alpha_{\text{OH}}$ ) is  $0.58(\pm 0.07)$  (Talukdar et al., 1996) at an average tropospheric temperature of 277 K (Prather and Spivakovsky, 1990) and for soil uptake ( $\alpha_{\text{sl}}$ ) is  $0.943(\pm 0.007)$  (Gerst and Quay, 2001; Rahn et al., 2002a). Next we determine the absolute soil sink strength in the NH using the amount of  $\text{H}_2$  that is oxidized by reaction with OH in the troposphere. This amount is calculated given the known reaction rate constant (DeMore et al., 1997) at an average tropospheric temperature of 277 K ( $= 4.52(\pm 0.516) \times 10^{-16} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ), an OH concentration of  $9.7(\pm 0.6) \times 10^5 \text{ molecules cm}^{-3}$  (Prinn et al., 1995), a global tropospheric  $\text{H}_2$  burden of  $155(\pm 2) \text{ Tg}$  (Novelli et al., 1999), and the ratio of  $\text{H}_2$  burdens in the NH to SH of 0.97 (Novelli et al., 1999). This results in the  $\text{H}_2$  oxidation by OH at  $9.4(\pm 1.3) \text{ Tg a}^{-1}$  and the NH soil sink therefore is  $62(\pm 10) \text{ Tg a}^{-1}$ . The uncertainty is calculated by error propagation for every parameter that was used in the calculation.

Finally, to estimate the global soil sink, we need to know the inter-hemispheric ratio of the “effective” soil surface area where  $\text{H}_2$  uptake occurs. Since  $\text{H}_2$  uptake is mainly controlled by diffusion through soil voids (Yonemura et al., 2000b), inundation and snow-cover of soil surface prevent  $\text{H}_2$  uptake. Therefore, the annual mean land areas excluding wetlands, rice paddies, glaciers, and snow-covered regions provide a ratio of the effective soil surface areas of SH to NH as  $0.4(\pm 0.03)$  (Table 4). This in turn leads to the global soil sink strength of  $88(\pm 11) \text{ Tg a}^{-1}$  since the fraction of soil uptake ( $h$ ) of the  $\text{H}_2$  sink in the SH can be derived by  $h = \frac{g\beta}{1-g(1-\beta)}$  accounting for the area dependency of soil sink, where  $\beta$  is the ratio of effective soil surface area of the SH to the NH. The value we calculated is 57% greater than the most recent estimate (Novelli et al., 1999). The derived global sink strength of  $107(\pm 11) \text{ Tg a}^{-1}$  implies the mean lifetime of  $\text{H}_2$  in the troposphere to be  $1.4(\pm 0.2)$  years, considerably shorter than

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the previous estimate of  $\sim 2$  years.

#### 4.3. Effect of variable $\delta D$ of source $H_2$ on the estimation of soil uptake rate

Among the sources, the  $\delta D$  value of the  $H_2$  from photochemical reactions of volatile organic compounds (VOCs) may vary due to change in the  $\delta D$  value of the VOCs involved, and due to the change in the OH concentration along the year. The annual variation of the  $\delta D$  value of  $CH_4$ , the longest-lived VOC and a dominant source of  $H_2$ , shows only  $\sim 2\text{‰}$  amplitude (Bergamaschi et al., 2000). This suggests insignificant seasonal variation of the  $\delta D$  value of combined VOCs unless the  $\delta D$  values of primary sources (e.g. biosphere) of non-methane volatile organic compounds (NMVOCs) would change much. This however is unlikely. The annual variation of the OH concentration on the hemispheric scale is substantial, however (Spivakovsky et al., 2000). Formaldehyde ( $CH_2O$ ), the very last precursor of  $H_2$  in the photochemical reaction chain, has two channels of photolysis one of which produces  $H_2$  and CO molecules and the other H and CHO radicals. A fraction also reacts with OH in the atmosphere. The yield of  $H_2$  and its corresponding  $\delta D$  value depend on the fraction of  $CH_2O$  that reacts with OH because the quantum yields for the two channels of  $CH_2O$  photolysis are nearly constant along year in the troposphere. The fraction of  $CH_2O$  that reacts with OH varies from 14 to 21% when using the photolysis rates of the two channels in the troposphere calculated by a 2-dimensional model (Bruehl and Crutzen, 1993), the rate constant of  $CH_2O$  (Sander et al., 2003), and the monthly OH concentration (Spivakovsky et al., 2000) normalized to the global mean value (Prinn et al., 1995). The  $\delta D$  values of the  $H_2$  that is produced by photolysis result in peak-to-peak variation of  $\sim 20\text{‰}$  according to the scheme of isotopic fractionation between  $CH_4$  and  $H_2$  under tropospheric condition (Rhee et al., 2005<sup>1</sup>). A one-box model simulation shows that the change in  $\alpha_{app}$

<sup>1</sup>Rhee, T. S., Brenninkmeijer, C. A. M., Braß, M., Röckmann, T., and Brühl, Ch.: The isotope composition of  $H_2$  from  $CH_4$  oxidation in the stratosphere and the troposphere, J. Geophys. Res., in review, 2005.

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remains within its uncertainty when including this seasonal variation of  $\delta D$  and given the source and sink strengths in the NH and their characteristic isotopic signatures in Table 1, and their seasonality in Hauglustaine and Ehalt (2002) but using a  $\sim 1.7$  times larger amplitude of the soil sink than they do.

#### 5 4.4. Southern hemispheric H<sub>2</sub> cycle

The in-phase variation of  $\delta D$  and H<sub>2</sub> in the SH (Figure 2d) indicates that its H<sub>2</sub> cycle is not primarily driven by sink processes, in contrast to the NH. Low H<sub>2</sub> mixing ratios and  $\delta D$  values during SH winter demonstrate the minor role of soil uptake. The effective soil surface area in the SH is significantly smaller (Table 4), and its seasonal variation also is negligible on account of the small snow-cover extent ( $\sim 1\%$ ) (Dewey and Heim, 1983). Also there is little seasonal variation in soil temperature because most of the continental area is at low latitudes. These factors render the SH H<sub>2</sub> cycle much weaker with a slower rate of turnover compared to the NH (Table 3). Therefore, this SH winter anomaly of the H<sub>2</sub> cycle must have an external influence. Seasonal observations of NH tracers (chiefly, SF<sub>6</sub>, Levin and Hesshaimer, 1996; CFCs, Prather et al., 1987; <sup>85</sup>Kr, Jacob et al., 1987; CO<sub>2</sub>, Nakazawa et al., 1991) in the SH show a strong NH influence during the SH winter following the northward shift of the ITCZ several months earlier. Moreover, the monsoon circulation enhances the injection of NH air into the south through the upper troposphere (Nakazawa et al., 1991; Newell et al., 1997). This NH air mass being supplied with the boundary layer air through convection near ITCZ has lower H<sub>2</sub> mixing ratios and is isotopically lighter than the SH air. We infer that this NH influence causes the H<sub>2</sub> and  $\delta D$  of the SH air to reach their lowest values simultaneously. In SH summer, however, the monsoon circulation is suppressed with the shift of the ITCZ to the south so that the NH influence tends to be minimal.

The synchronous increase of H<sub>2</sub> and  $\delta D$  in SH late spring and early summer suggests the major source of H<sub>2</sub> in the SH to be isotopically heavier than the atmospheric H<sub>2</sub> reservoir itself. It has been postulated that biomass burning dominates the SH seasonal cycle of H<sub>2</sub> (Hauglustaine and Ehalt, 2002; Novelli et al., 1999). In particular,

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the increase of  $H_2$  in SH late spring and early summer makes this plausible as it coincides with the biomass burning period in the SH. However, the seasonal cycle of  $\delta D$  based on CARIBIC contradicts this hypothesis, unless  $\delta D$  of  $H_2$  from biomass burning would be much higher than previously estimated using a laboratory experiment (Gerst and Quay, 2001).

### 4.5. $\delta D$ of the $H_2$ emitted from biomass burning

Our data allow an independent estimate of  $\delta D$  of  $H_2$  from biomass burning. As mentioned, during all three flight sections in the equatorial tropics the aircraft intercepted air masses carrying entrained boundary layer air (Fig. 1). The observed enhancement of CO and its actual isotopic compositions of  $^{13}CO$ ,  $C^{18}O$ , and  $^{14}CO$  (not shown) demonstrate a dominant influence of biomass burning effluents. In strong contrast to this,  $H_2$  mixing ratios actually do not reflect the enhancement of CO. For instance, in July,  $H_2$  and  $\delta D$  both were lower in the equatorial tropics whereas CO increased to 200 ppb due to biomass burning (Möhle et al., 2002). Therefore, there must be a counterbalance to the emissions of  $H_2$  from biomass burning, e.g.  $H_2$  uptake by soil. Another cause one could think of is a substantial photochemical loss due to increased OH. This however can be ruled out because the reaction rate constant of  $H_2$  with OH is  $\sim 50$  times slower than that for CO.

We estimate  $\delta D$  of  $H_2$  from biomass burning based on mass conservation for the major (H) and minor (D) isotopes of  $H_2$  in one box with the correction of the isotopic fractionation associated with the soil uptake:

$$[H_2]_{ob} = [H_2]_{bg} - [H_2]_{sl} + [H_2]_{bb} \quad (2)$$

$$\delta D_{ob} = \left( (\delta D_{bg} + 1000) \times (1 - g_{sl})^{\alpha_{sl}-1} - 1000 \right) \times (1 - f_{bb}) + \delta D_{bb} \times f_{bb} \quad (3)$$

where  $[H_2]_i$  is the  $H_2$  mixing ratio,  $\alpha_{sl}$  is the isotopic fractionation factor for  $H_2$  removal by soil uptake (Gerst and Quay, 2001; Rahn et al., 2002a),  $f_{bb}$  is the ratio of

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H<sub>2</sub> emitted from biomass burning to the H<sub>2</sub> mixing ratio observed ( $= \frac{[H_2]_{bb}}{[H_2]_{ob}}$ ),  $g_{sl}$  is the ratio of H<sub>2</sub> consumed by soil to the background H<sub>2</sub> mixing ratios ( $= \frac{[H_2]_{sl}}{[H_2]_{bg}}$ ), and indices are: *ob* (observation); *bg* (background); *bb* (biomass burning); *sl* (soil uptake). In applying this model to our observations in the equatorial tropics we assume (1) that the background mixing ratios of CO ( $[CO]_{bg}$ ) and H<sub>2</sub> ( $[H_2]_{bg}$ ) are the same as for the adjacent air sample to the southern or northern free troposphere. In the case of the air sample in the middle of the equatorial tropics, the mean values of both air samples are representative except the air samples collected in the latitude of 6.3° N in May and 12.6° S in December. According to the 5-day backward trajectories (see the web site [http://www.knmi.nl/samenw/campaign\\_support/CARIBIC/190500](http://www.knmi.nl/samenw/campaign_support/CARIBIC/190500) and [http://www.knmi.nl/samenw/campaign\\_support/CARIBIC/031200](http://www.knmi.nl/samenw/campaign_support/CARIBIC/031200)), these air masses in May and December originated in the NH and the SH, respectively. We further assume (2) that the increase of the CO mixing ratio as observed in the equatorial tropics is solely due to the emissions from biomass burning, (3) that the CO uptake by soil is negligible, (4) that other anthropogenic emissions and the photochemical oxidation and production of H<sub>2</sub> by the OH radical are not significant, and (5) that in the background air parcel H<sub>2</sub> was consumed by soil prior to uplifting and mixing with a plume from biomass burning. We draw a relation between ER and  $\delta D_{bb}$  by using a least squares minimization between the modeled and the observed  $\delta D$  at a given ER value. Repeating this procedure at different ER value, one can obtain an inverse relation between ER and  $\delta D_{bb}$  as shown in Fig. 3a. Combining Eqs. (2) and (3) with the definition of the enhancement ratio of H<sub>2</sub> ( $ER = \Delta H_2 / \Delta CO = \frac{[H_2]_{bb}}{[CO]_{bb}}$  and  $[CO]_{bb} = [CO]_{ob} - [CO]_{bg}$ ), it is readily noticeable that the ER and  $\delta D_{bb}$  in the equations above have a pseudo-inverse relation, which can be expressed as

$$\delta D_{bb} \approx \frac{[H_2]_{ob}}{[CO]_{bb}} (\delta D_{ob} - \delta D_{bg}) + \alpha \delta D_{bg} + \varepsilon \quad (4)$$

by applying a Taylor series expansion. In Eq. (4),  $\varepsilon = (\alpha - 1) \times 1000$ . While optimizing

the model to the observation, 2 data points that result in negative values of  $g_{sl}$  are excluded (WAS-25-6 and WAS-30-6; see Table 2). This artifact is mainly due to the large  $[H_2]_{ob}$  despite small addition of  $[H_2]_{bb}$ .

As Fig. 3a shows, the model results appear to be in good agreement with the only available set of laboratory measurements taking into account the scatter of the enhancement ratios (ER) of  $H_2$  to CO emissions from biomass burning for the same biomass material (Gerst and Quay, 2001). The excellent agreement, within the uncertainty, between the observed and the predicted  $\delta D$  strongly confirms the correctness of the model (Fig. 3b). As our model shows, the  $\delta D$  value of  $H_2$  from biomass burning differs depending on the actual region (Fig. 3a). Since it is known that soil moisture  $\delta D$  values determine to a high degree  $\delta D$  of the hydrogen in plant organic matter (Yapp and Epstein, 1982), it is plausible to assume that  $\delta D$  of  $H_2$  from biomass burning follows the gradient of  $\delta D$  in meteoric water with latitude (Dansgaard, 1964). Our model shows that tropical forest fires emit  $H_2$  with a high  $\delta D$  value of  $-30(\pm 20)\text{‰}$  and extra-tropical forest and savanna fires have values of  $-150(\pm 100)\text{‰}$  and  $-170(\pm 120)\text{‰}$ , respectively. Weighting the emission rates in those regions (Andreae and Merlet, 2001), we compute the global mean  $\delta D$  value of  $-90(\pm 40)\text{‰}$ . This value is much higher than the previous estimate of a global mean value of  $-290(\pm 60)\text{‰}$  (Gerst and Quay, 2001). Nevertheless, our model still predicts that biomass burning emits  $H_2$  that is isotopically lighter than the atmospheric  $H_2$  reservoir itself. Therefore, direct emission of  $H_2$  from biomass burning is not the primary source for the increase of  $H_2$  in austral summer. The photochemical oxidation of  $CH_4$  and probably many NMVOCs constitute a specific source that maintains the atmospheric  $H_2$  reservoir isotopically heavy. Biomass burning also emits VOCs that can be photochemically degraded to produce  $H_2$ . Our results indicate that the secondary photochemical production of  $H_2$  from the VOCs emitted from biomass burning and biosphere must play a substantial role in the seasonal cycle of  $H_2$  in the SH and further in the global budget of tropospheric  $H_2$ .

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#### 4.6. Global H<sub>2</sub> source strengths

Although it has been debated whether the global H<sub>2</sub> budget is in steady state or not (Khalil and Rasmussen, 1990; Novelli et al., 1999; Simmonds et al., 2000), the results from the NOAA/CMDL observations over the last decade (Novelli et al., 1999) show no significant inter-annual variation or trend in either hemisphere. In assuming steady state for  $\delta D$  as well, the global ( $\delta D_{QG}$ ), NH ( $\delta D_{QN}$ ), and SH ( $\delta D_{QS}$ ) source values of  $\delta D$  are derived (Table 1) while taking into account the asymmetric hemispheric distribution of H and D:

$$\delta D_{QG} = \frac{\sum_j L_{jN} (\alpha_j \delta D_N + \epsilon_j) + \sum_j L_{jS} (\alpha_j \delta D_S + \epsilon_j)}{\sum_j L_j} \quad (5)$$

$$\delta D_{QN} = \frac{\sum_j L_{jN} (\alpha_j \delta D_N + \epsilon_j) - km \frac{\delta D_S - \gamma \delta D_N}{1+\gamma}}{\sum_j L_{jN} - km \frac{1-\gamma}{1+\gamma}} \quad (6)$$

$$\delta D_{QS} = \frac{\sum_j L_{jS} (\alpha_j \delta D_S + \epsilon_j) + km \frac{\delta D_S - \gamma \delta D_N}{1+\gamma}}{\sum_j L_{jS} + km \frac{1-\gamma}{1+\gamma}} \quad (7)$$

The subscripts indicate: *G* (global); *N* (northern hemisphere); *S* (southern hemisphere); *Q* (source); *j* (respective sink processes). Further,  $L_j$  is the sink strength,  $\alpha_j$  are the isotopic fractionation factors for sink processes,  $\epsilon_j$  is  $(\alpha_j - 1) \times 1000$ ,  $k$  is the hemispheric exchange rate ( $=1 \text{ a}^{-1}$ ) (Jacob et al., 1987),  $m$  is the tropospheric burden of H<sub>2</sub> ( $=155 \text{ Tg}$ ) (Novelli et al., 1999), and  $\gamma$  is the ratio of the H<sub>2</sub> burdens in the NH to SH ( $=0.97$ ) (Novelli et al., 1999). The right-hand side of denominator and numerator in

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the equations for  $\delta D_{QN}$  and  $\delta D_{QS}$  play a role in the imbalance of the  $H_2$  source strength in both hemispheres. Inserting the values into the equations, the isotopic signatures of combined sources are:  $\delta D_{QG} = -7.2\text{‰}$ ,  $\delta D_{QN} = -2.6\text{‰}$ , and  $\delta D_{QS} = -16\text{‰}$ . The calculation of these values does not account for the input of stratospheric  $H_2$  providing that the tropospheric and stratospheric  $H_2$  mixing ratios are the same (Ehhalt et al., 1977). However, stratospheric  $H_2$  is more enriched in D than tropospheric  $H_2$  (Rahn et al., 2003; Röckmann et al., 2003), leading to input of D from the stratosphere. We estimate the mean  $\delta D$  value of stratospheric  $H_2$  ( $=168\text{‰}$ ) at the stratospheric mean  $CH_4$  ( $=1640$  ppb) on the basis of their mutual linear relation (Röckmann et al., 2003). Multiplying the difference of the  $\delta D$  values between the stratosphere and the troposphere (e.g. for NH,  $40\text{‰}$ ) to the fraction of the  $H_2$  flux across the tropopause at the 380 K isentropic surface (e.g., for NH,  $12.5 \text{ Tg a}^{-1}$ ) to the annual  $H_2$  turnover rate in each hemisphere, the increase of  $\delta D$  in the NH and SH will be  $7\text{‰}$  and  $11\text{‰}$ , respectively. Accounting for the impact of stratospheric input,  $\delta D_{QN}$  would be  $\sim 5\text{‰}$ , which is similar to the  $\delta D$  of combined source ( $=10\text{‰}$ ) obtained in Fig. 4 applying the Rayleigh distillation model (see Appendix). This clearly supports the isotopic equilibrium of the NH  $H_2$  cycle and underscores the robust approach of our  $H_2$  budget estimation. In contrast, the SH  $H_2$  cycle does not reach isotopic equilibrium, but is perturbed by the NH intrusion as  $\delta D_{QS}$  is far different from the value of  $390\text{‰}$  derived from the observations (Fig. 4).

The asymmetric distribution of the isotopes of  $H_2$  in the two hemispheres allows us to estimate the contribution of sources between the hemispheres according to:

$$\delta D_{QG} = f \delta D_{QN} + (1 - f) \delta D_{QS} \quad (8)$$

The NH fraction of the global  $H_2$  source strength,  $f=0.65$ , turns out to be the same as that for the NH fraction of the global CO source (e.g. Logan et al., 1981), which is commonly used as a surrogate for the source strength of atmospheric  $H_2$ . The values for  $f$ ,  $\delta D_{QG}$ , and  $\delta D_{QN}$  (or  $\delta D_{QS}$ ) constrain the estimates of the global and hemispheric source strengths in conjunction with the isotopic signature of each source ( $\delta D_i$ ) and

the NH fraction of the global source strength ( $\chi_i$ ):

$$\sum_i q_i = 1 \quad (9)$$

$$\sum_i \chi_i q_i = f \quad (10)$$

$$\sum_i \delta D_i q_i = \delta D_{QG} - \zeta (\delta D_{SS} - \delta D_{TS}) \quad (11)$$

$$\sum_i \chi_i \delta D_i q_i = f \{ \delta D_{QN} - \zeta_N (\delta D_{SS} - \delta D_N) \} \quad (12)$$

where  $q_i$  indicates the fraction of source  $i$ ,  $\zeta$  is the ratio of the  $H_2$  flux across the tropopause at the 380 K isentropic surface (Appenzeller et al., 1996) to the annual  $H_2$  turnover rate,  $\zeta_N$  is the same parameter as  $\zeta$  but for the NH,  $\delta D_{SS}$  is the value for the stratospheric  $H_2$ ,  $\delta D_{TS}$  is the mean value for the tropospheric  $H_2$ ,  $\delta D_N$  is the mean value for the northern hemispheric  $H_2$ .  $\delta D_i$ 's are available from the literature and this study (see Table 1).

The fraction  $\chi_i$  for fossil fuel combustion is estimated from the updated Emission Database for Global Atmospheric Research (EDGAR) CO emission inventories (Oliver and Berdowski, 2001). The fraction  $\chi_i$  for biomass burning reflects the ratios of CO emissions from biomass burning in the two hemispheres (Duncan et al., 2003), while  $\chi_i$  for ocean and microbial  $N_2$  fixation are based on the ratios of land and ocean (Levitus, 1982). The fraction  $\chi_i$  for the photochemical production is uncertain particularly because of the large uncertainty in the amount of  $H_2$  produced by photochemical oxidation of NMVOCs. Thus, this parameter is considered unknown, and is confined by our observations of  $H_2$  and  $\delta D$  in the SH. As discussed, the photochemical production of  $H_2$  was larger than that from biomass burning during the peak biomass burning period (late spring and early summer) in the SH. Assuming that  $H_2$  emission from biomass

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burning concentrates during this period, we estimate the photochemical production of  $H_2$  ( $P_{hv}$ ) in this season considering that VOCs concentrations ( $[VOC_i]$ ), the OH concentration ( $[OH]$ ), and the fraction of  $CH_2O$  that photolyzed to produce  $H_2$  ( $\phi_i(H_2)$ ) are key factors controlling  $H_2$  production ( $P_{hv} = \sum_i k_i [OH][VOC_i]\phi_i(H_2)$ , where  $k_i$  is rate

constant for the reaction of  $VOC_i$  and OH).  $CH_4$  and isoprene may be major VOCs producing  $H_2$  in the atmosphere, and both do not have substantial seasonal variation in the SH. Therefore, we presume an annual mean in this season. The OH concentration in the SH from November to January is  $\sim 30\%$  greater than annual mean (Spivakovsky et al., 2000). A 2-dimensional model calculation of photolysis rates of  $CH_2O$  (Bruehl and Crutzen, 1993) and photochemical reaction rate of  $CH_2O$  and OH indicate nearly constant fraction of  $CH_2O$  to produce  $H_2$  along year. Therefore, over all photochemical production of  $H_2$  would be  $\sim 30\%$  greater in summer than annual mean, which results in  $\sim 33\%$  ( $=1.3/4 \times 100$ ) of the annual photochemical production of  $H_2$  during the biomass burning period in the SH. This implies that in the SH the biomass burning emission of  $H_2$  would be less than  $\sim 33\%$  of the annual photochemical  $H_2$  production. This fraction should be considered as a lower limit because we assume the same VOCs concentrations as the annual mean, which might not be correct because biomass burning is one of the major sources of VOCs. Sensitivity test shows that  $\chi_i$  for the photochemical production increases merely 0.02 with a factor of 2 increase (33% to 66%) in the fraction of  $H_2$  from biomass burning to the photochemical production of  $H_2$  in the SH because photochemical production is the major source of atmospheric  $H_2$  and occurs mainly in the NH (Table 1). However, the factor of 2 increase leads to 70% increase of biomass burning emissions and 10% decrease of the photochemical production of  $H_2$  on a global scale.

Finally, the source strengths are determined by means of mass conservation equations for the H and D isotopes of  $H_2$  on global and hemispheric scales. The uncertainties in the sources are estimated from the sensitivity runs with several  $\delta D$  values of sources from the literature. We adopt  $\delta D$  for fossil fuel combustions of  $-270\%$  (Rahn et al., 2002b) and  $-196\%$  (Gerst and Quay, 2001),  $\delta D$  for biomass burning of  $-90\%$  (this

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study) and  $-290\text{‰}$  (Gerst and Quay, 2001),  $\delta D$  for photochemical production of  $213\text{‰}$  (Rahn et al., 2003) and  $113\text{‰}$  (Gerst and Quay, 2001),  $\delta D$  for ocean and microbial  $N_2$  fixation of  $-700\text{‰}$  (Rahn et al., 2003) and half of it. Of the source strengths calculated we choose the uncertainty that results in the largest difference from the standard set of isotopic signatures shown in Table 1. For sink strengths, the uncertainties are propagated in each step of the calculation as mentioned earlier. As listed in Table 1, the individual source strengths calculated by our independent top-down approach are larger than the values previously estimated by Novelli et al. (1999). In particular, our study shows that the photochemical production of  $H_2$  is 60% higher than the former estimates (Novelli et al., 1999). The large anticipated input of  $H_2$  from photochemical oxidation indicates a substantial contribution by the photochemical oxidation of VOCs, which are ubiquitous atmospheric compounds (Singh et al., 2001). This also explains fairly homogeneous mixing ratios in both hemispheres in spite of short lifetime and major sink on soil surface.

**5. Conclusions**

Measurements of the stable isotope composition of free tropospheric  $H_2$  across the hemispheres allowed us to investigate atmospheric  $H_2$  cycle and budget in global and hemispheric scale at the limit of the number of observations. To our knowledge this is the first measurement of free tropospheric  $H_2$  covering both hemispheres. Although we have observed only during three discrete time slices, the spatial coverage of the air samples is large enough to represent the tropospheric  $H_2$  of the time slot in both hemispheres. Further observations especially at other time slots shall improve our understanding of global  $H_2$  cycle. The following is summary of our findings:

1. The NH  $H_2$  cycle is mainly driven by the soil sink for which we conjecture the snow-cover extent to play a dominant role. The large peak-to-peak seasonal cycle of the NH snow-cover extent covering  $\sim 40\%$  of the NH continents, and its precisely corresponding phase to the cycle of the NH  $H_2$  render our hypothesis plausible.

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2. We determined the global soil sink strength to be  $88(\pm 11) \text{ Tg a}^{-1}$  using the seasonal variations of  $\text{H}_2$  and its D/H ratio in the NH. Since the two sink processes have strongly differing kinetic isotope effects, measurement of the D/H ratio allows the complex soil sink to be directly scaled against the better known photochemical sink. Our results reduce the uncertainty of the soil sink strength of  $\text{H}_2$ , and in particular demonstrate that soil uptake is much stronger than previously estimated and dominates the global  $\text{H}_2$  cycle. Continued global warming will increase the sink strength of soils on the basis of a positive correlation with soil temperature (Yonemura et al., 2000b). Moreover the expected shrinking of permafrost and annual snow-cover over the NH (Armstrong and Brodzik, 2001; Folland et al., 2001), both of which are associated with the global warming, will further enhance the soil sink in future.

3. The SH  $\text{H}_2$  cycle is mainly controlled by both photochemical production of  $\text{H}_2$  from variety sources of VOCs in summer and the NH intrusion enforced by monsoon circulation in winter which are evidenced by in-phase cycle of D and H. This is however contrary to the argument that biomass burning dominates the SH  $\text{H}_2$  cycle based only on the measurement of  $\text{H}_2$  mixing ratios (Novelli et al., 1999) and from a 3-dimensional modeling study (Hauglustaine and Ehhalt, 2002).

4. The biomass burning signature of  $\delta D$  appears to vary depending on the region, likely associated with the spatial gradient of  $\delta D$  in meteoric water (Dansgaard, 1964). Weighting the emission rates in various regions, global mean value is estimated to be  $-90(\pm 40)\%$ . The value is far larger than a value estimated from a laboratory experiment (Gerst and Quay, 2001).

5. A top-down approach allowed us to independently determine the global and hemispheric source strengths being constrained by the sink strengths determined in this study and the characteristic isotopic compositions of sources. Our approach discloses far larger emissions of  $\text{H}_2$  from photochemical oxidation in the atmosphere than the previous estimates in terms of not only the absolute amounts ( $64 \text{ Tg a}^{-1}$ ) but also the relative fraction (60%) among all sources (Table 1).

## A modification of the Rayleigh distillation model

The change in the isotopic ratio of H<sub>2</sub> by a fractionation process is described by the Rayleigh distillation model (Rayleigh, 1902):

$$\frac{R_f}{R_i} = \left( \frac{C_f}{C_i} \right)^{\alpha-1} \quad (\text{A1})$$

where  $R_i$  and  $C_i$  are the initial isotopic ratio and mixing ratio of H<sub>2</sub>,  $R_f$  and  $C_f$  are those observed along the fractionation process, and  $\alpha$  is the isotopic fractionation factor. Equation (A1) can be converted by means of “ $\delta$ ” notation into:

$$\ln \left( \frac{\delta D_f \times 10^{-3} + 1}{\delta D_i \times 10^{-3} + 1} \right) = (1 - \alpha) \ln \left( \frac{C_i}{C_f} \right) \quad (\text{A2})$$

This can be approximated by applying a Taylor series expansion as follows (Bergamaschi et al., 2000):

$$\delta D_f \approx \frac{(\delta D_i + 1000)(1 - \alpha)C_i}{C_f} + \delta D_Q \quad (\text{A3})$$

where  $\delta D_Q = \alpha \delta D_i + (\alpha - 1) \times 1000$  which is the same expression as that derived from the definition of isotopic fractionation factor at isotopic equilibrium. According to Eq. (A3), one can obtain  $\alpha$  from the slope of the relationship between  $\delta D$  and the inverse of the H<sub>2</sub> mixing ratios observed during the isotopic fractionation. Equation (A3) also can be utilized to verify whether a system is at an isotopic equilibrium or not, because  $\delta D_Q$  in Eq. (A3) depends on  $\alpha$  and  $\delta D_i$  at isotopic equilibrium (e.g. Fig. 4).

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**Table 1.** The global budget of atmospheric H<sub>2</sub> (Tg a<sup>-1</sup>). Isotopic signatures of sources are shown under the column,  $\delta D_i$ . For the sink processes, the isotopic fractionation factors are shown as,  $\alpha_j$ , which is dimensionless.

	NH fraction		Novelli et al. (1999)	This study		
	$\delta D_i$ (‰)	$\chi_i$	Global (Tg a <sup>-1</sup> )	Global (Tg a <sup>-1</sup> )	NH (Tg a <sup>-1</sup> )	SH (Tg a <sup>-1</sup> )
Sources						
Fossil fuel combustion	-270 <sup>a</sup>	0.9	15±10	15±6	13	1.5
Biomass burning	-90	0.53	16±5	16±3	8.4	7.5
Photochemical production	190 <sup>b</sup>	0.65	40±16	64±12	42	23
Biogenic N <sub>2</sub> fixation	-700 <sup>c</sup>	0.6	3±1	6±5	3.6	2.4
Oceans	-700 <sup>c</sup>	0.4	3±2	6±5	2.4	3.6
Total sources			77±16	107±15	69	38
Sinks						
OH oxidation	0.58±0.07 <sup>d</sup>	$\chi_j$ 0.49	19±5	19±3	9.4	9.7
Soil uptake	0.943±0.007 <sup>e</sup>	0.71	56±41	88±11	62	26
Total sinks			75±41	107±11	72	35

<sup>a</sup> Rahn et al. (2002b); <sup>b</sup> Rhee et al. (2005); <sup>c</sup> Rahn et al. (2003); <sup>d</sup> Talukdar et al. (1996) at 277 K; <sup>e</sup> average from Gerst and Quay (2001) and Rahn et al. (2002a)

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**Table 2.** Logistic information on the air samples, their H<sub>2</sub> and CO mixing ratios, and  $\delta D$  values.

Sample ID	Date	Lon. (° E)	Lat. (° N) <sup>§</sup>	[H <sub>2</sub> ] (ppb) <sup>*</sup>		$\delta D$ (‰) <sup>*</sup>		No. of replicate	[CO] (ppb) <sup>  </sup>
				Mean	sd	Mean	sd		
WAS-22-1	05/19/2000	15.43	-15.81	528	2	139	3	3	76
WAS-22-2	05/19/2000	13.72	-9.98	550	1	129	4	2	95
WAS-22-3	05/19/2000	11.66	-4.57	545	3	139	3	1	82
WAS-22-4	05/19/2000	9.84	0.70	524	3	141	3	1	106
WAS-22-5	05/19/2000	9.33	6.31	552	0.1	125	3	2	126
WAS-22-6	05/19/2000	8.54	12.40	552	3	127	3	1	116
WAS-22-7	05/19/2000	7.95	18.29	557	3	126	3	1	91
WAS-22-8	05/19/2000	7.37	23.95	562	3	122	3	2	108
WAS-22-9	05/19/2000	6.86	29.43	557	3	125	3	1	98
WAS-22-10	05/19/2000	6.72	34.97	558	0.3	129	2	2	75
WAS-22-11	05/19/2000	7.67	40.82	558	3	129	3	1	89
WAS-22-12	05/19/2000	10.55	46.18	557	3	122	3	1	87
WAS-25-1	07/28/2000	15.68	-16.96	524	3	131	3	1	97
WAS-25-2	07/28/2000	14.18	-11.92	543	4	131	5	3	74
WAS-25-3	07/28/2000	12.46	-6.85	538	9	133	1	2	76
WAS-25-4	07/28/2000	10.33	-1.70	523	1	126	0.4	2	154
WAS-25-5	07/28/2000	9.66	3.71	525	3	125	3	1	150
WAS-25-6	07/28/2000	8.93	9.42	545	0.1	125	8	2	114
WAS-25-7	07/28/2000	8.22	15.29	534	3	129	3	1	93
WAS-25-8	07/28/2000	7.67	21.27	539	3	128	3	1	85
WAS-25-9	07/28/2000	7.00	27.16	544	3	125	3	1	84
WAS-25-10	07/28/2000	6.80	32.89	538	3	129	3	1	80
WAS-25-12	07/28/2000	9.36	44.09	544	3	129	3	1	66
WAS 30-1	12/03/2000	18.37	-27.74	550	3	138	3	1	65
WAS 30-2	12/03/2000	17.44	-22.70	544	3	136	3	1	90
WAS 30-3	12/03/2000	15.89	-17.71	543	3	138	3	1	96
WAS 30-4	12/03/2000	14.38	-12.61	538	3	137	3	1	99
WAS 30-5	12/03/2000	12.75	-7.56	533	3	135	3	1	110
WAS 30-6	12/03/2000	10.71	-2.61	545	3	137	3	1	90
WAS 30-7	12/03/2000	9.65	2.77	530	3	129	3	1	141
WAS 30-8	12/03/2000	9.03	8.72	528	3	133	3	1	97
WAS 30-9	12/03/2000	8.28	14.67	534	3	132	3	1	95
WAS 30-10	12/03/2000	7.76	20.46	533	5	129	2	2	93
WAS 30-11	12/03/2000	7.12	26.04	533	3	133	3	1	77
WAS 30-12	12/03/2000	6.84	31.41	517	3	135	3	1	83

<sup>§</sup> Negative values indicate the southern hemisphere.

<sup>\*</sup> Uncertainties in the H<sub>2</sub> mixing ratio and  $\delta D$  for single measurement are assumed to be the mean of the uncertainties of the replicate measurements. sd designates 1 standard deviation of the mean.

<sup>||</sup> Mean CO mixing ratios of the in situ measurements during whole air sampling period.

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**Table 3.** Fitting parameters for  $H_2$  and  $\delta D$  representing their seasonal variations in the northern (NH) and southern hemisphere (SH).  $H_2$  mixing ratios and  $\delta D$  values in both hemispheres are fitted to a function,  $y = a \cos(2\pi(x - \phi) + m)$ .

	$[H_2]$ (ppb)		$\delta D$ (‰)	
	NH	SH	NH	SH
Amplitude ( $a$ )	18.2±1.6	8.1±3.2	4.0±0.9	4.2±1.6
Phase* ( $\phi$ )	0.28±0.01	0.10±0.07	0.85±0.05	0.13±0.06
Average ( $m$ )	543.4±0.8	542.9±1.8	128.3±0.7	135.9±1.1

\* Units for phase are year.

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**Table 4.** Surface areas ( $\times 10^6$  km<sup>2</sup>) for several types of land in both hemispheres.

	Northern Hemisphere	Southern Hemisphere	Reference
Continental area	103	46	Butcher et al. (1992)
Snow-cover	23.1 ( $\pm 4.8$ )	14.5 <sup>§</sup>	Armstrong and Brodzik (2001) and Dewey and Heim (1983)
Wetlands <sup>‡</sup>	4.1 ( $\pm 0.2$ )	1.6 ( $\pm 0.3$ )	Aselmann and Crutzen (1989)
Rice paddies <sup>†</sup>	1.3 ( $\pm 0.2$ )	–	Aselmann and Crutzen (1989)
Effective soil surface	74.5 ( $\pm 4.9$ )	30.0 ( $\pm 0.3$ )	

<sup>§</sup> Including the area of Antarctica ( $= 14 \times 10^6$  km<sup>2</sup>)

<sup>‡</sup> The uncertainty of the wetlands is assumed to be the difference of areas estimated by Aselmann and Crutzen (1989) and Matthews and Fung (1987)

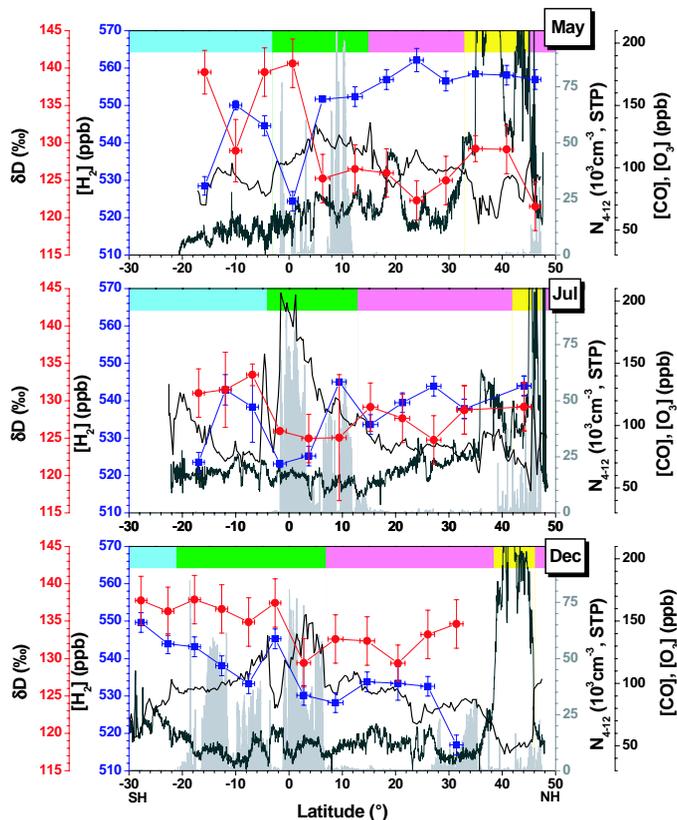
<sup>†</sup> The uncertainty of rice paddy area is assumed to be the difference of areas estimated by Aselmann and Crutzen (1989) and FAO Regional Office for Asia and Pacific (2003).

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**Fig. 1.** The measured spatial variability of the mixing ratios of  $\text{H}_2$  (blue squares) and its  $\delta D$  values (red circles) in May, July, and December. The horizontal bars indicate the sampling distance and the vertical bars represent the analytical uncertainty ( $1\sigma$ ). Furthermore the in situ observations of ultra-fine aerosol ( $N_{4-12}$ ) (shaded areas), CO (thick line) and  $\text{O}_3$  (thin line) are shown. Color codes on top of each panel: cyan (southern hemisphere), green (equatorial tropics), and magenta (northern hemisphere), and yellow (the lowermost stratosphere).

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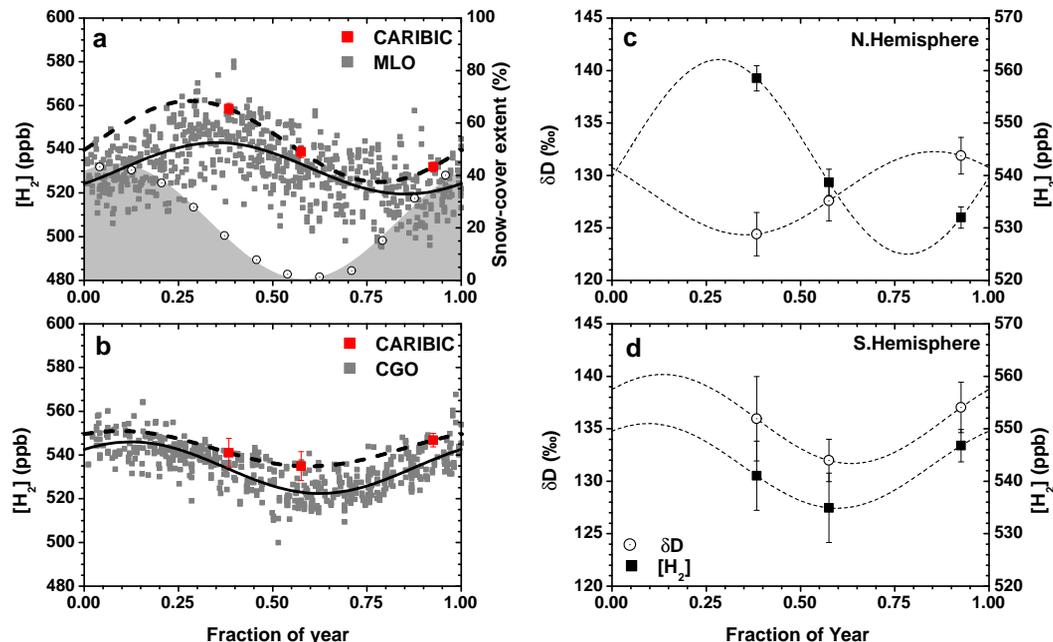
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**Fig. 2.** Seasonal variations of the  $H_2$  mixing ratios and the  $\delta D$  values. **(a)** and **(b)** Comparison of the  $H_2$  mixing ratios between the airborne observations (CARIBIC) and the surface observations (NOAA/CMDL) (Novelli et al., 1999). MLO and CGO indicate the monitoring stations of Mauna Loa and Cape Grim. Dashed and solid lines are sinusoidal fits to the CARIBIC and NOAA/CMDL data sets, respectively. In (a), the fraction of snow-cover extent from NOAA satellite observations (Armstrong and Brodzik, 2001) in the northern hemisphere is reproduced with gray shading (sinusoidal fit) and dotted circles (mean monthly data for 20 year observations). **(c)** and **(d)** Seasonal variations of the  $\delta D$  values and the  $H_2$  mixing ratios in the northern and southern hemisphere. The error bars represent 1 standard deviation of the mean.

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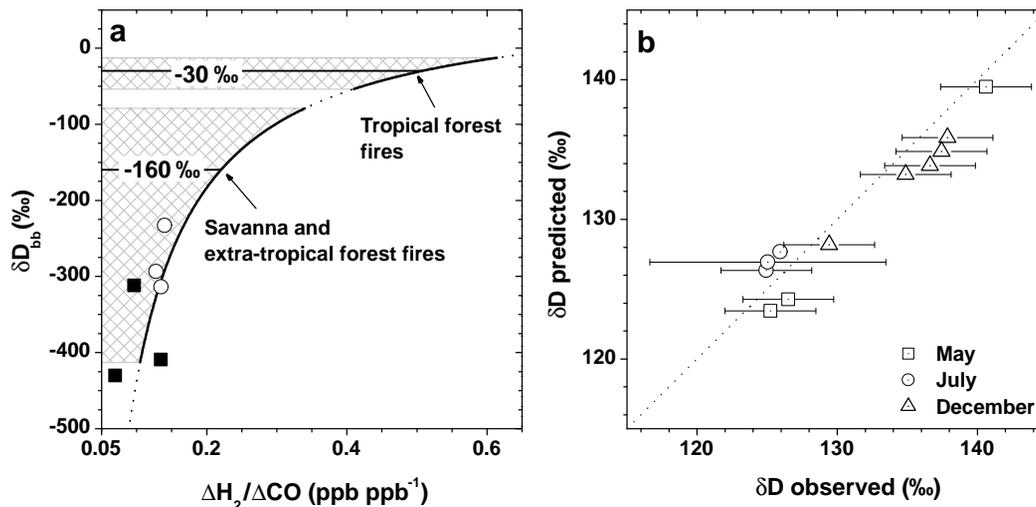
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**Fig. 3.** (a) The deuterium (D) content of  $H_2$  emitted from biomass burning ( $\delta D_{bb}$ ) as a function of the enhancement ratio ( $ER = \Delta H_2 / \Delta CO$ ) derived from the model. The dotted curve depicts the relation between  $\delta D_{bb}$  and ER predicted by the model ( $\delta D_{bb} = 70 - \frac{51}{ER}$ ). The fat sections of the dotted curve confine the range of ERs for the tropical, extra-tropical, and savanna regions. The ERs for these regions are after Andreae and Merlet (2001). The gray hatched areas highlight the corresponding range of  $\delta D$ . The  $\delta D$  values of  $-30\text{‰}$  and  $-160\text{‰}$  corresponds to the mean of ERs for the tropical forest fires and the extra-tropical and savanna fires, respectively. The symbols indicate the results from a laboratory experiment (Gerst and Quay, 2001) with Idaho white pine needles (solid squares) and Lodgepole pine branches (open circles). (b) Comparison of  $\delta D$  from the model prediction and the observation in the equatorial tropics for all 3 flights. The dotted line is one-to-one relation.

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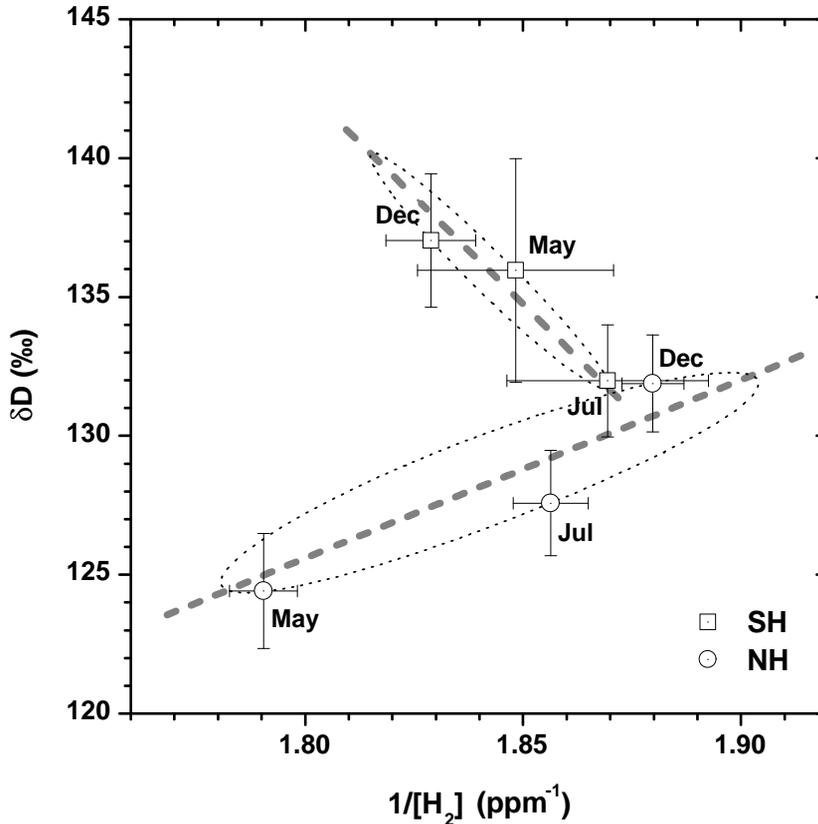
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**Fig. 4.** Relationship between  $\delta D$  and the inverse of the  $H_2$  mixing ratios in the southern and northern hemispheres. The error bars represent 1 standard deviation of the mean. The ellipses are derived from the sinusoidal fits of Fig. 2c and d. The thick dashed lines represent the Rayleigh model. At isotopic equilibrium, its slope is related to the apparent isotopic fractionation factor and the intercept with the vertical axis represents the isotopic signature of all combined sources.

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