

## A | Introduction

Why is hydrogen an important research topic?

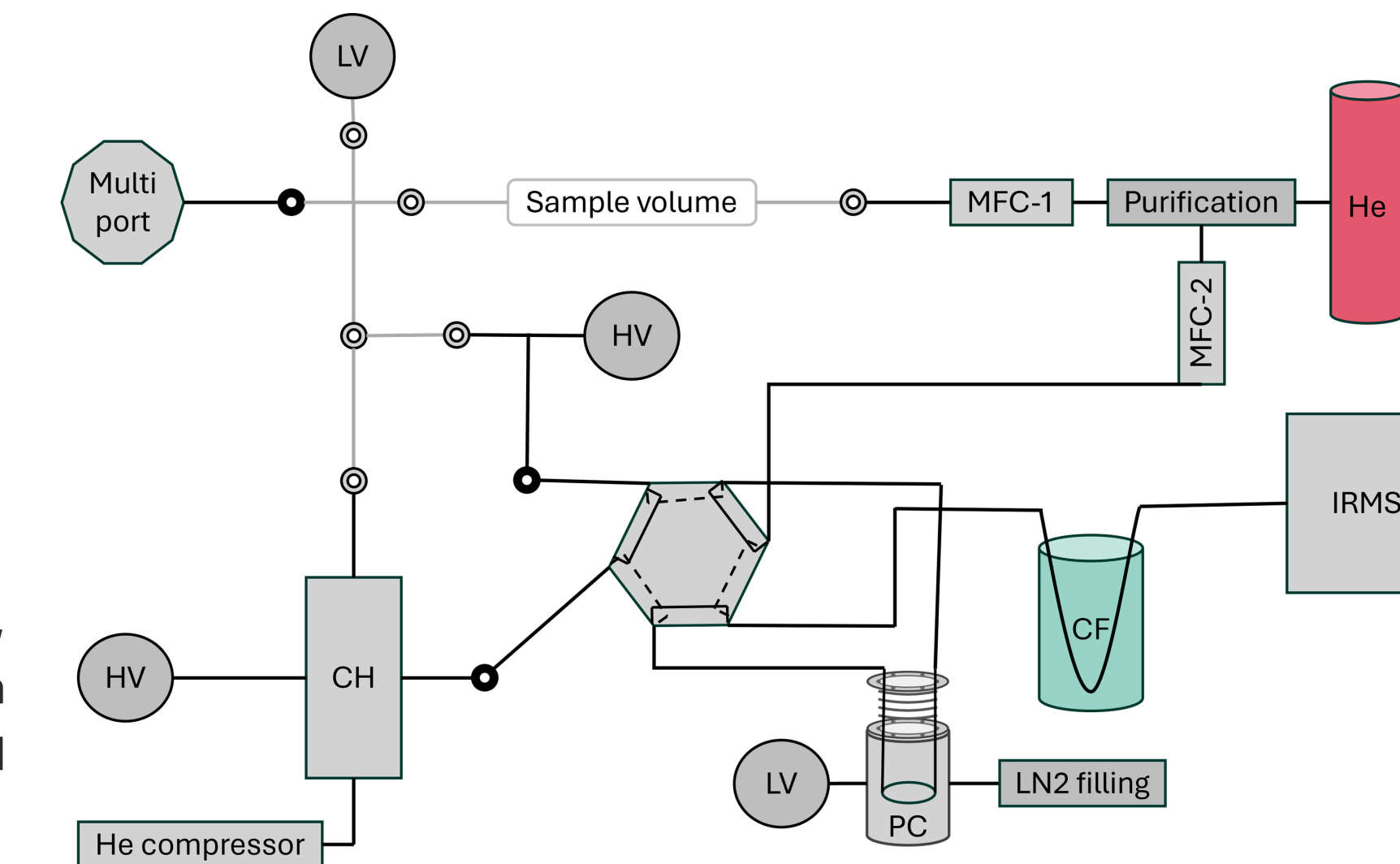
- Atmospheric molecular **hydrogen** (H<sub>2</sub>) is considered a promising **future energy carrier**, but also an indirect greenhouse gas.
- The **indirect warming effect** is caused by the reaction of H<sub>2</sub> with OH, causing increased:
  - methane mole fraction
  - stratospheric water vapour
  - tropospheric ozone, which all lead to extra warming.
- H<sub>2</sub> contributed **0.020 °C** over the past decade (2010 – 2020) to the increase of global surface air temperature, Ouyang et al., 2025.

What gaps does this study fill?

- Stable isotope measurements can help to **constrain source and sink terms** in the hydrogen budget, because of the very different deuterium content of sources.
- Recent **observations** of δD-H<sub>2</sub> are very **scarce**
- Despite its importance as an indirect greenhouse gas, important features of the hydrogen cycle remain **poorly constrained** by observations, for example **seasonal variability** and **latitudinal gradients**.

## B | Methods

- Atmospheric air samples from **ground-based sampling stations** and **ship transects** across Atlantic and Pacific Ocean collected in framework of the FETCH4 and ISAMO project (see world map).
- Analysis carried out using **continuous-flow isotope-ratio mass spectrometry** (IRMS), with the method developed and described by Rhee et al., 2004.
- Instrumental **stability** (from sample remeasurements, n = 33, one point calibration): **4.8 ppb** for H<sub>2</sub> and **2.3‰** for δD. Precision from lab standard stability (over 2.5 weeks): 7.0 ppb for H<sub>2</sub> and 4.6‰ for δD.



H<sub>2</sub> is separated from sample air matrix in three steps:

- Cryogenic separation using a cold head (CH)** – the sample air matrix is condensed at 40 K, except the most volatile gases (H<sub>2</sub>, He, Ne).
- Pre-concentration of H<sub>2</sub> (PC)** – non-condensed components are collected in a 5 Å molecular sieve at 83 K.
- Cryo-focus purification (CF)** – the hydrogen is flushed with He from PC to CF, consisting of a capillary filled with 5 Å molecular sieve, immersed in liquid nitrogen (77 K).

After separation, the H<sub>2</sub> is measured using ThermoFisher IRMS for H<sub>2</sub> and δD.

## C | Results

Seasonal and latitudinal patterns in H<sub>2</sub> and δD

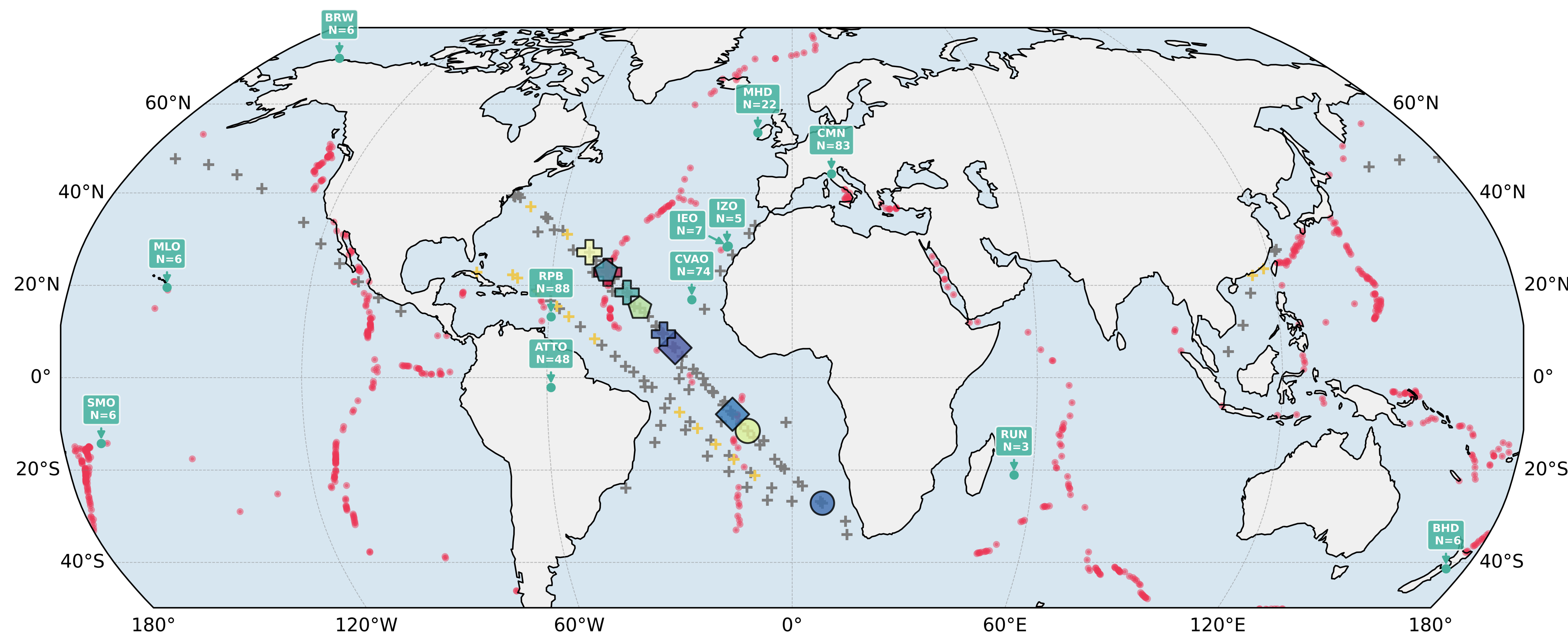
- Both H<sub>2</sub> and δD are **higher** in the **Southern Hemisphere** in all seasons, which is consistent with previous measurements by e.g. Batenburg, 2012.
- In the months June, July and August, the **interhemispheric difference** is the smallest.
- Measurements from the stations and ships differ the most during December, January and February.

Identifying polluted samples from ship transects

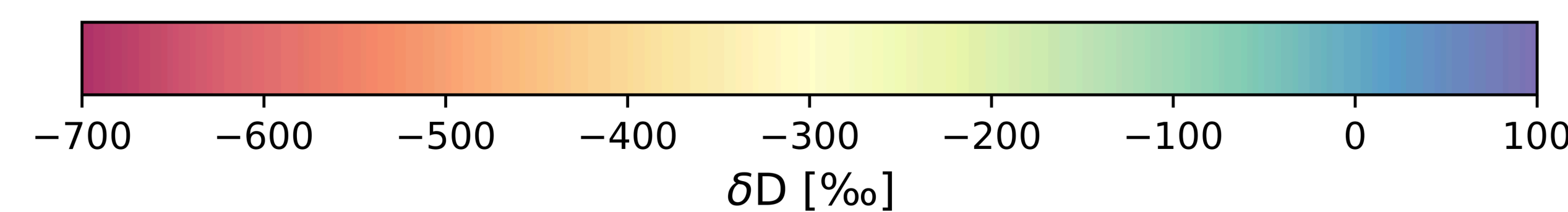
Outliers sampled during ship transects are selected based on a 10% deviation from the median of the measurements for both H<sub>2</sub> and δD.

Polluted samples cluster into two distinct source groups:

- Combustion** origin (yellow + on map); in these samples elevated H<sub>2</sub> mole fractions are associated with high CO. Keeling plot analysis points to a combustion origin with a source signature of **-286 ± 94 ‰** (R<sup>2</sup> = 0.51).
- Geological or biological** origin (large colour coded markers on map); no contamination in CO is found for these samples. Keeling plot analysis yields source signature of **-735 ± 9 ‰** (R<sup>2</sup> = 0.998). Interestingly, most of these samples seem to overlap quite well with the hydrothermal vent regions in the ocean.



- Hydrothermal vent regions
- ⊕ Sampling location ship (N=132)
- ⊕ Contaminated samples (N=16)
- STN Sampling stations



Outliers low source signature

- January
- ◆ April
- ⊕ June
- ⬠ October

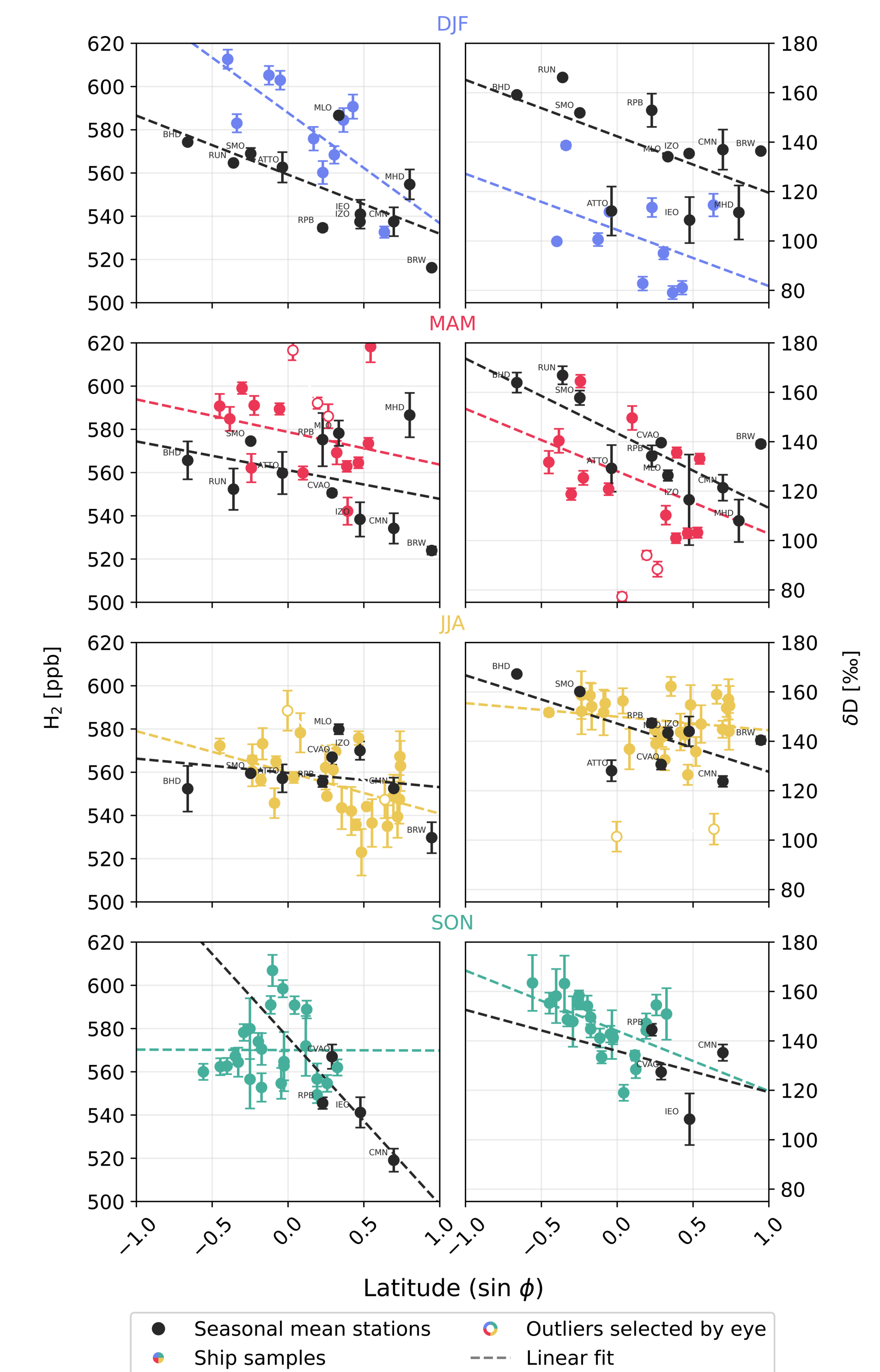


Table with sample information from outliers with a low source signatures

Date (DD-MM)	10-01	14-01	01-04	04-04	07-06	09-06	10-06	11-06	27-10	29-10
Latitude	27°S	12°S	8°S	6°N	9°N	18°N	23°N	27°N	15°N	23°N
H <sub>2</sub> (ppb)	650	1004	671	612	609	702	5893	1103	891	671
δD (‰)	48	-213	36	77	63	-39	-653	-273	-160	-12

Dataset used for hydrothermal vent regions: InterRidge Vents Database version 3.4, June 21, 2025. Downloaded from: Pacific Data Hub.

## D | Conclusions

- This extended dataset of H<sub>2</sub> and δD provides new **observational constraints** for **understanding and modeling** the global hydrogen cycle.
- The results show a robust latitudinal gradient, with **higher** H<sub>2</sub> and δD in the **Southern Hemisphere**. The latitudinal gradient is **weakest** in **boreal summer**.
- Outliers in ship samples point towards two different sources of contamination: **combustion** originated, and with a **geo-/biological** origin.
- The association of geo-/biological identified outliers with **hydrothermal vent regions** suggests an underexplored oceanic H<sub>2</sub> source, deserving further investigation.