δD(H_2) in the tropopause region probed by the CARIBIC aircraft

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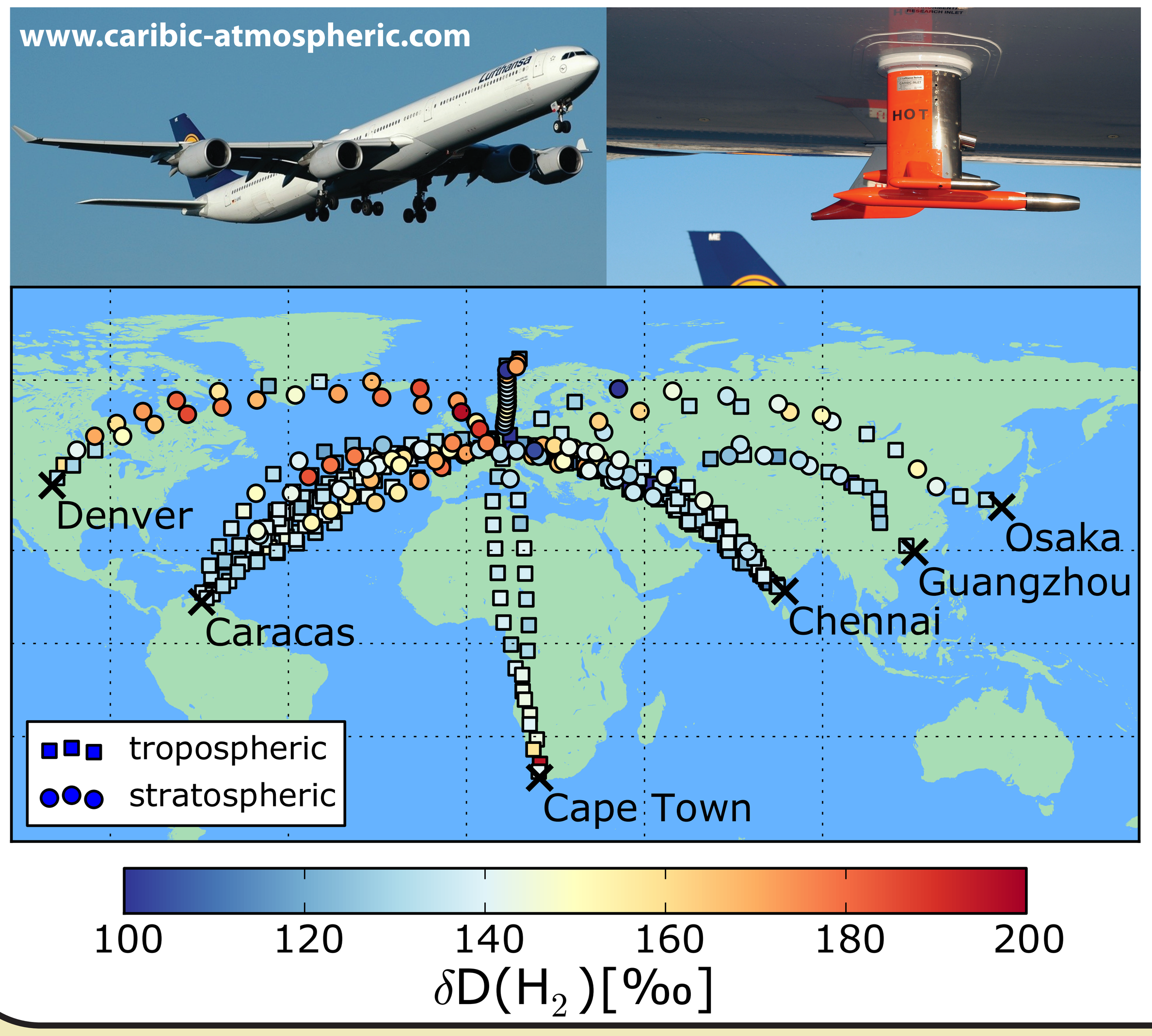
Atmospheric H_2 and the CARIBIC project

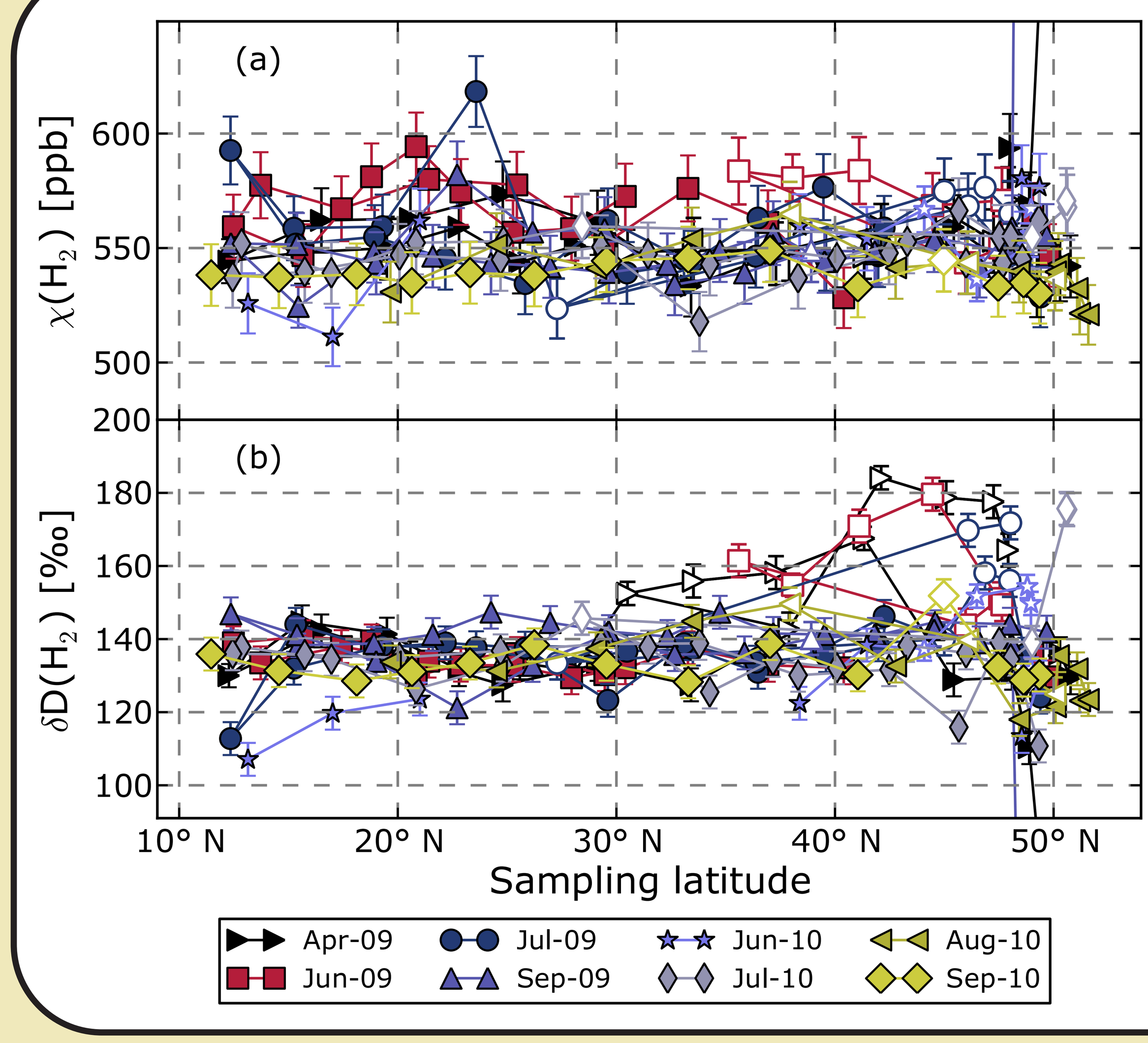


H_2 leakage from H_2-powered vehicles may cause a large increase in atmospheric H_2 mixing ratios ($\chi(H_2)$), necessitating a better understanding of the H_2 cycle. Measurements of the isotopic composition (deuterium content, $\delta D(H_2)$) can help distinguish different source and sink processes, as those have very different isotopic effects.

The CARIBIC project uses an automated instrument container on board of a commercial passenger aircraft to carry out in-situ measurements and collect air samples. The resulting samples are mostly from the Upper Troposphere-Lower Stratosphere (UTLS) region.

Fig.1: Top: the aircraft (Lufthansa Airbus A340-600) and the attached inlet system used for CARIBIC. Bottom: sampling location of all samples analysed for $\chi(H_2)$ and $\delta D(H_2)$, color coded with $\delta D(H_2)$ value.

General features of the data



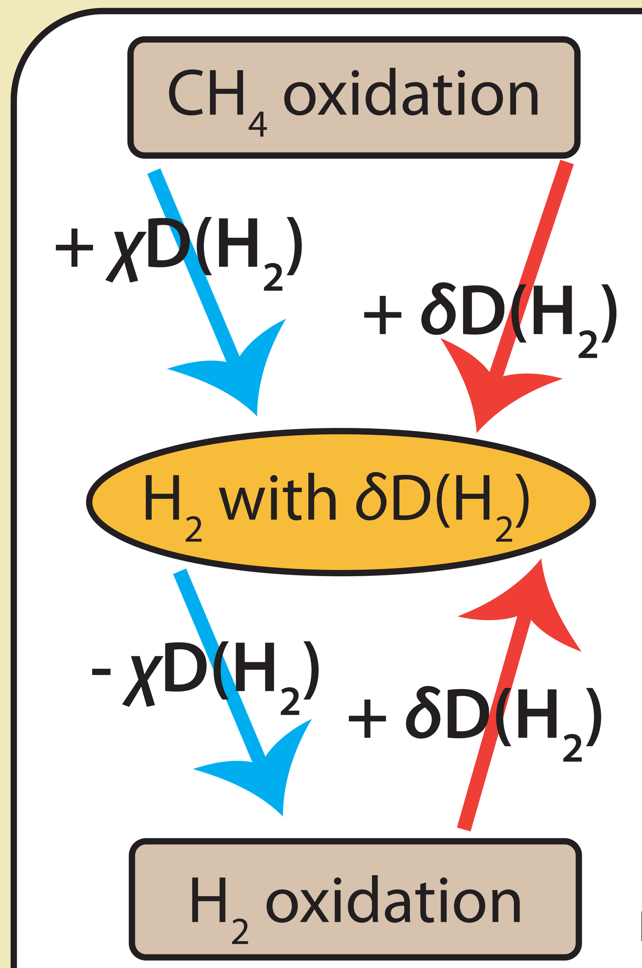
490 samples from 37 flight legs have been analyzed for $\chi(H_2)$ and $\delta(D,H_2)$ at the IMAU isotope laboratory. Fig. 2 shows the results of all 7 return flights to Caracas.

Some samples seem affected by pollution (high $\chi(H_2)$ and low $\delta D(H_2)$). This tends to occur in samples that were taken around take-off and landing of the aircraft (e.g. in April and September, values are off the figure scale).

With ozone data, stratospheric samples can be identified. These samples often show a clear elevation in $\delta D(H_2)$.

Fig.2: $\chi(H_2)$ **(a)** and $\delta D(H_2)$ **(b)** data from flights to Caracas, Venezuela. Stratospheric samples are shown with open symbols.

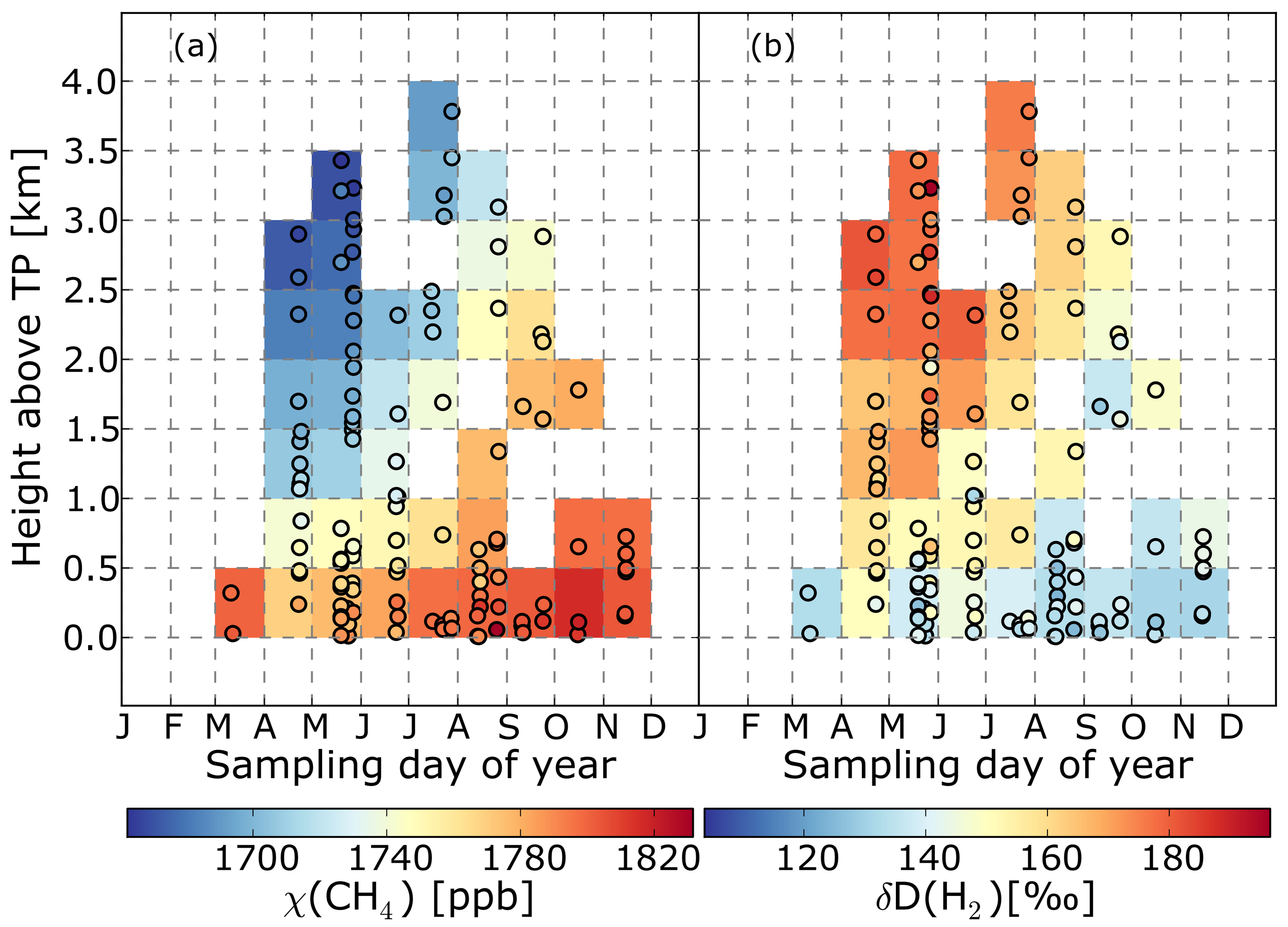
Stratospheric samples



Literature shows that in the stratosphere, the competing production and destruction processes for H_2 balance out, but do cause a strong deuterium enrichment (Fig. 3). Inverse correlations exist between $\delta D(H_2)$ and methane (CH_4), which is destroyed as H_2 is produced.

120 CARIBIC samples contain air from the lower stratosphere. Fig. 4(a) and (b) show that $\delta D(H_2)$ is high when and where $\chi(CH_4)$ has decreased. Fig 4(c) shows that this results in a compact inverse correlation. This correlation can be used to parameterize $\delta D(H_2)$ of H_2 that is imported into the troposphere from the lowermost stratosphere in global chemistry models.

Fig.3: A cartoon representation of the the stratospheric H_2 cycle



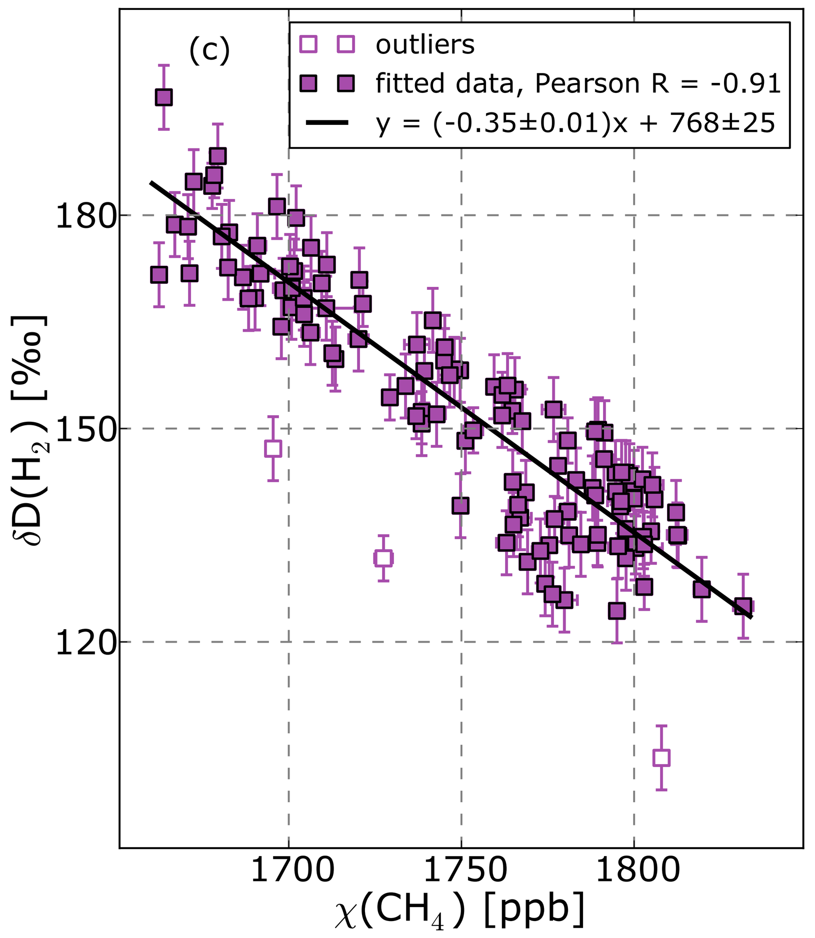
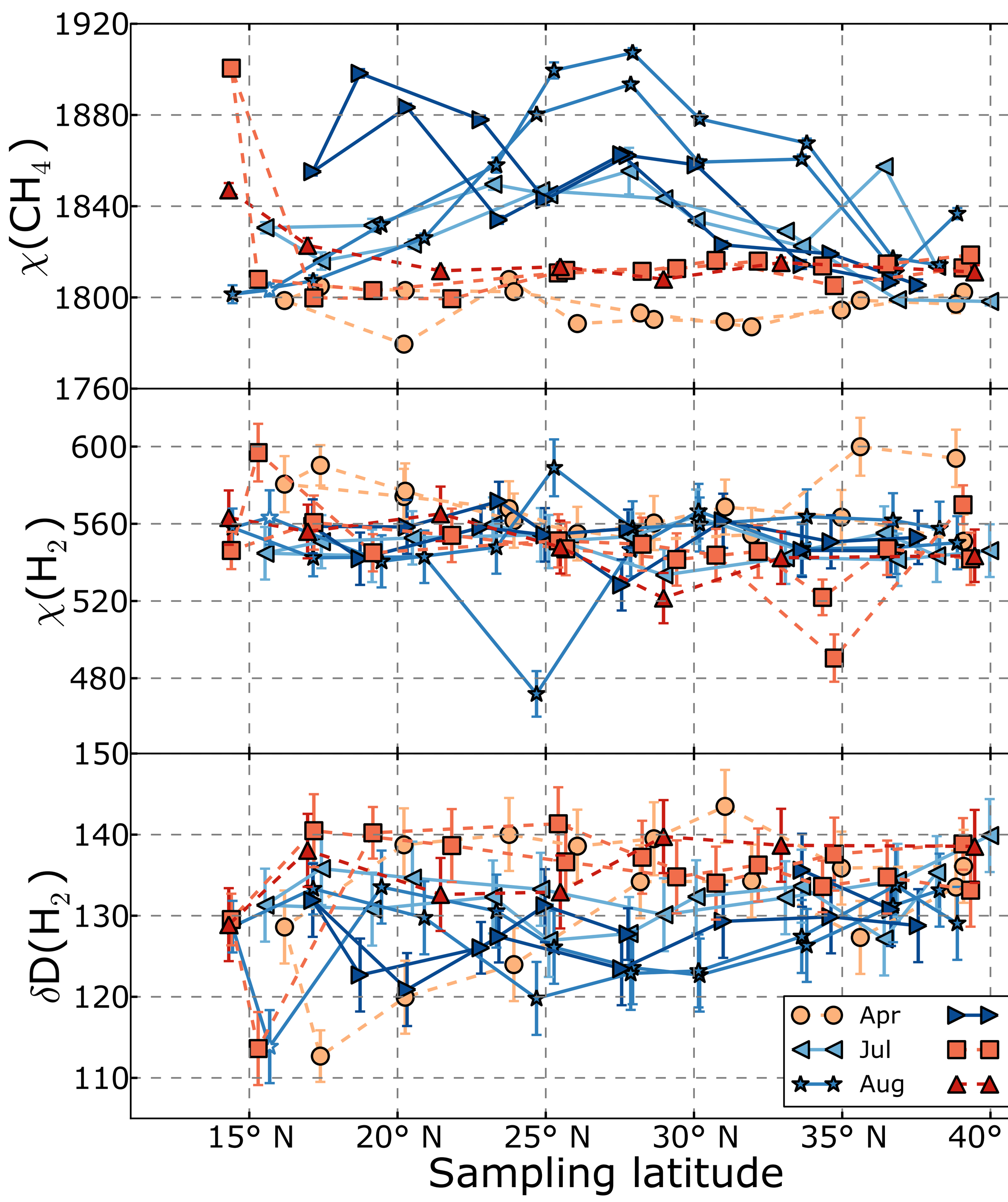


Fig.4: $\chi(CH_4)$ **(a)** and $\delta D(H_2)$ **(b)** plotted against time of year and height above the tropopause **(c):** $\delta D(H_2)$ plotted against $\chi(CH_4)$, with bivariate fit.

Monsoon flights

Previously, increased levels of CH_4 were found in CARIBIC flights to India during the summer monsoon (Fig. 5(a)). No enhancement was found in $\chi(H_2)$ (Fig 5(b)), but the samples with increased methane showed a decrease in $\delta D(H_2)$ (Fig. 5(c)), which is correlated to $\chi(CH_4)$ (Fig. 5 (d)).

The absence of a concomitant $\chi(H_2)$ increase and the correlation with $\chi(CH_4)$ indicate that the $\delta D(H_2)$ decrease may at least partly be caused by microbial production of H_2, which has an extremely depleted source signature (-700 ‰, in contrast to e.g. the -196 ‰ source signature of H_2 produced by fossil fuel combustion).



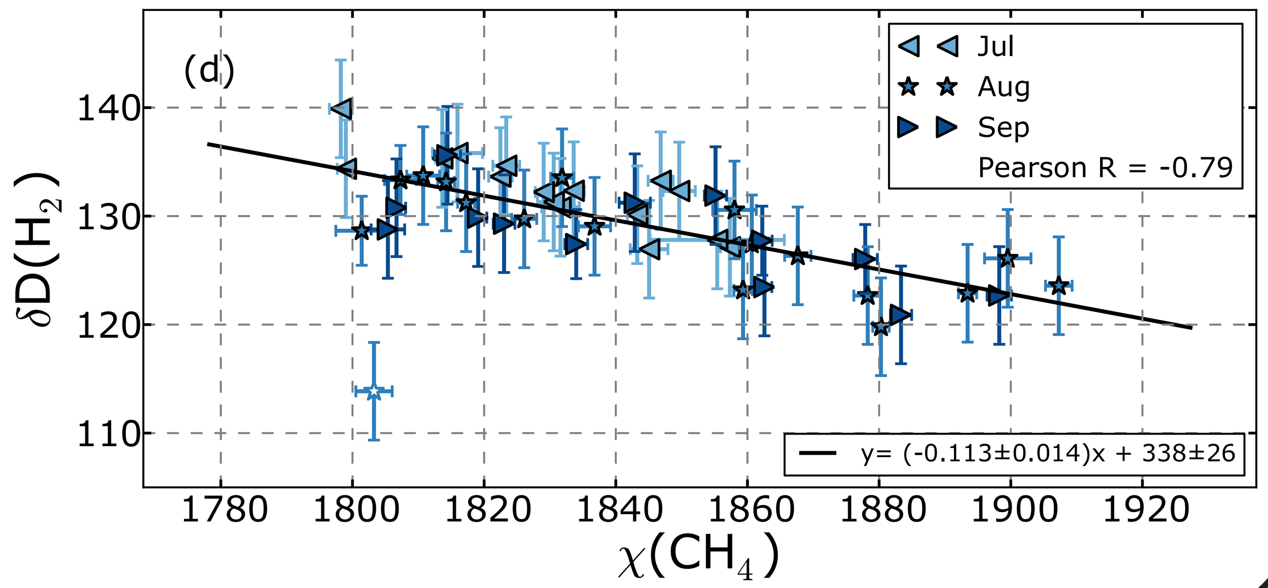


Fig.5: $\chi(CH_4)$ **(a),** $\chi(H_2)$ **(b)** and $\delta D(H_2)$ **(c)** measured on tropospheric samples from flights to India south of 40° N in the summer monsoon (July-Sept, blue shades) and other seasons(Okt-Apr, orange shades). **(d):** $\delta D(H_2)$ plotted against $\chi(CH_4)$, with bivariate fit.

Conclusions / Outlook

A large number of UTLS samples were analyzed for $\chi(H_2)$ and $\delta D(H_2)$.

- For the *lowermost stratosphere* the $\delta D(H_2)$ observations provide information about the stratospheric H_2 and CH_4 cycles.
- First observations of $\delta D(H_2)$ in the *Indian summer monsoon* show an interesting correlation with $\chi(CH_4)$, which may point to an as yet unstudied microbial H_2 source.

These UTLS data complement observations from ground stations and ship cruises and will help in constraining the uncertainties in the H_2 budget and in validating models.

Read more

These data are published in:
Batenburg et al., *The stable isotopic composition of molecular hydrogen in the tropopause region probed by the CARIBIC aircraft*, Atmos. Chem. Phys. Discuss., 2011, 12, 589-622