Modeling the isotopes of hydrogen

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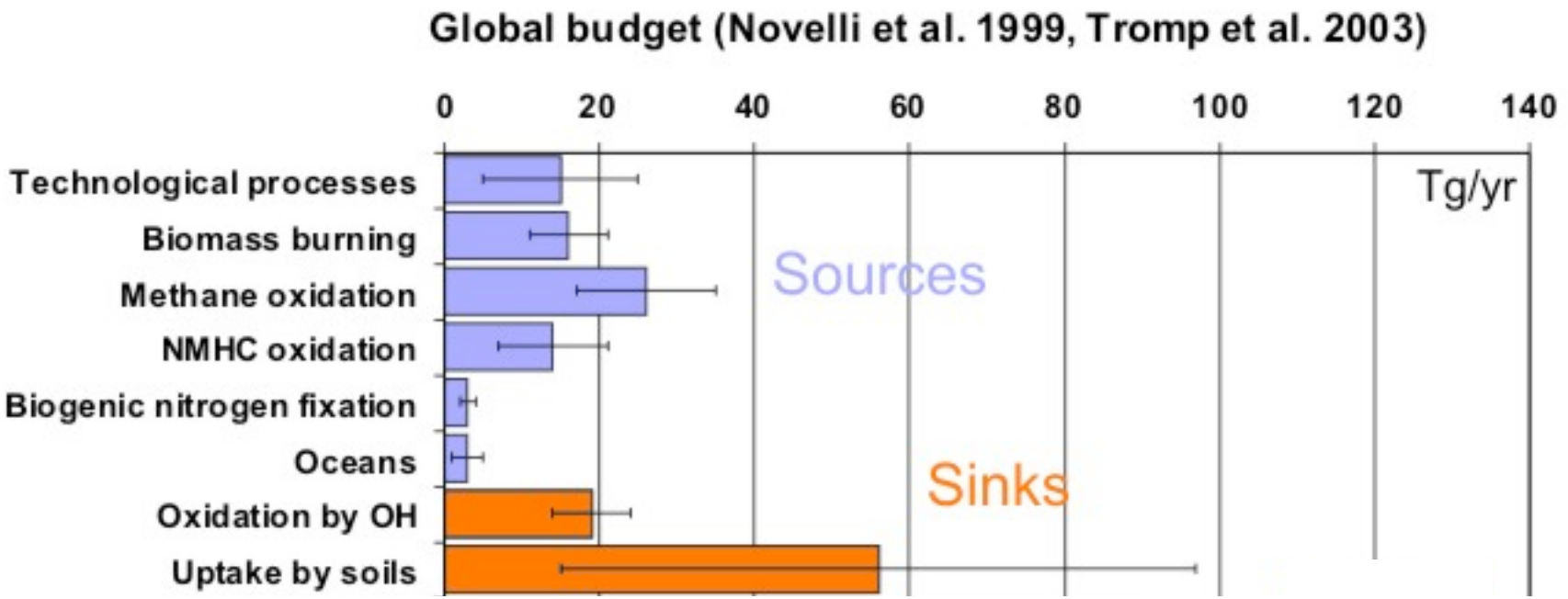
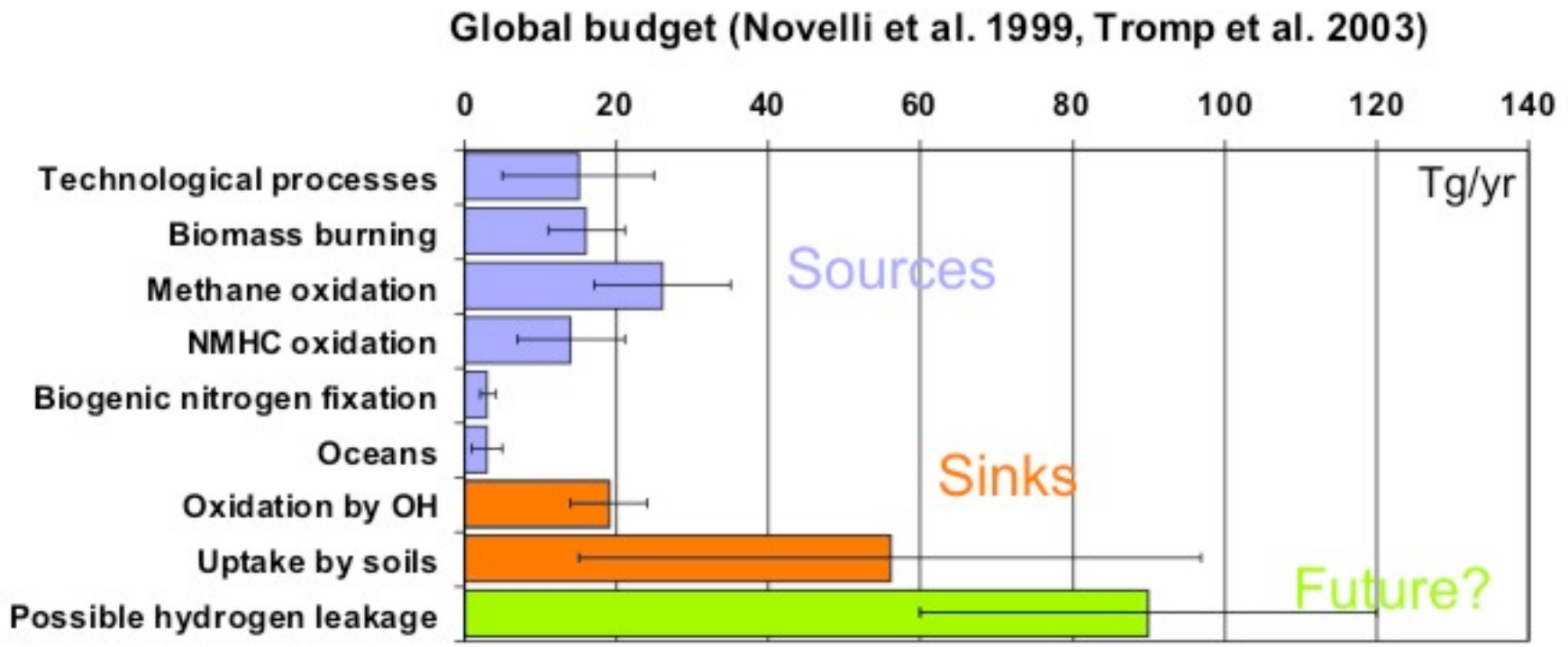
Introduction: The H_2 budget



- Linked to methane cycle
- Larger mixing ratios in SH than NH
- Large uncertainties exist in the global H_2 budget
- Expected `Hydrogen economy'

Introduction: The H_2 budget



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- Larger mixing ratios in SH than NH
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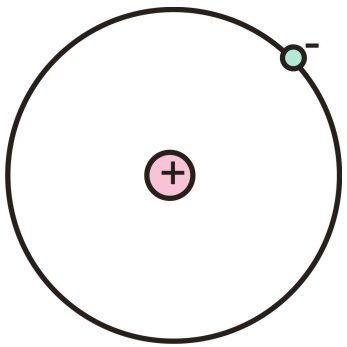
Introduction: Hydrogen isotopes

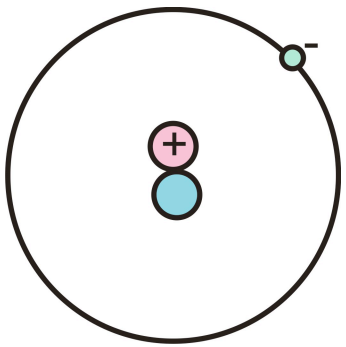
Isotopes: atoms of the **same chemical element**, with **different mass**

Isotopes of hydrogen:



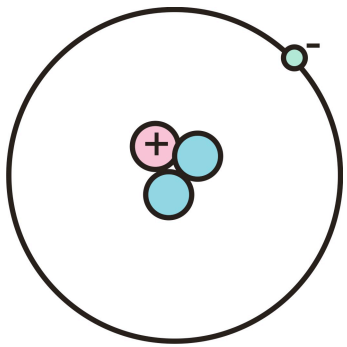
^{1}H or H

Protium/hydrogen



^{2}H or D

Deuterium

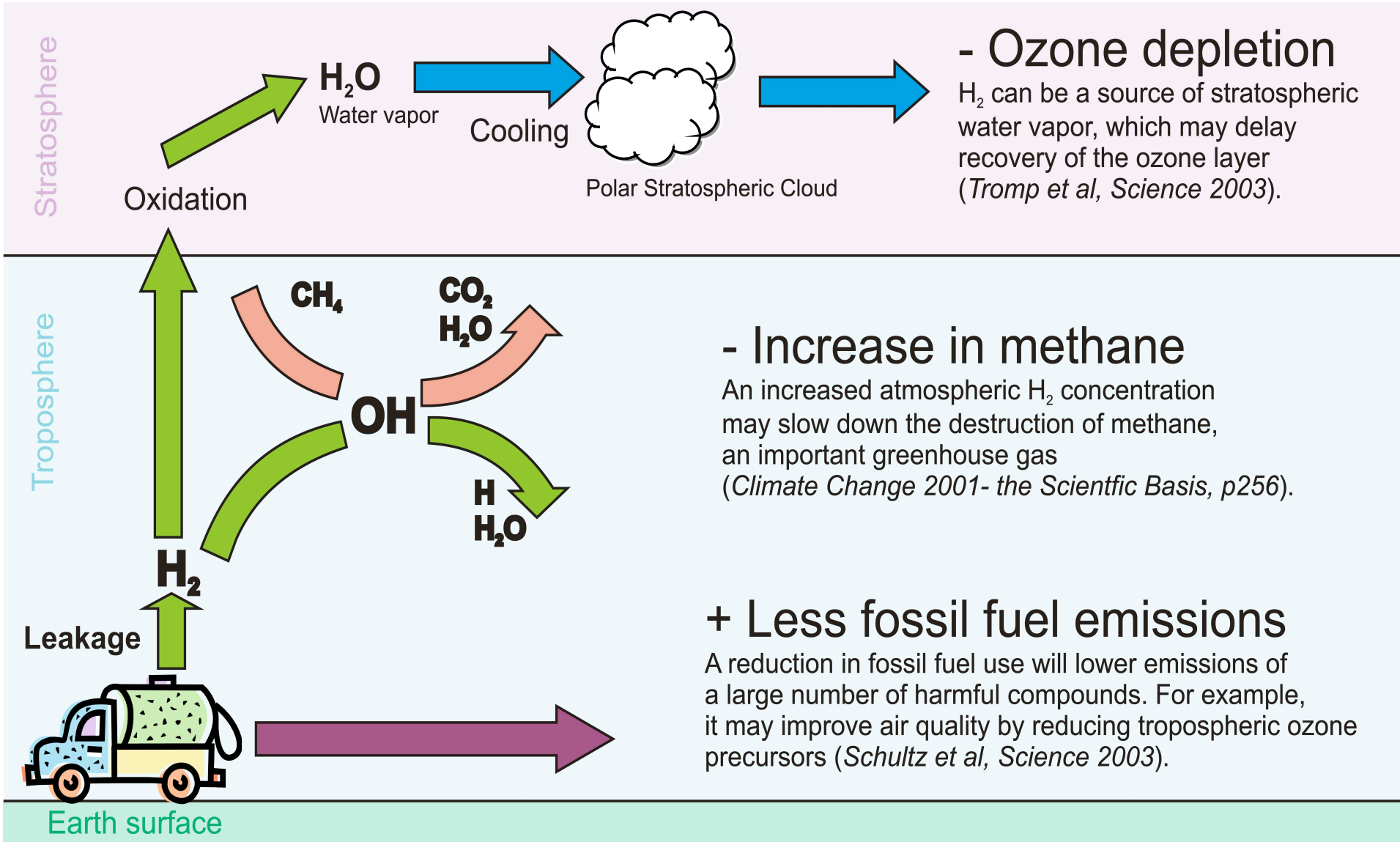


^{3}H or T

Tritium (unstable)

Deuterium atoms undergo the same reactions as `ordinary' hydrogen atoms, but at **different rates**.

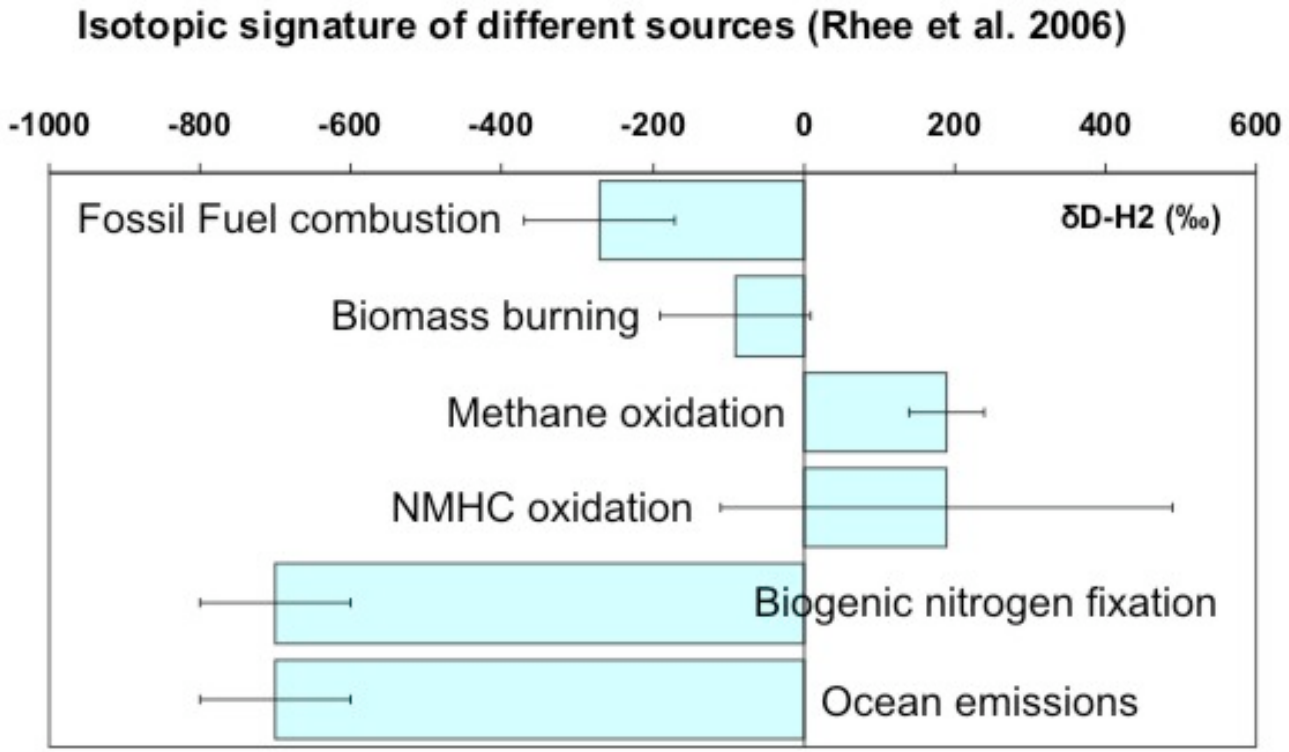
Effects of an hydrogen economy



Introduction: Hydrogen isotopes

Result: H_2 from different sources has a different deuterium content.

Also the different sinks have a different effect on the relative deuterium content of H_2

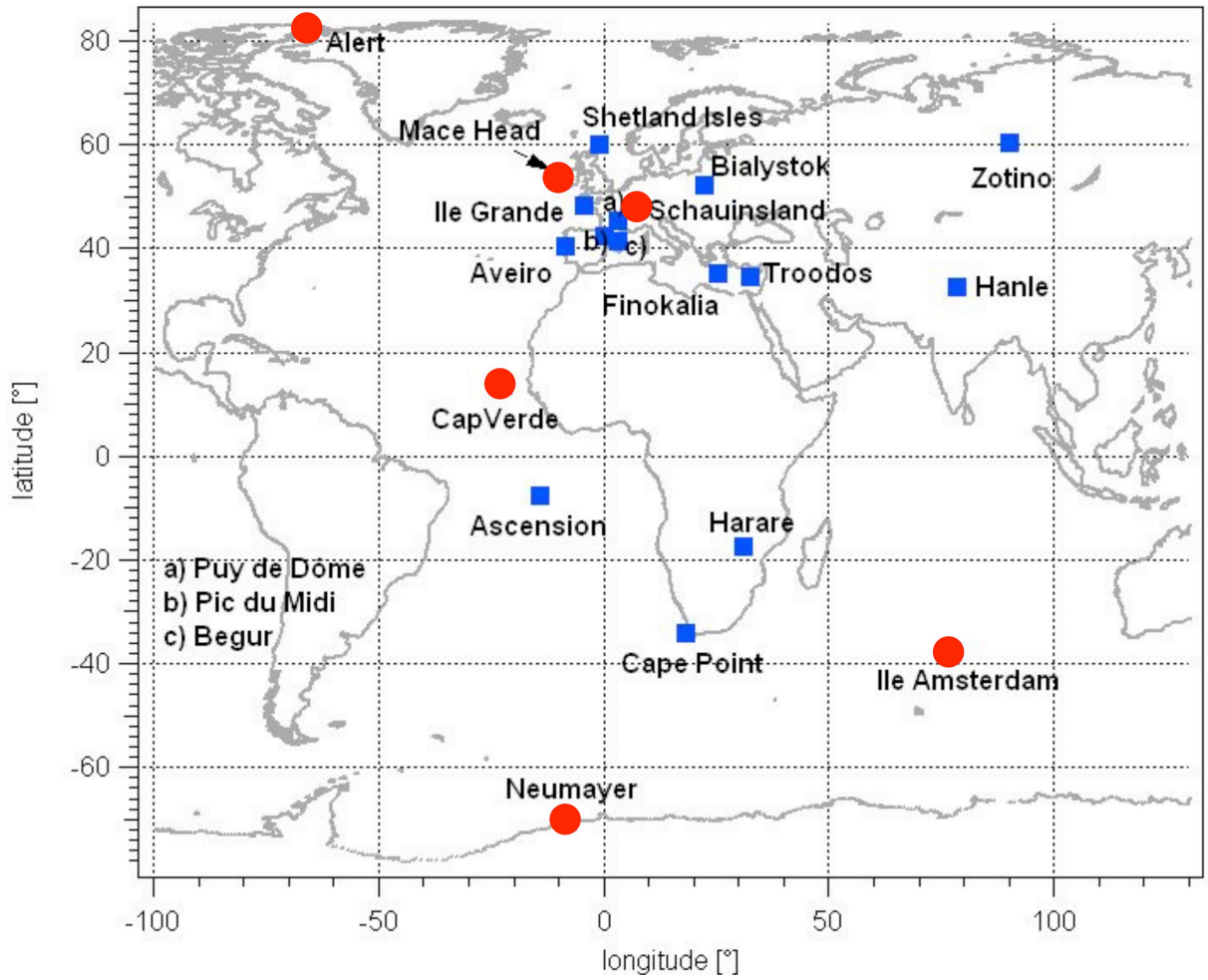


Isotopes can be used to distinguish between different sources and sinks.

Task ACTS

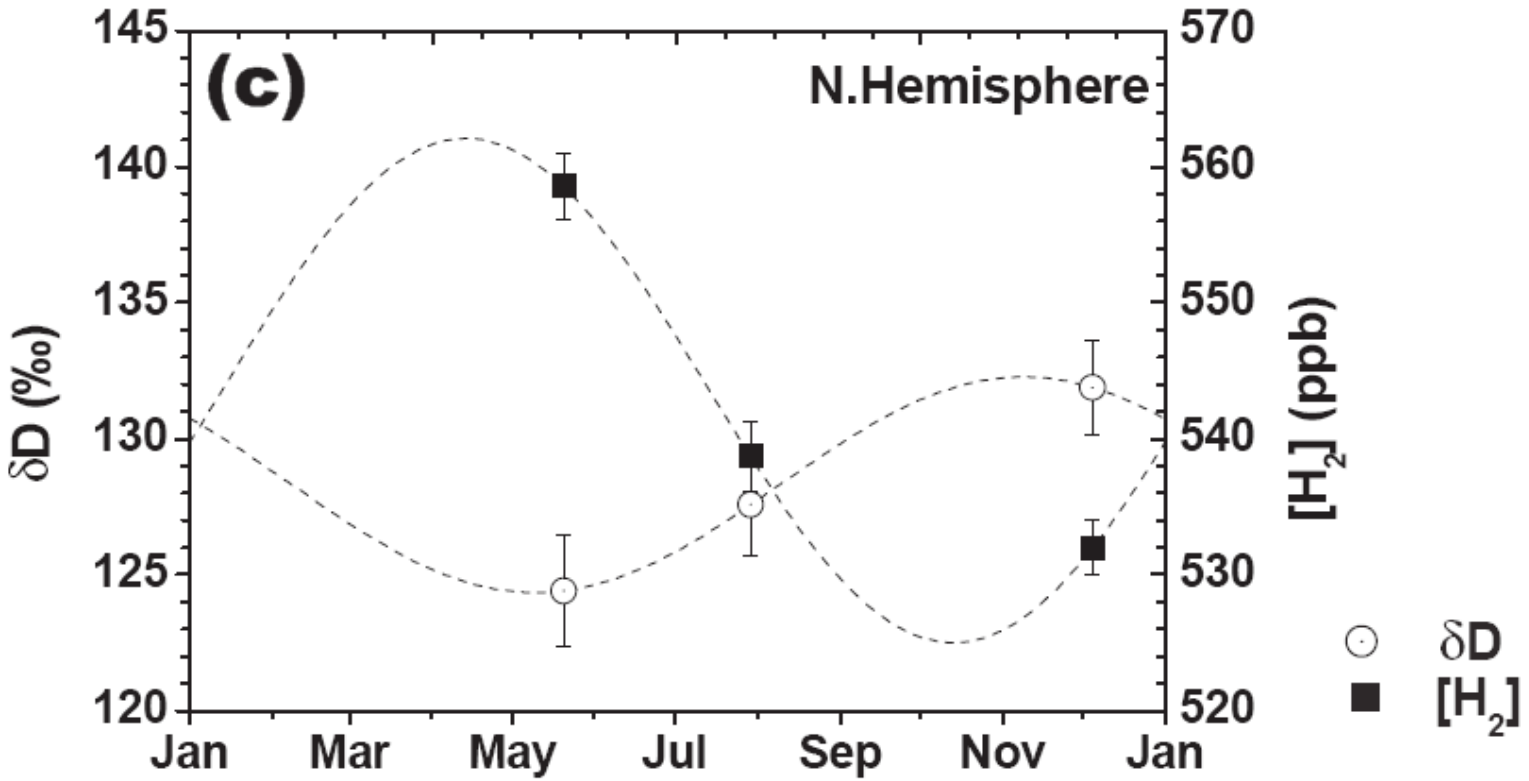
- Implement an isotope scheme in TM5 to interpret atmospheric measurements
  - Definitions
    - KIE: kinetic isotope effect
    - IBs: isotope branching ratios
    - MIE: molecular isotope enrichment
- Previous studies show:
  - H2 & CH4 enriched due to CH4 oxidation
  - Due to MIE
  - Uncertainties: CH2O photolysis

Isotope monitoring stations



The EUROHYDROS flask sampling locations. Red circles indicate the stations used for isotope measurements.

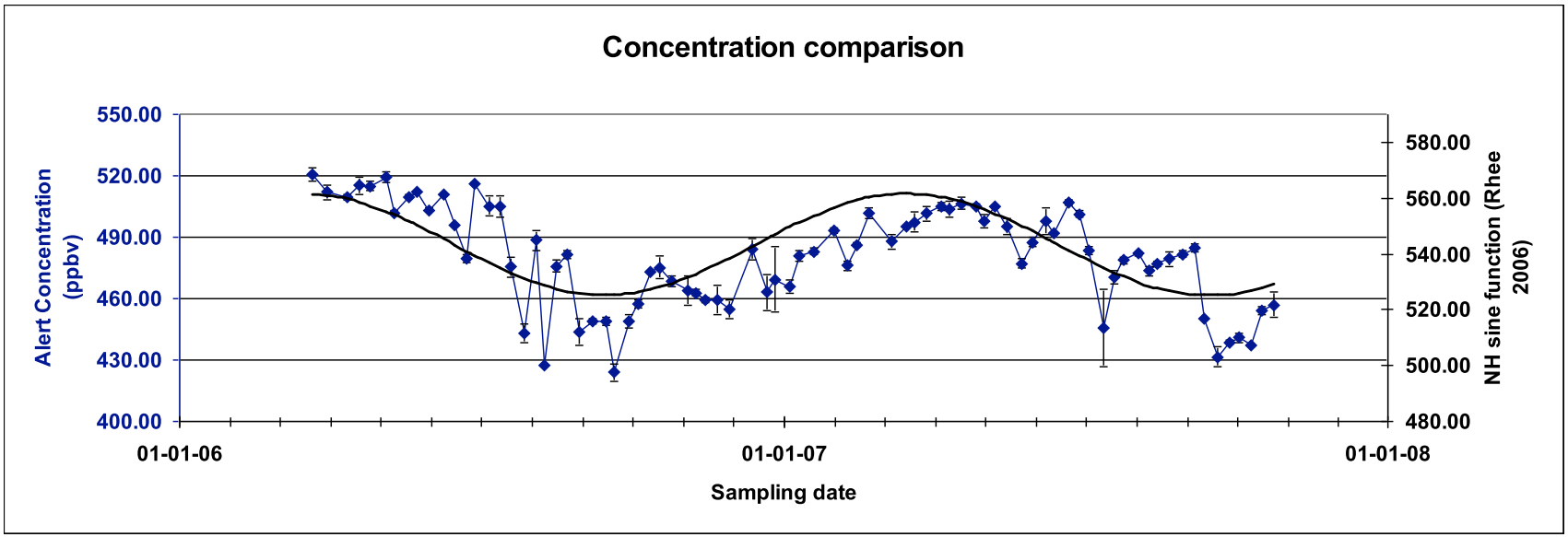
Out of phase behavior in NH

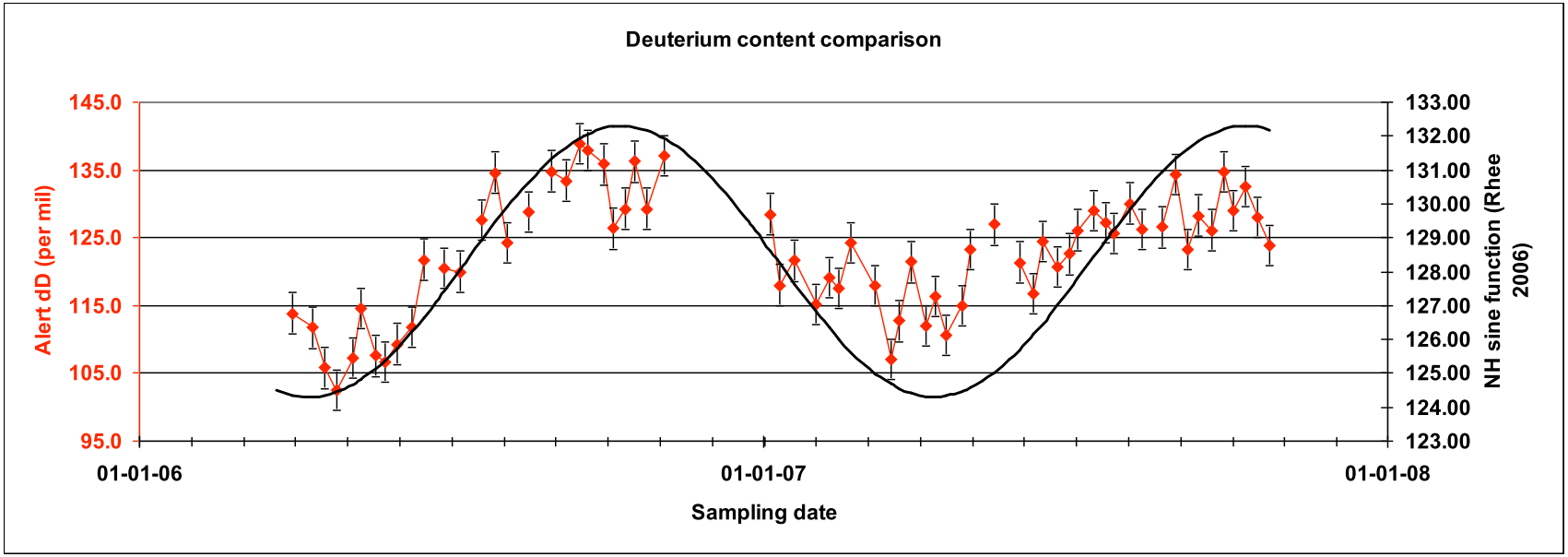


T.S. Rhee 2006: seasonal cycle derived from samples from 3 CARIBIC flights (sampling from commercial aircraft)

Shows the dominant role of soil uptake in the NH.

Comparison Alert – NH mean





We can follow this cycle with much larger precision.

TM5 model (6x4) 2004

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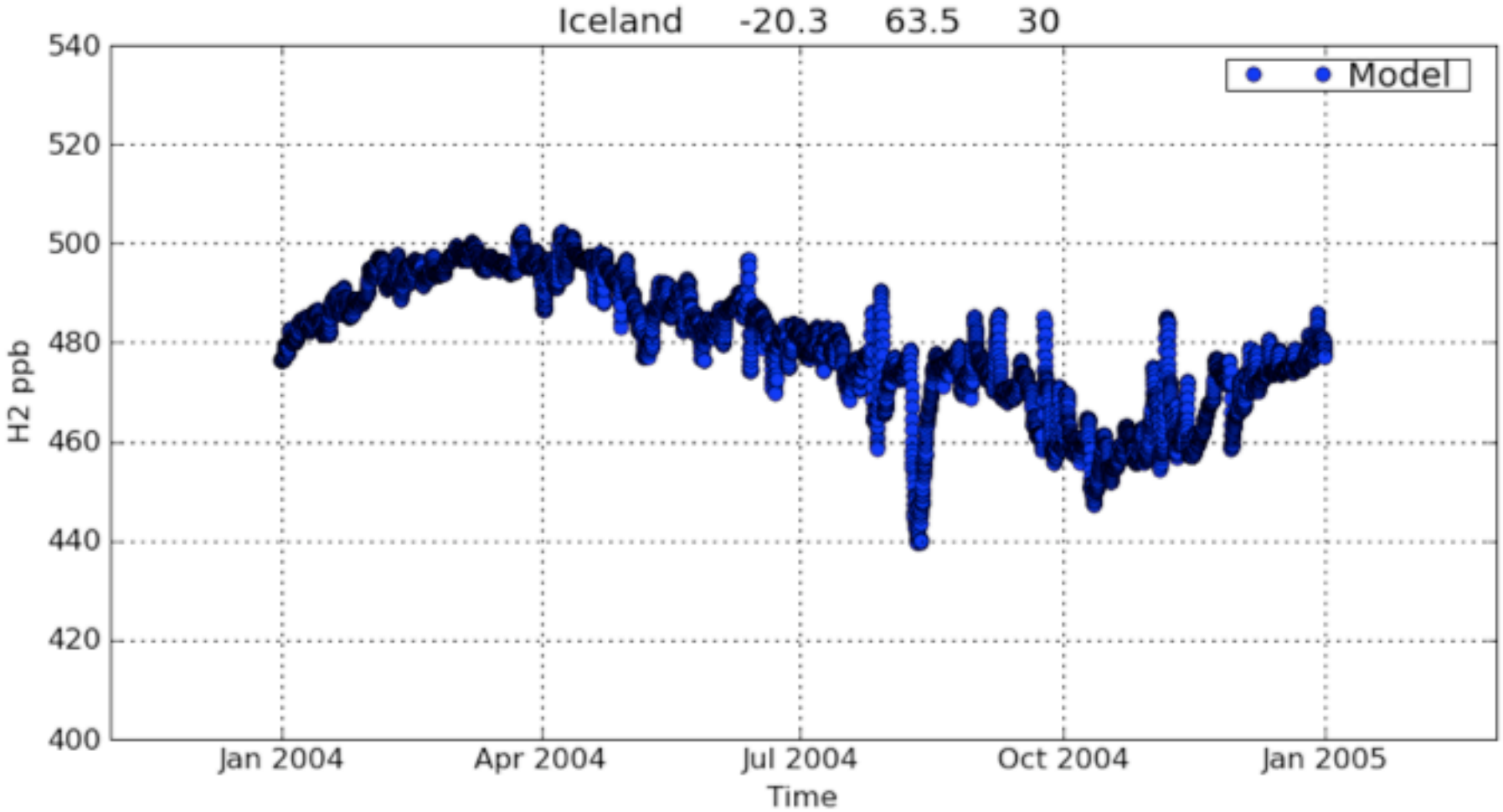
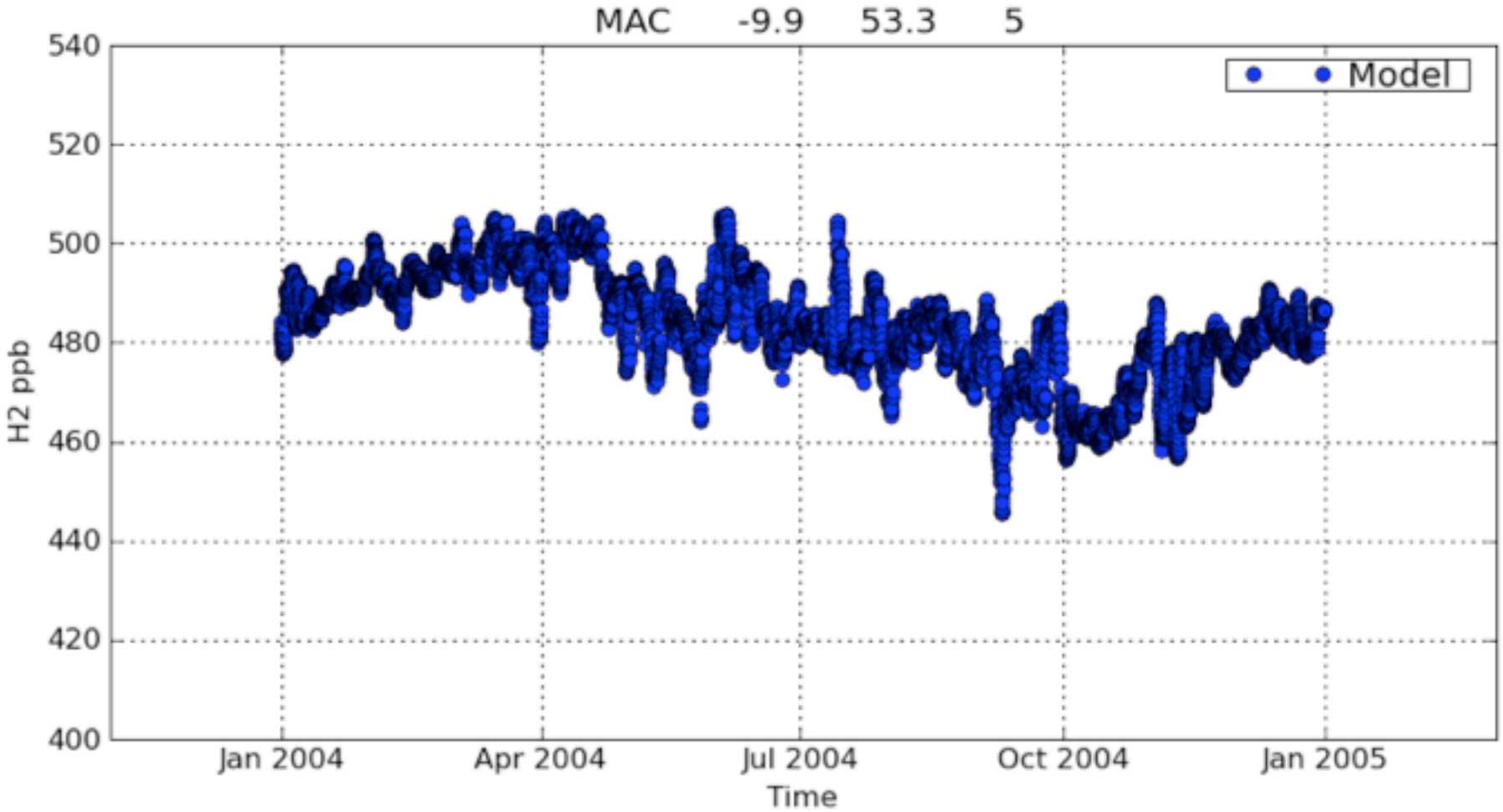


TM5 model (6x4) 2004



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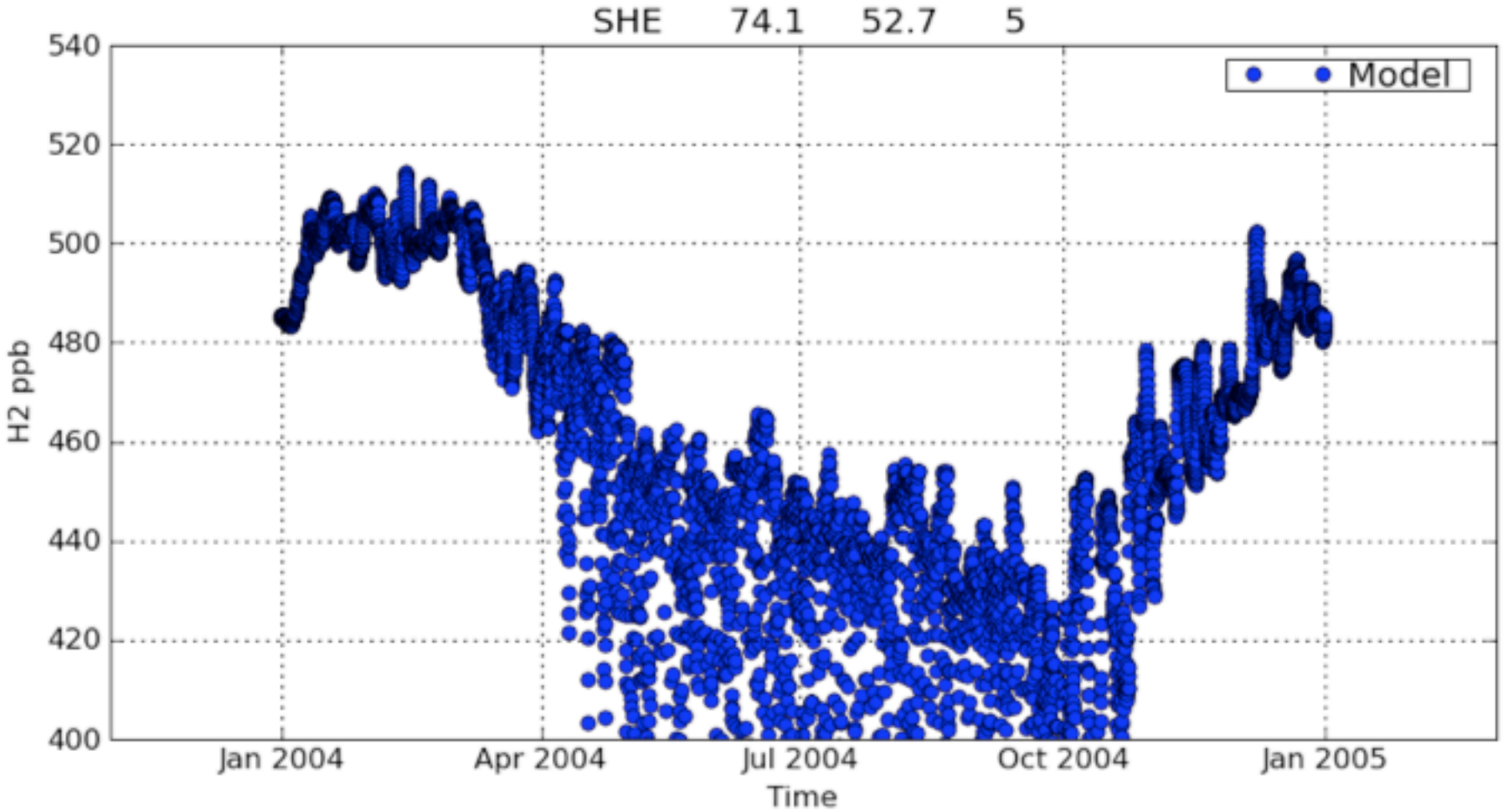

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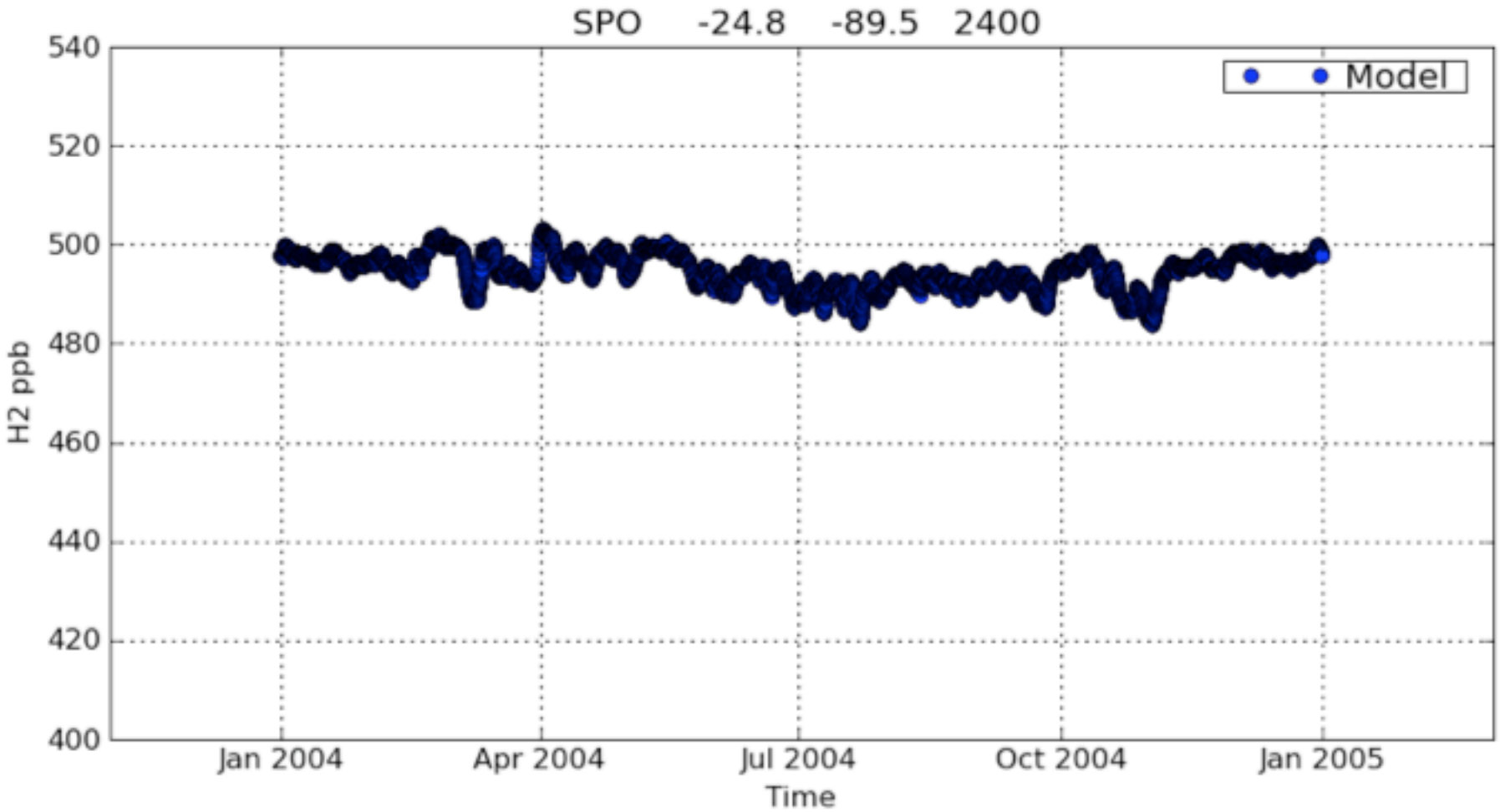
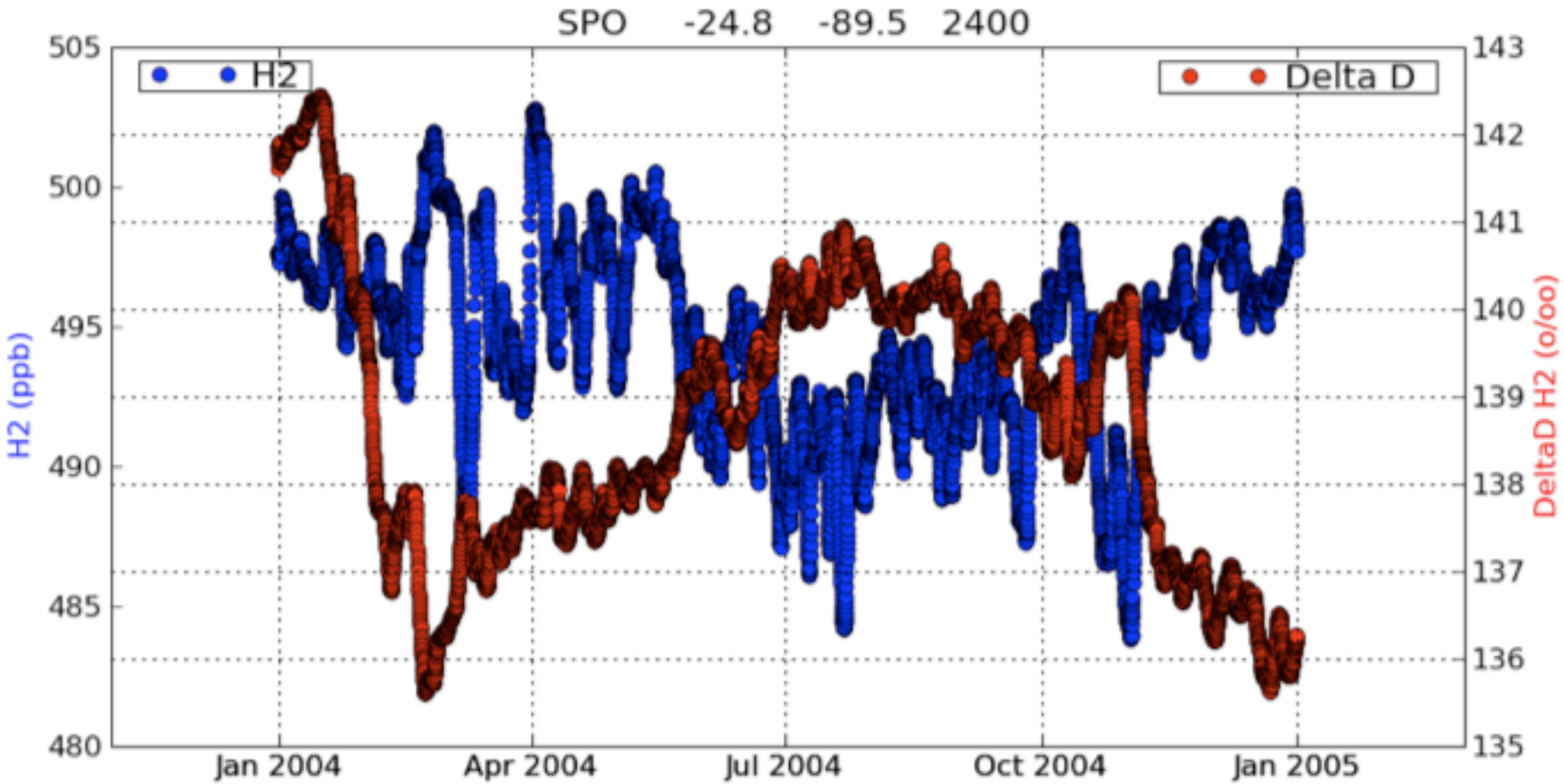


10

DeltaD H2 (Alert/Neumaver)



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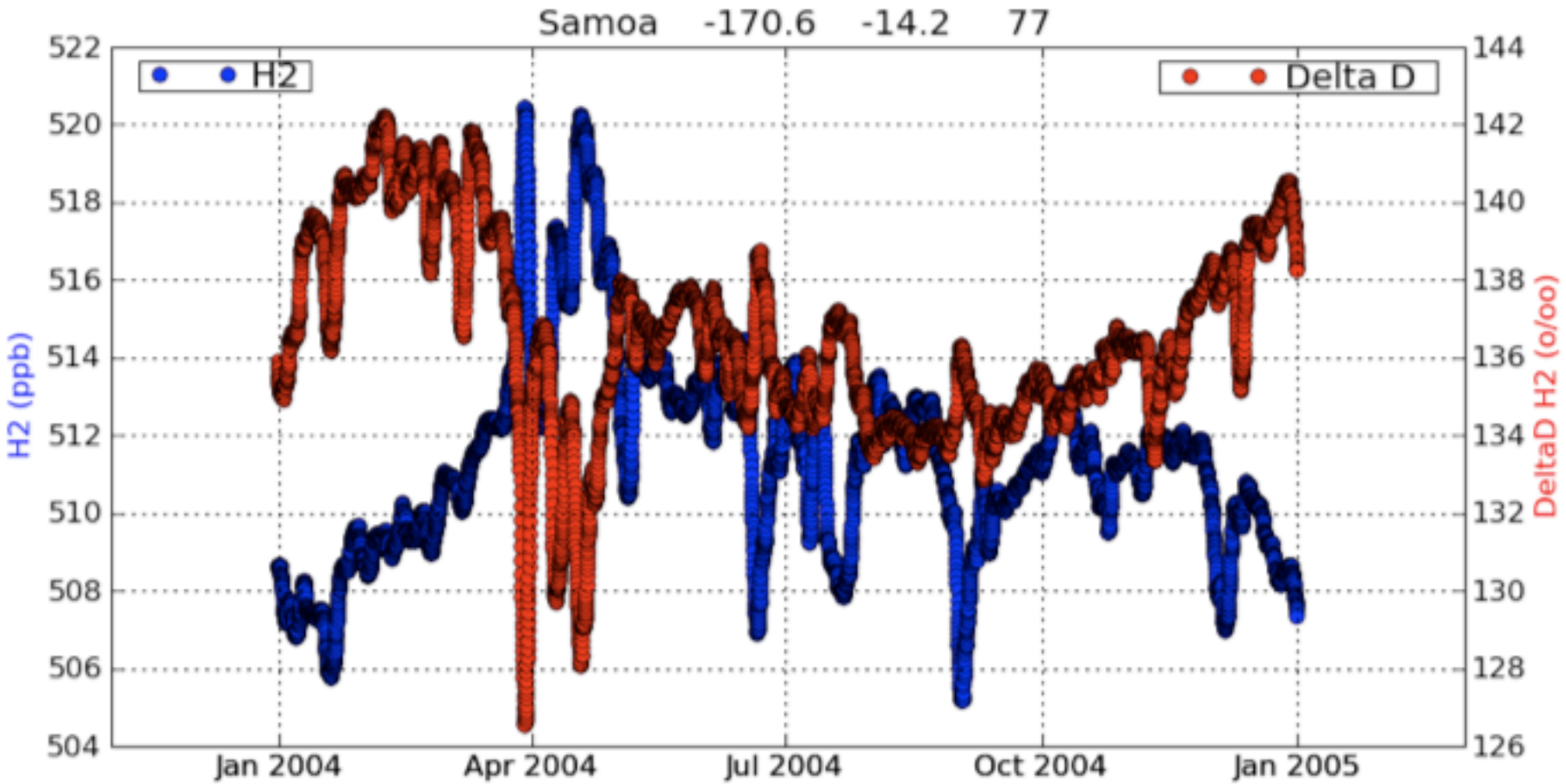

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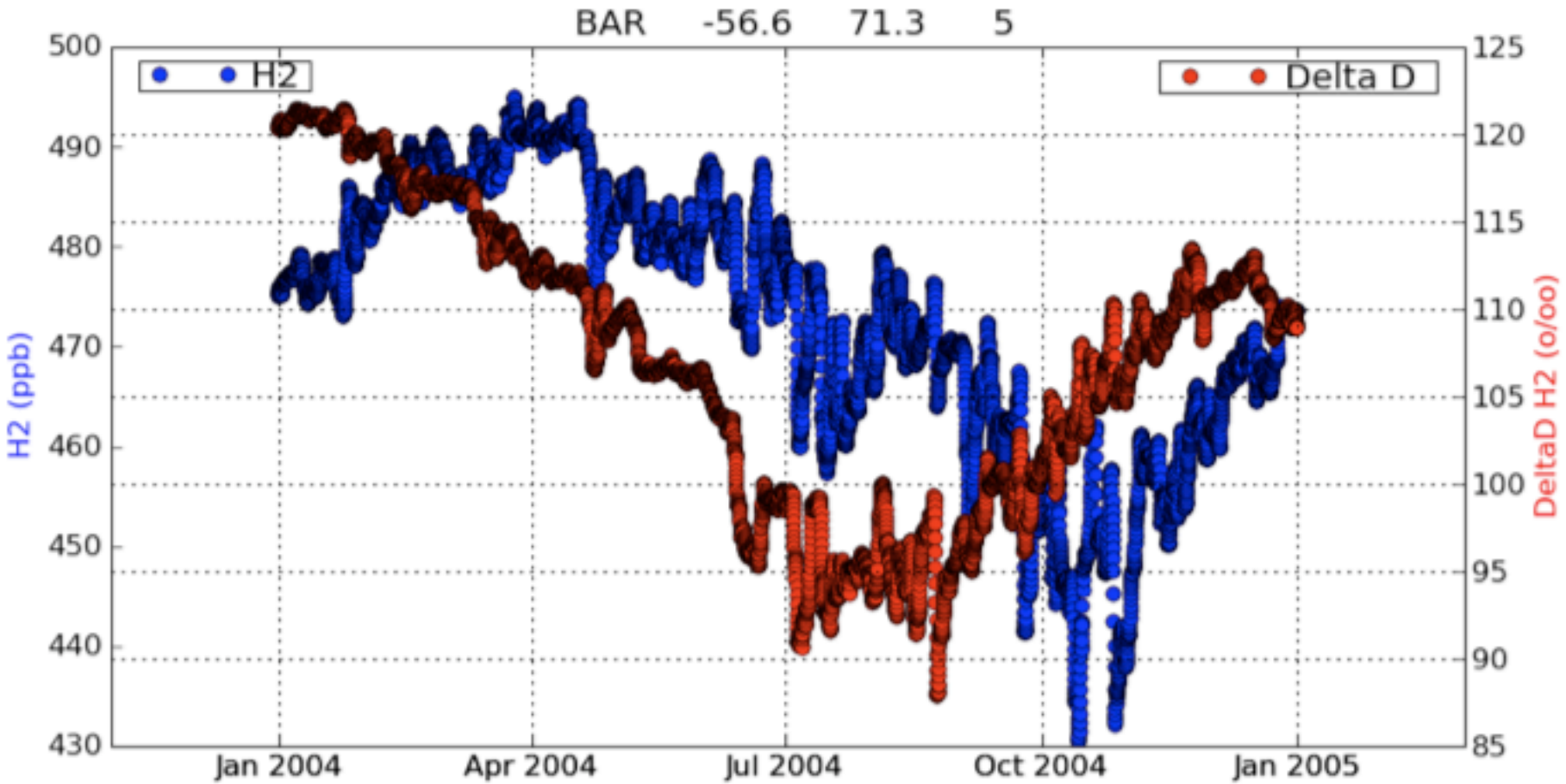

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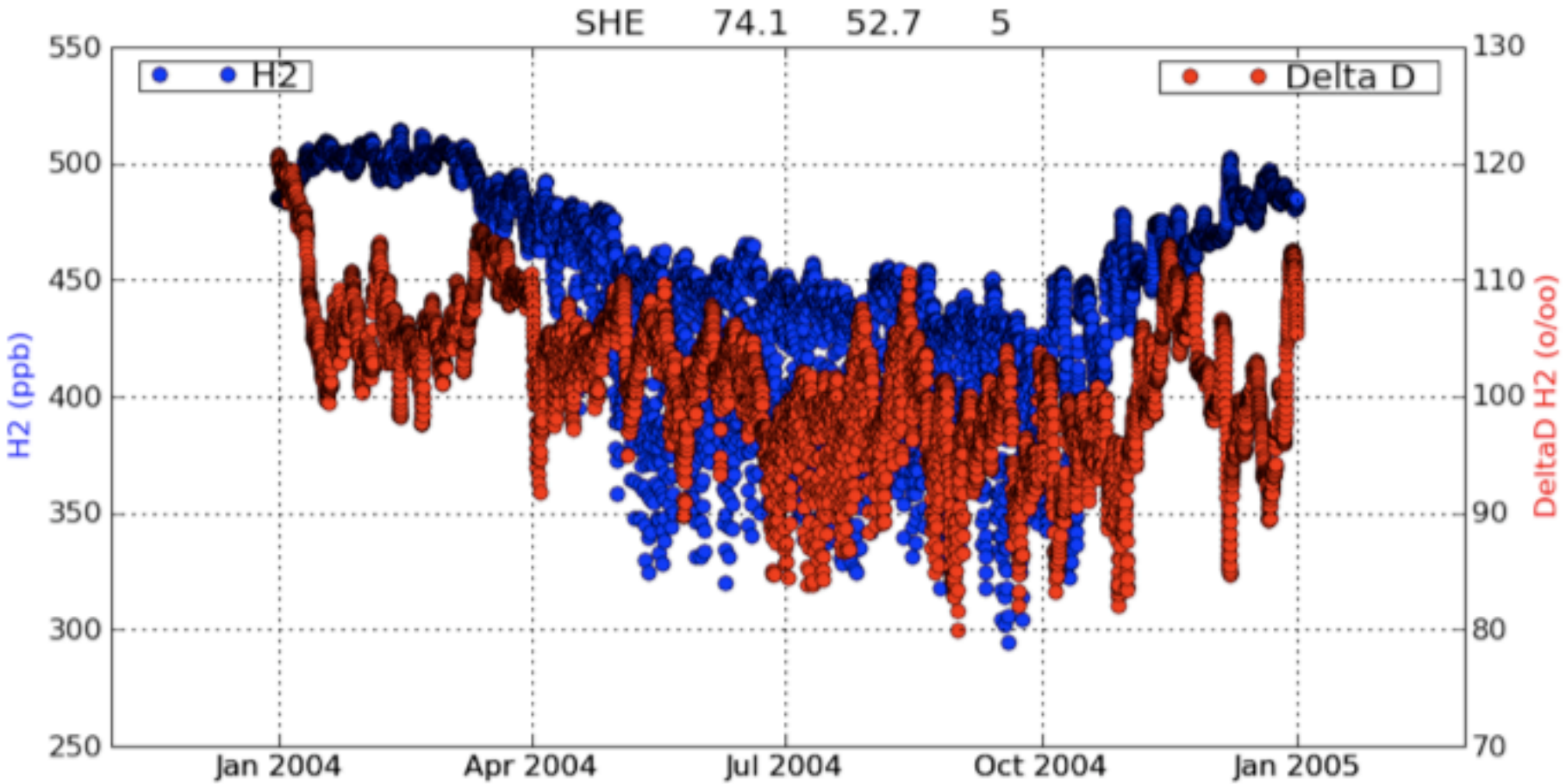
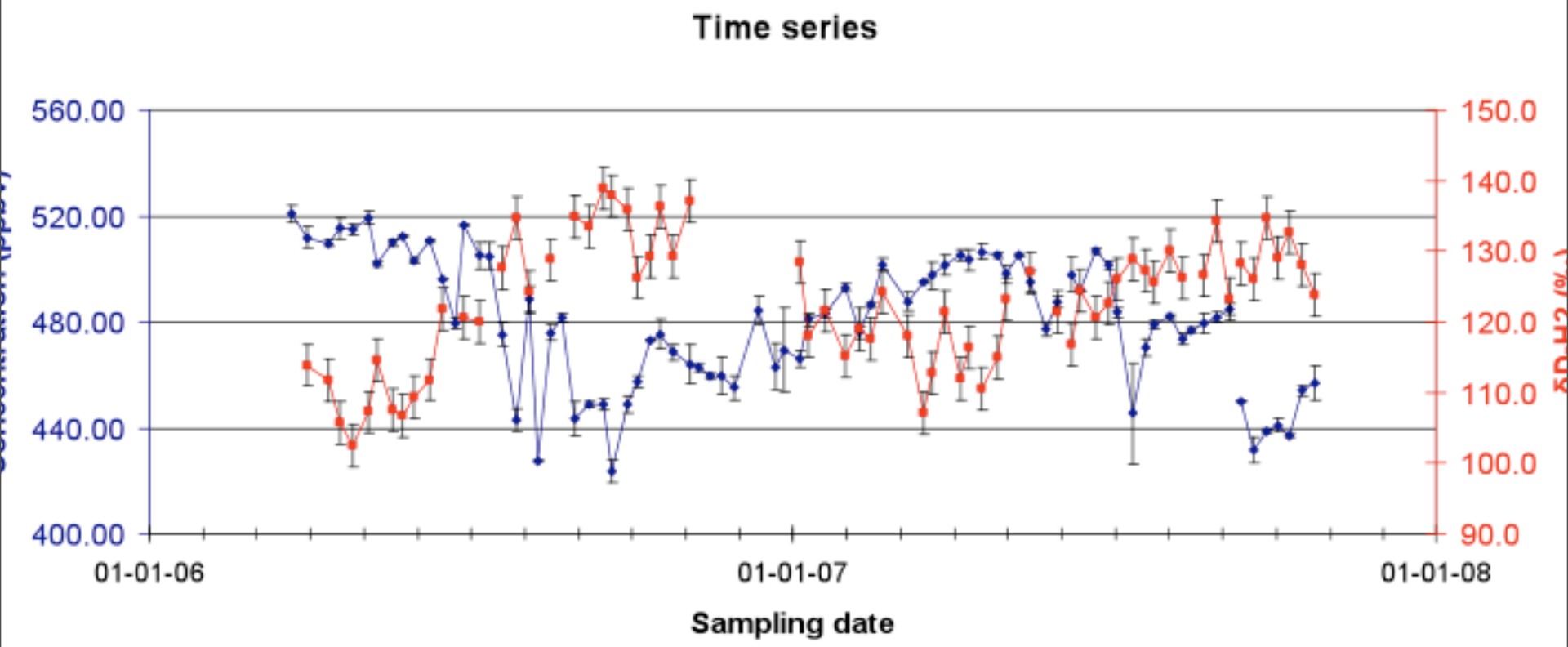
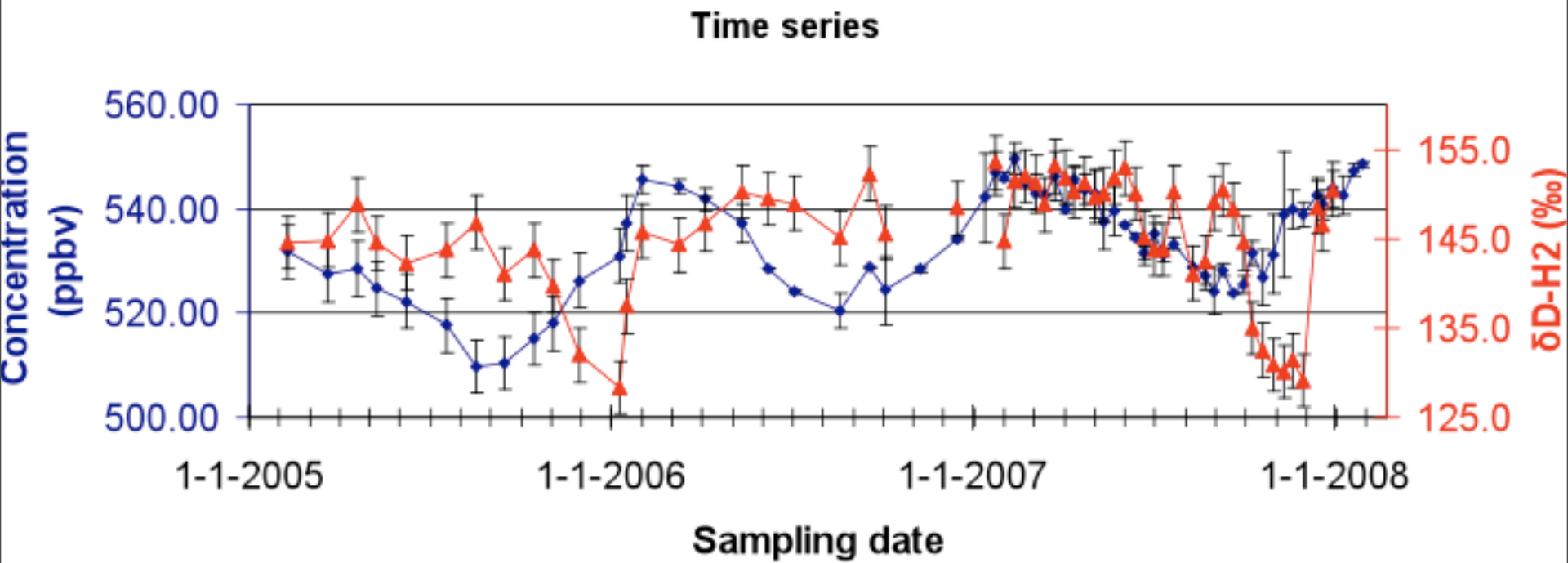


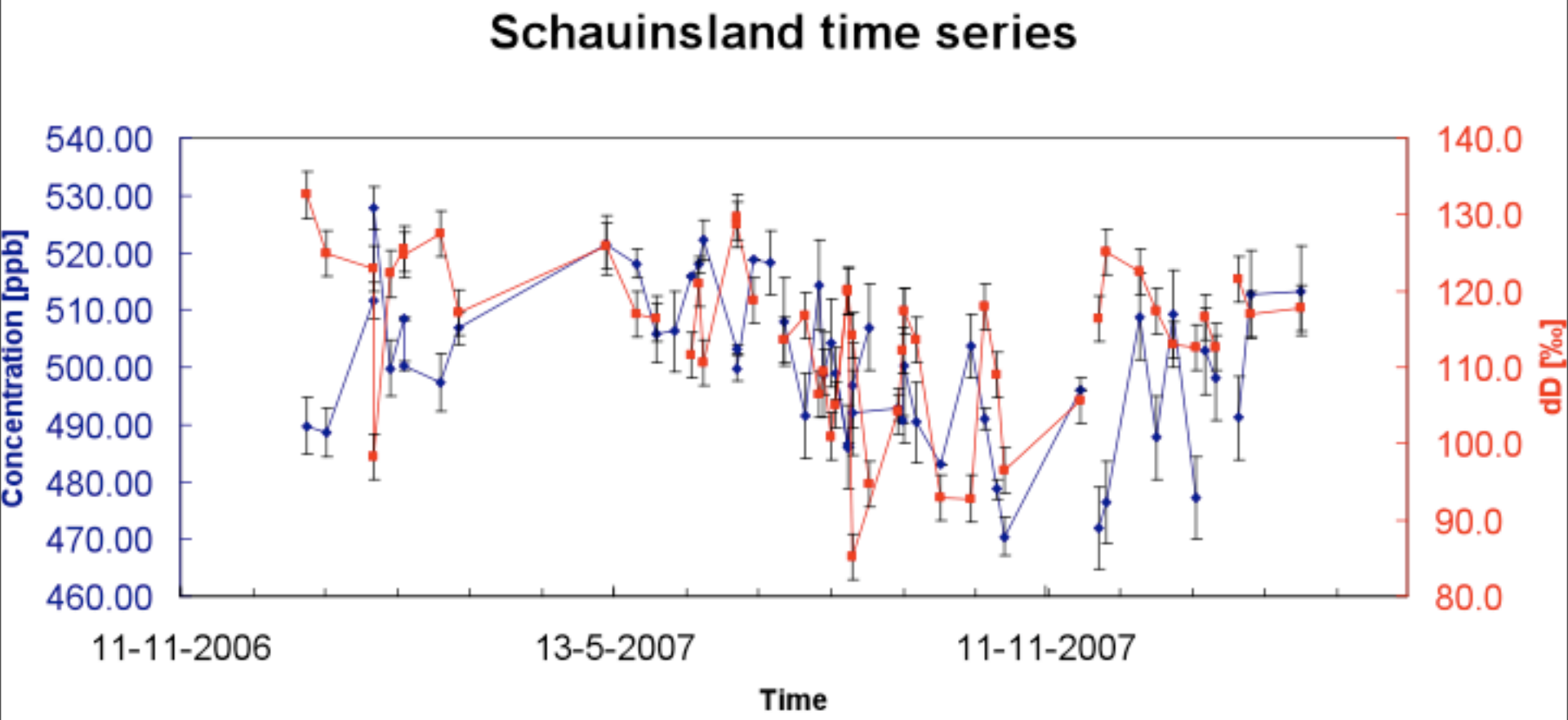
DeltaD H2 (Alert/Neumayer)



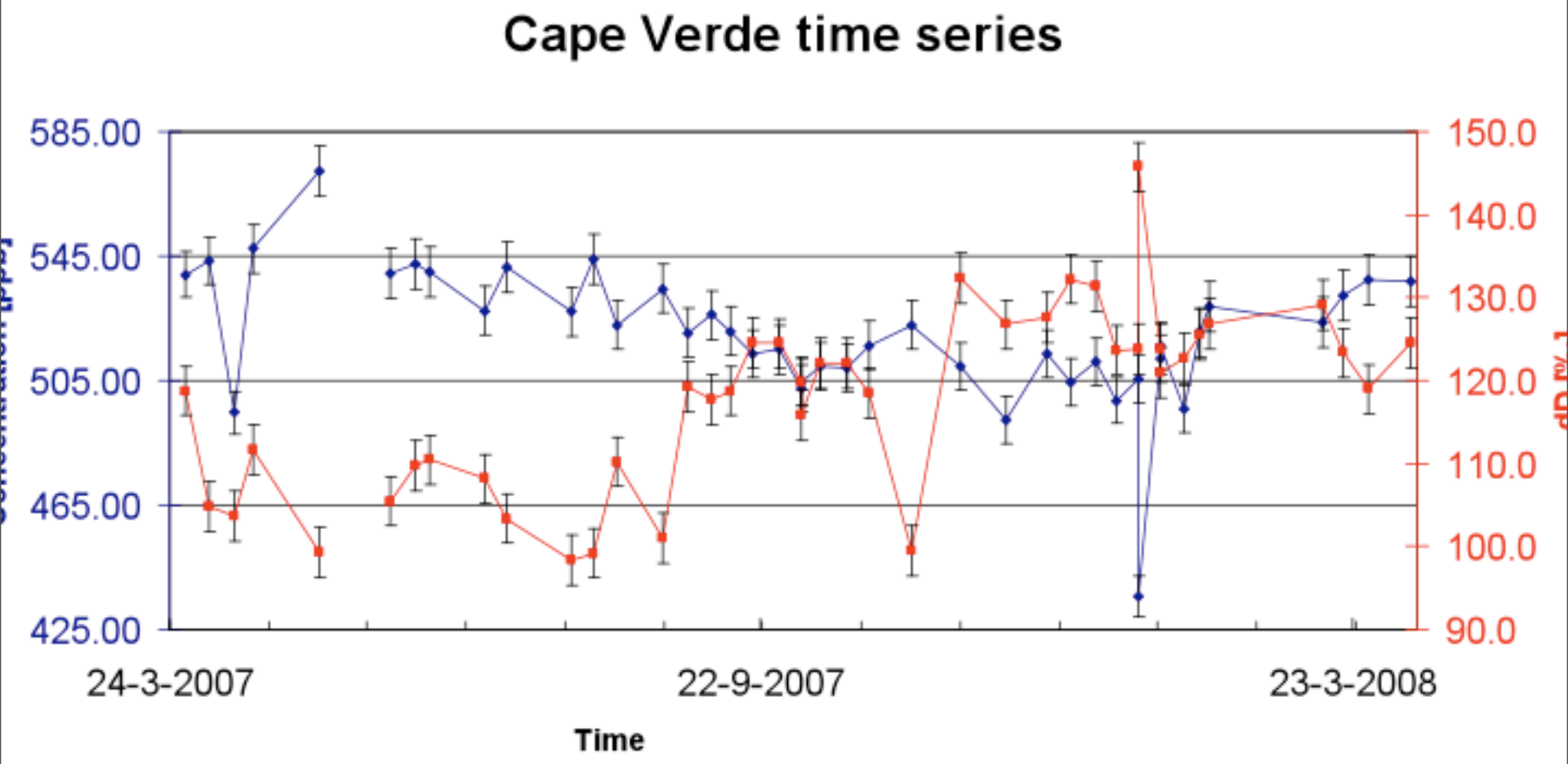
DeltaD H2 (Alert/Neumayer)



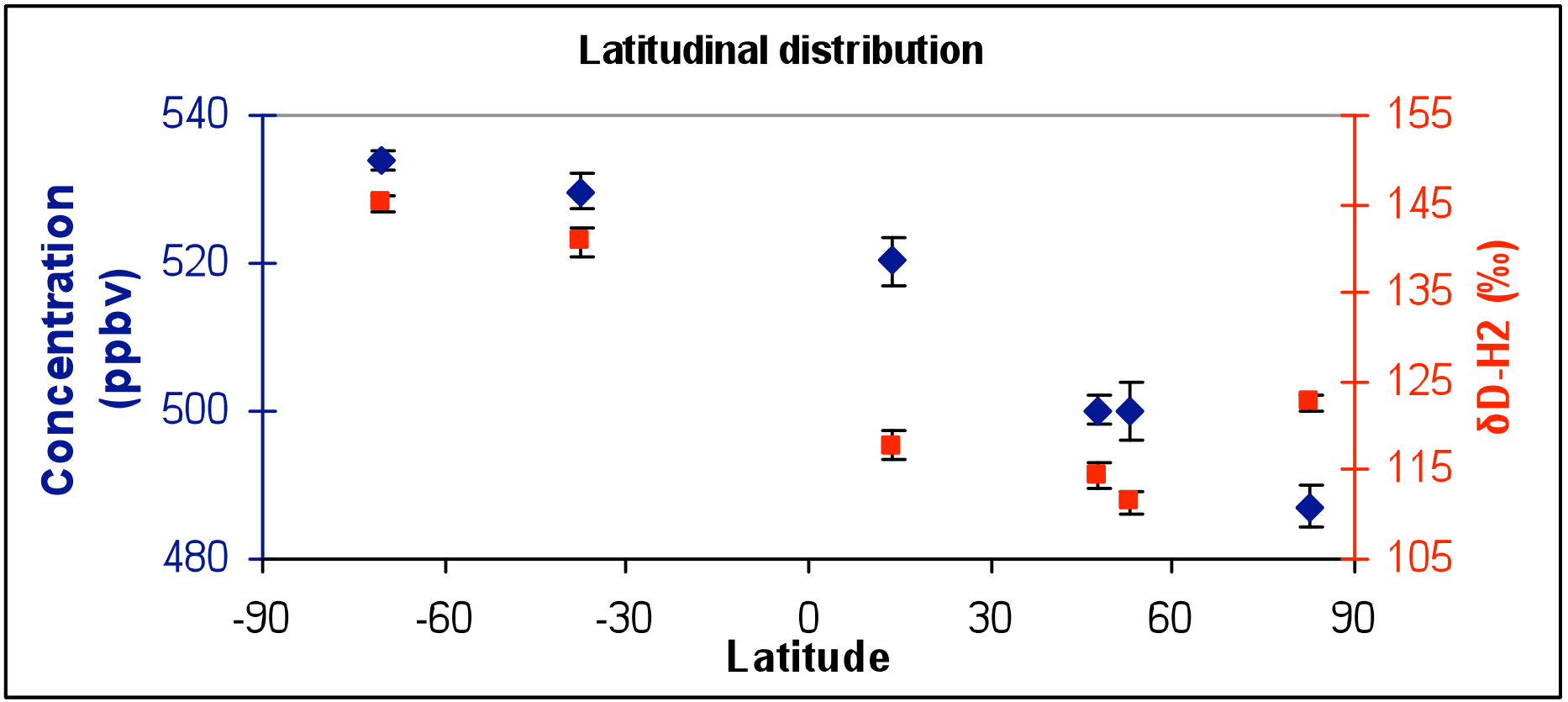
DeltaD H2 (Alert/Neumayer)

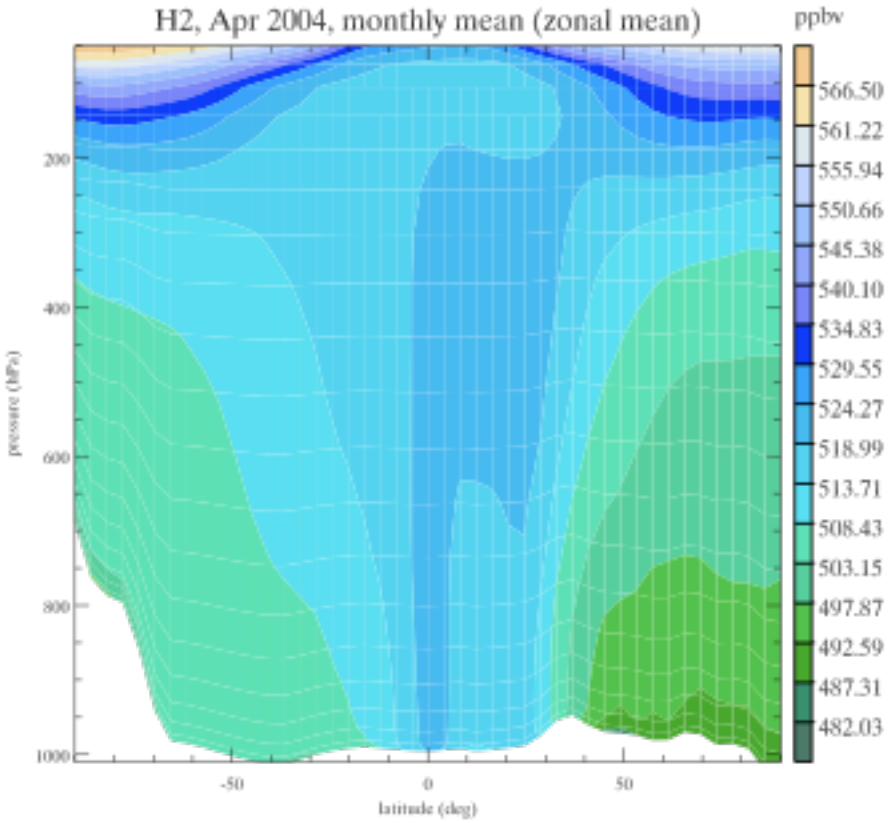


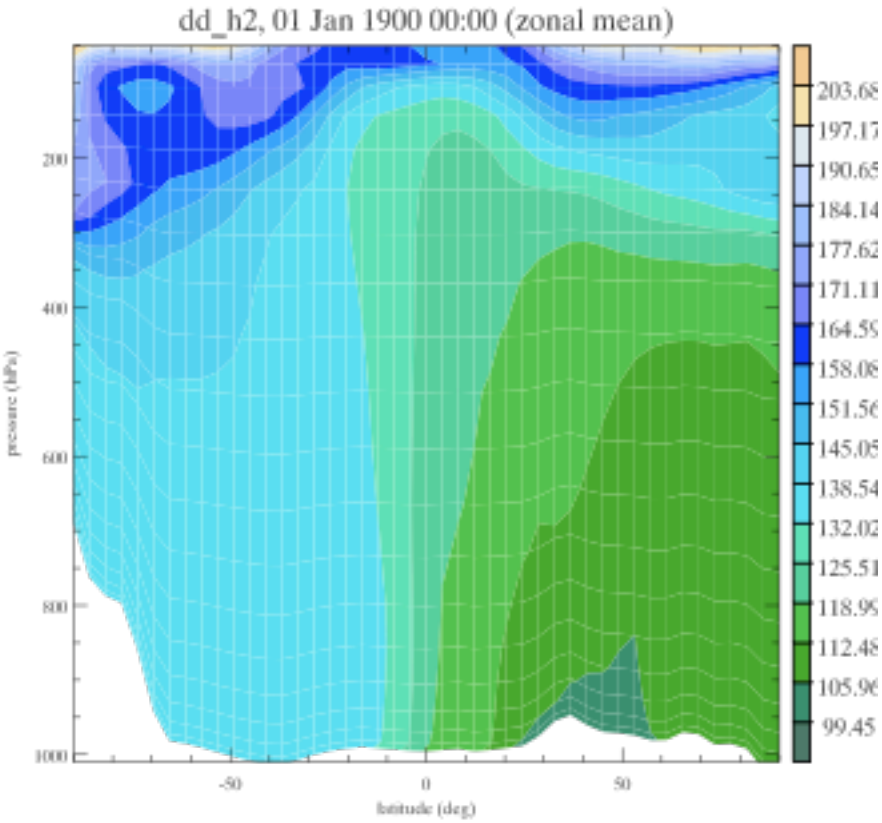
DeltaD H2 (Alert/Neumayer)

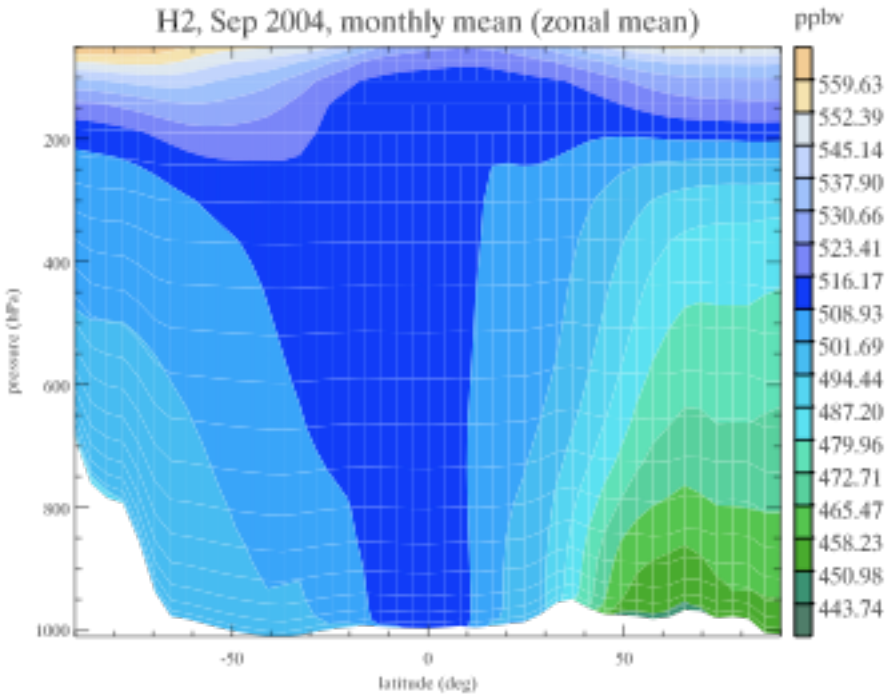


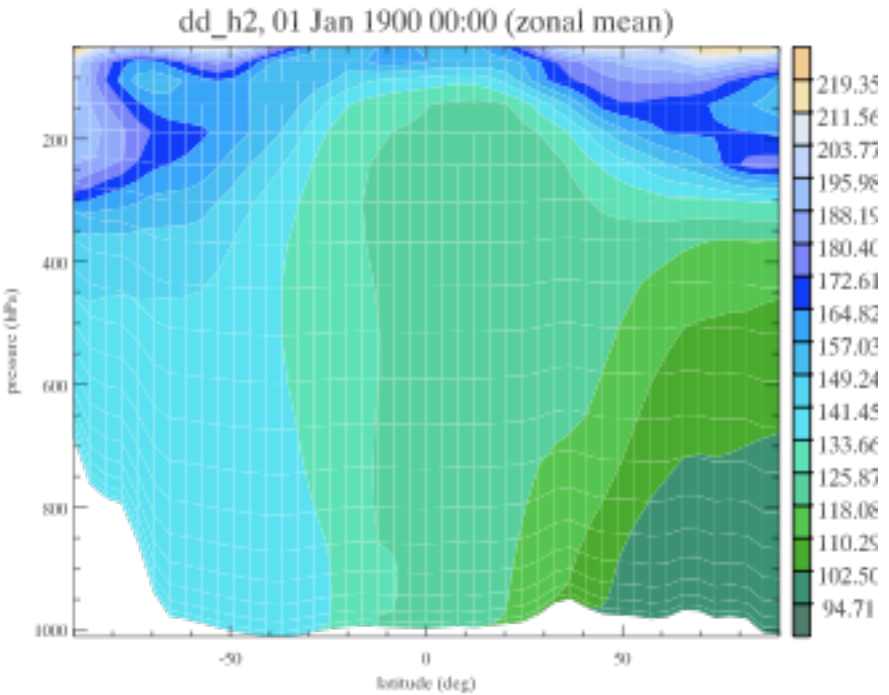
Latitudional Distribution

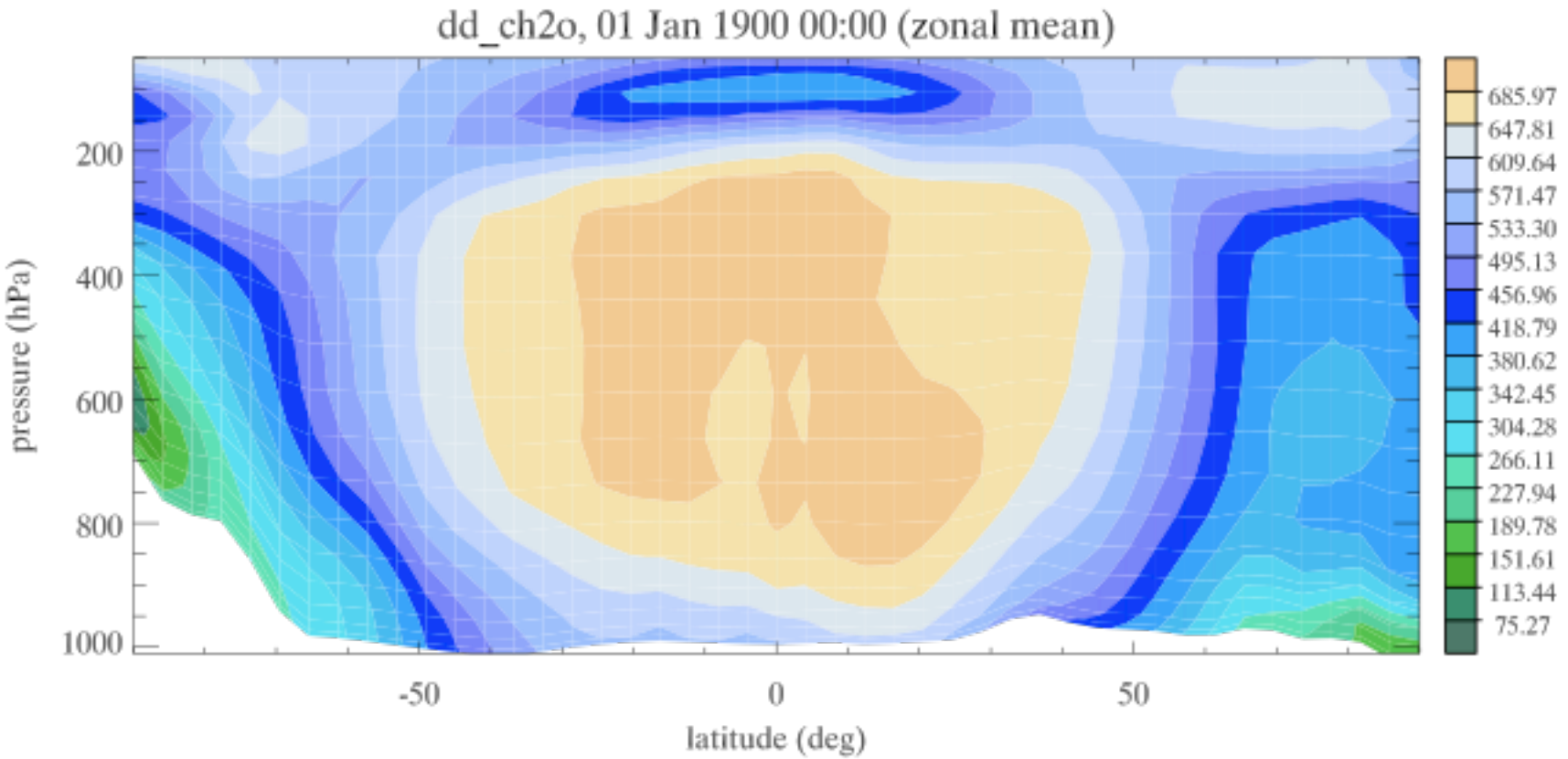



H2, Apr 2004, monthly mean (zonal mean)
ppbv
566.50
561.22
555.94
550.66
545.38
540.10
534.83
529.55
524.27
518.99
513.71
508.43
503.15
497.87
492.59
487.31
482.03
pressure (hPa)
200
400
600
800
1000
-50
0
50
latitude (deg)


dd_h2, 01 Jan 1900 00:00 (zonal mean)
203.68
197.17
190.65
184.14
177.62
171.11
164.59
158.08
151.56
145.05
138.54
132.02
125.51
118.99
112.48
105.96
99.45
pressure (hPa)
200
400
600
800
1000
-50
0
50
latitude (deg)

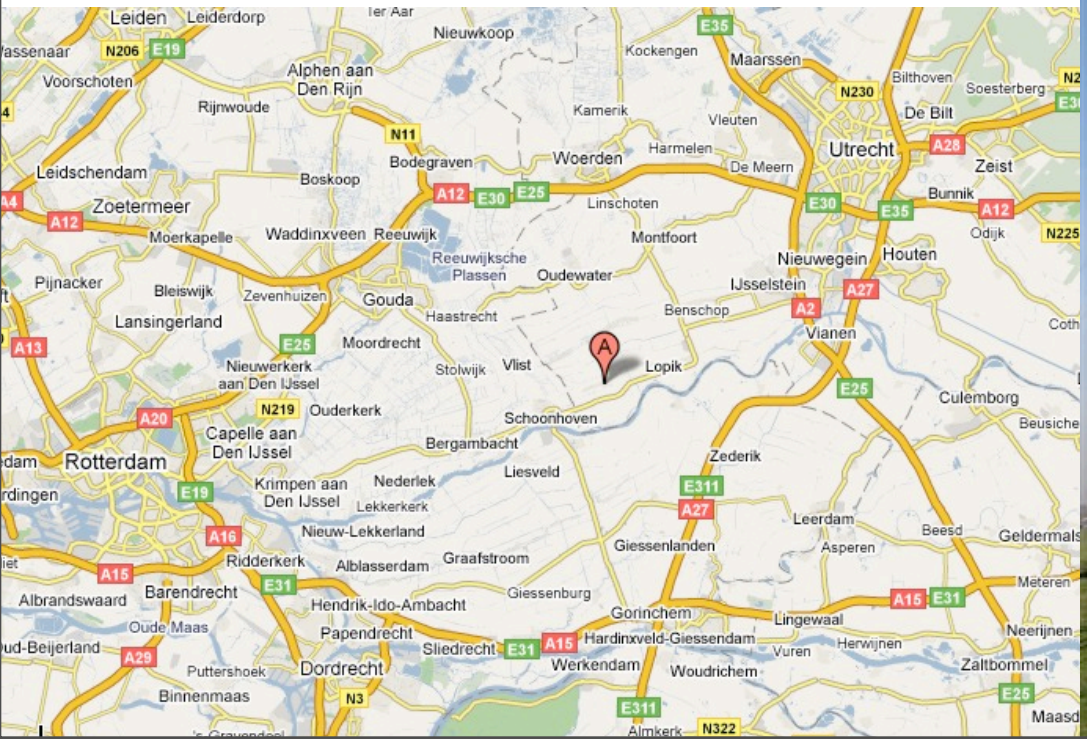

H2, Sep 2004, monthly mean (zonal mean)
ppbv
559.63
552.39
545.14
537.90
530.66
523.41
516.17
508.93
501.69
494.44
487.20
479.96
472.71
465.47
458.23
450.98
443.74
200
400
600
800
1000
-50
0
50
latitude (deg)


dd_h2, 01 Jan 1900 00:00 (zonal mean)
200
400
600
800
1000
-50
0
50
latitude (deg)

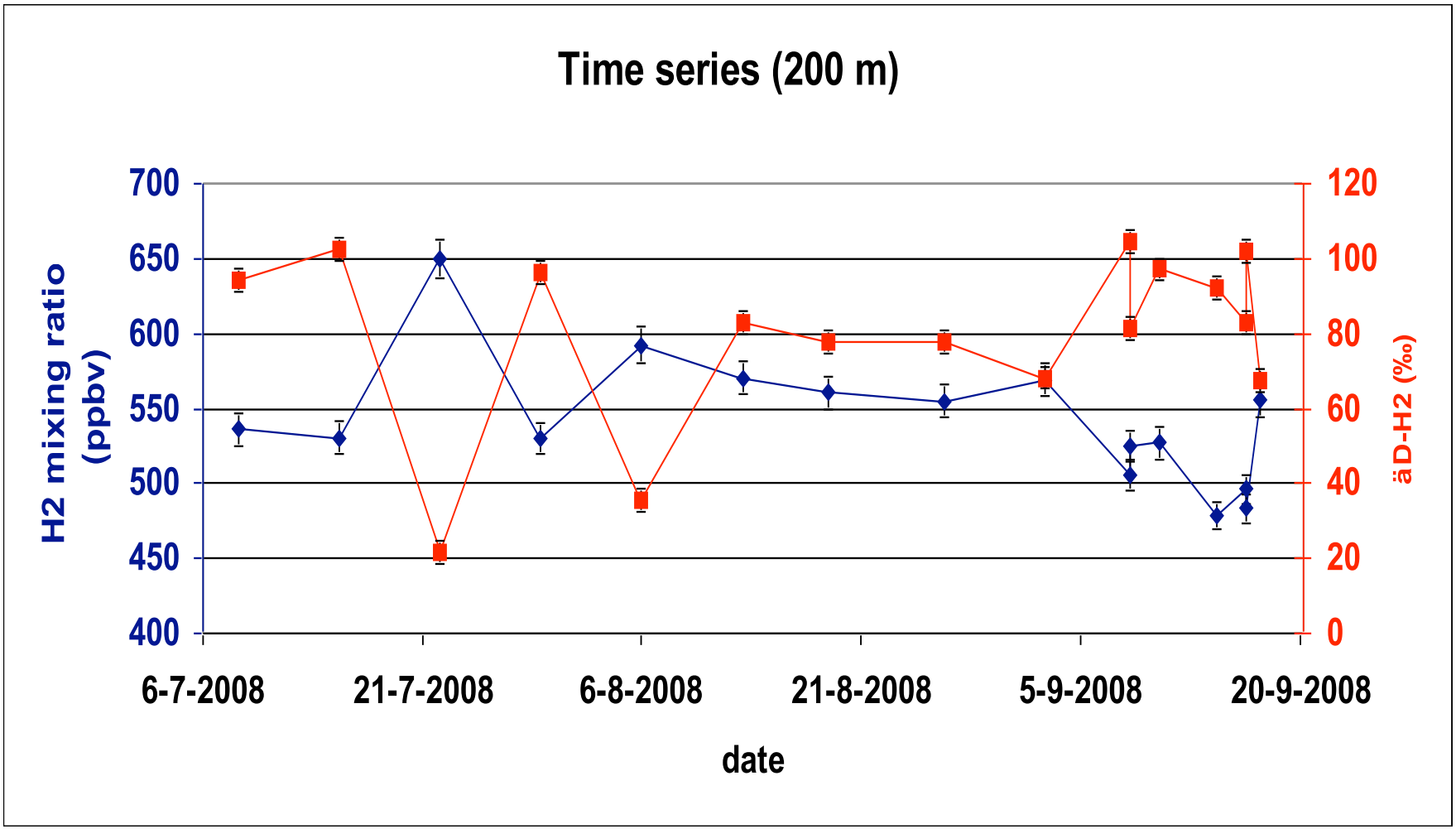

dd_ch2o, 01 Jan 1900 00:00 (zonal mean)
pressure (hPa)
200
400
600
800
1000
-50
0
50
latitude (deg)
685.97
647.81
609.64
571.47
533.30
495.13
456.96
418.79
380.62
342.45
304.28
266.11
227.94
189.78
151.61
113.44
75.27

The Cabauw tower

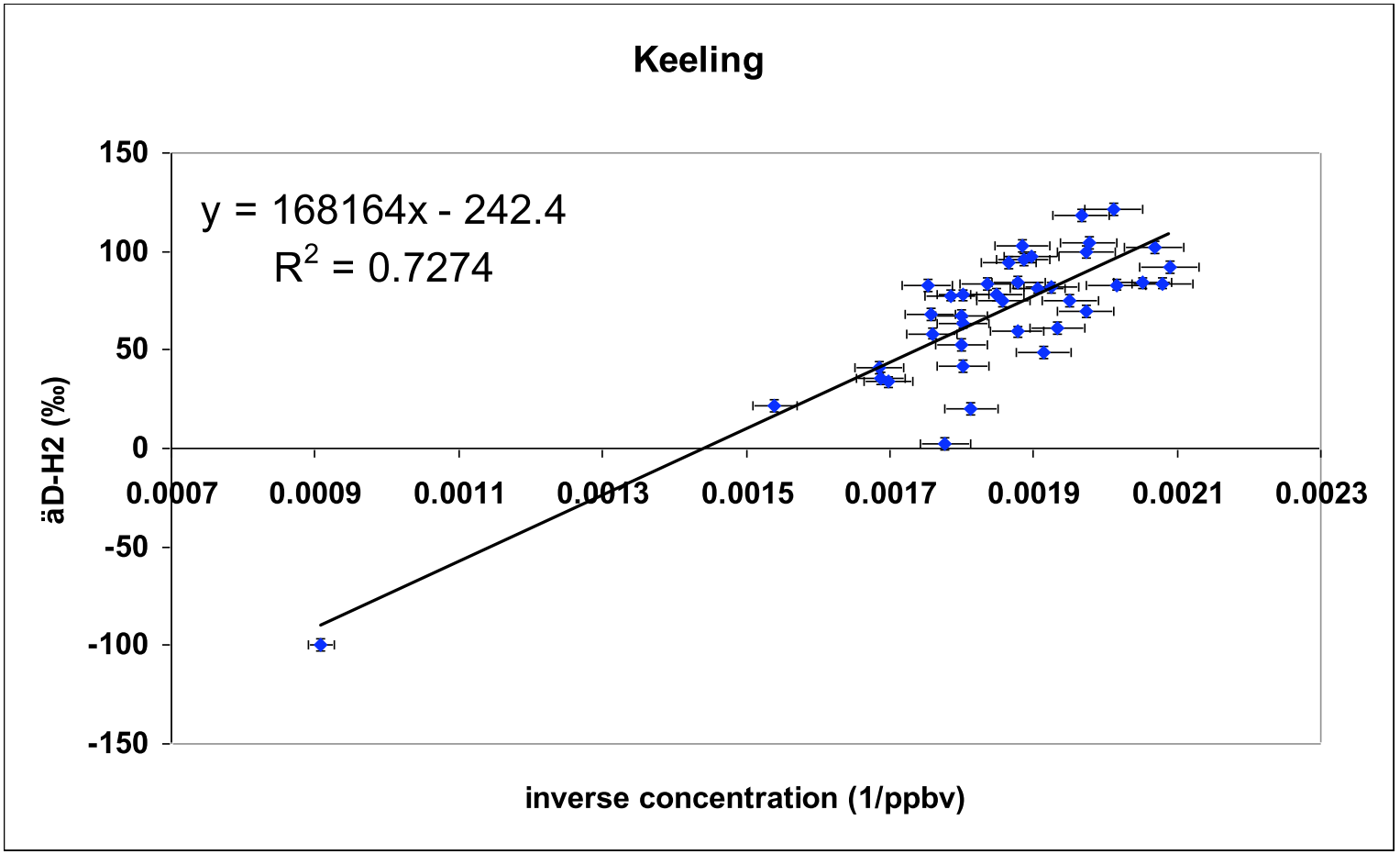
- 213 m high tower with instruments at different heights
- ECN can sample air from 20, 60, 120 and 200 m
- Continuous measurements of H_2 and other trace gases already running



Cabauw: time series



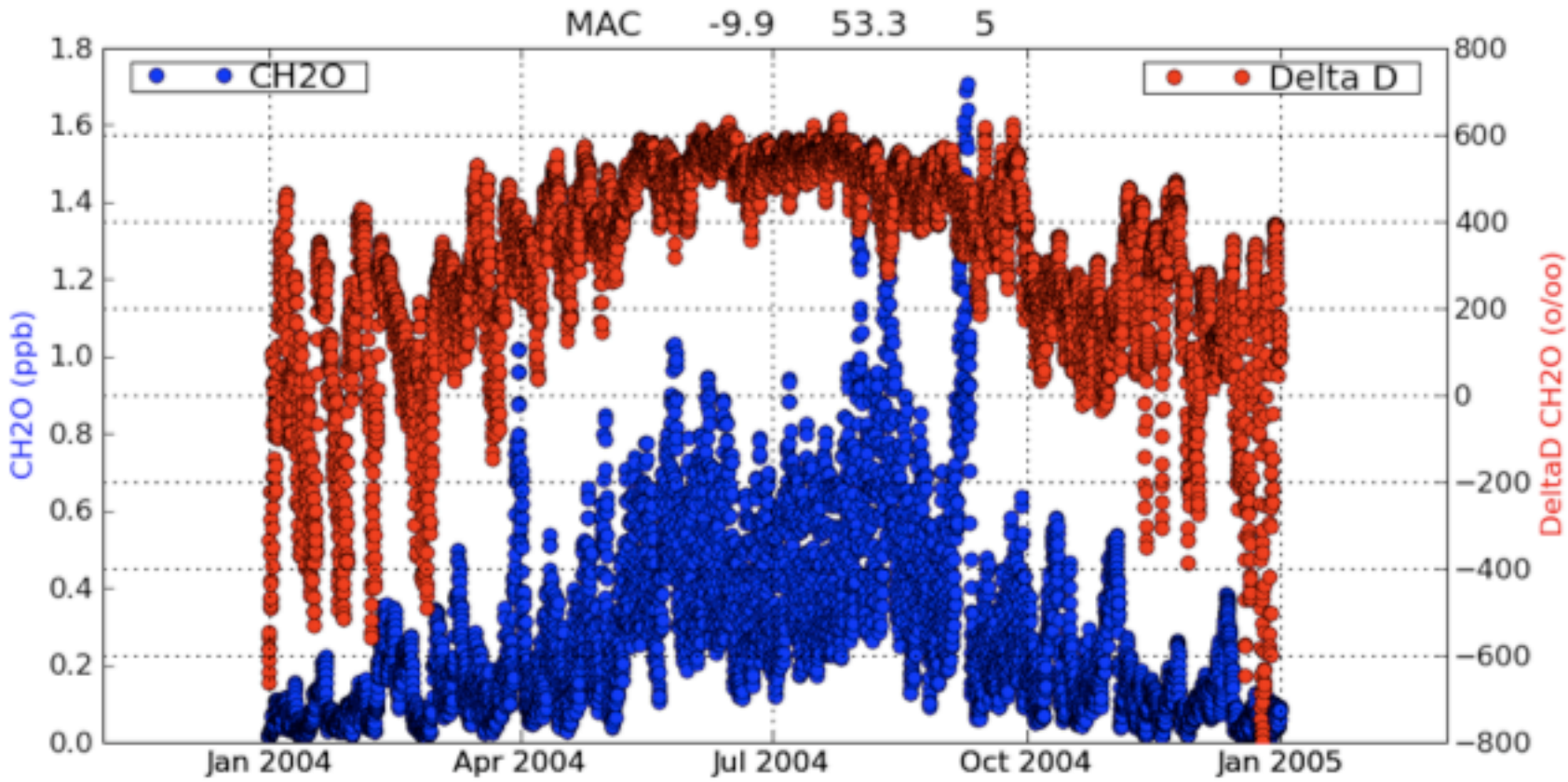
Cabauw; source signature

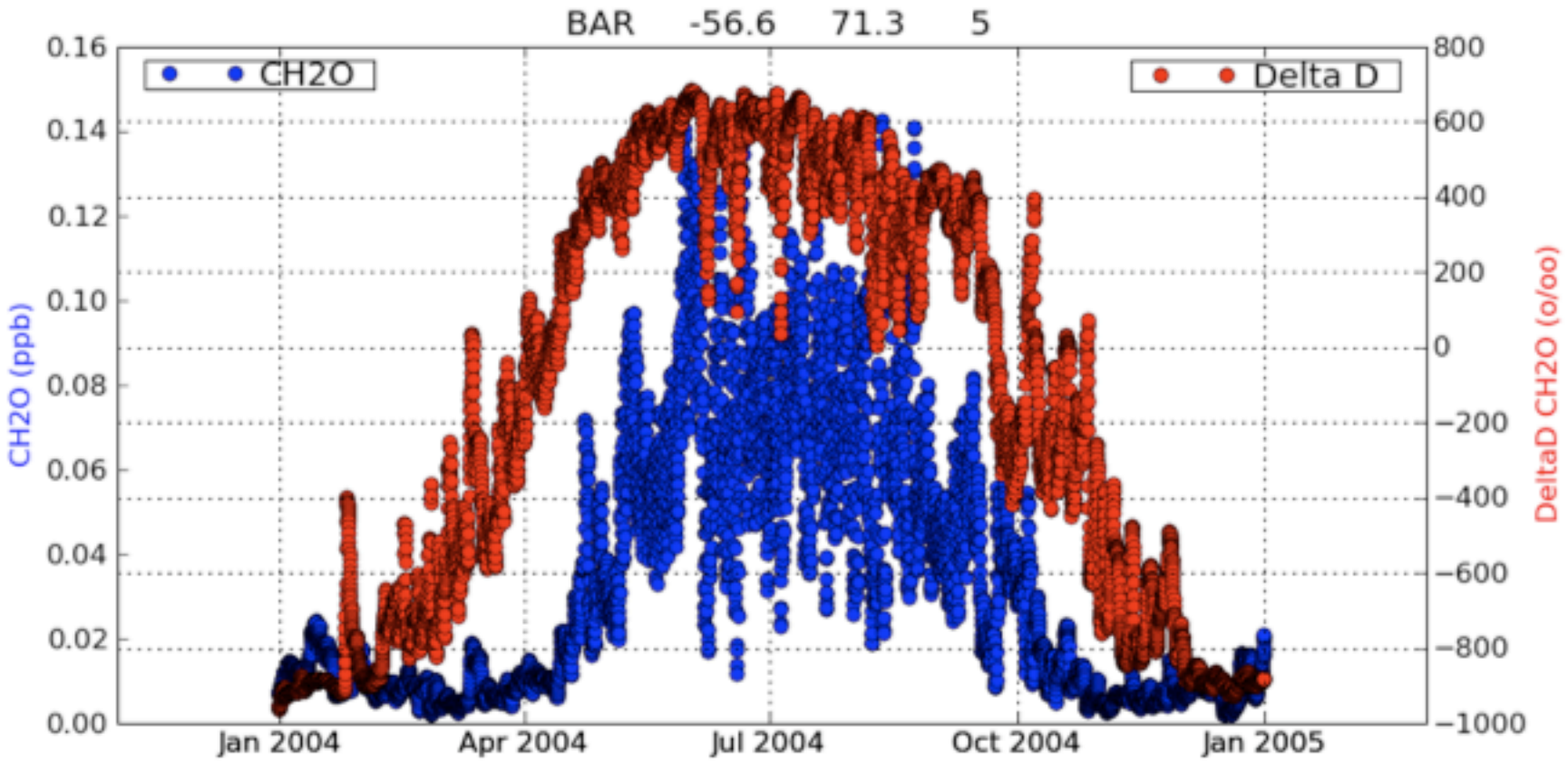


- Axis intercept of a Keeling plot (δD vs. inverse concentration) gives an estimate of the dominant source signature.
- At Cabauw, fossil sources seem to dominate (negative intercept)

Conclusions

- First H2-isotope version TM5 performs reasonable (i.e. Some latest updates need to be included)
- SH: H2 slightly underpredicted & too light
- Competition between chemical production and depostion: isotopic signatures uncertain!
- Intermediate CH2O shows very variable isotopic composition!
- First measurements: -294 > +210 o/oo


MAC -9.9 53.3 5
CH2O
Delta D
CH2O (ppb)
DeltaD CH2O (o/oo)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
800
600
400
200
0
−200
−400
−600
−800
Jan 2004
Apr 2004
Jul 2004
Oct 2004
Jan 2005


BAR -56.6 71.3 5
CH2O
Delta D
CH2O (ppb)
DeltaD CH2O (o/oo)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
800
600
400
200
0
−200
−400
−600
−800
−1000
Jan 2004
Apr 2004
Jul 2004
Oct 2004
Jan 2005

Novelli et al., *Molecular hydrogen in the atmosphere, global distribution and budget,* JGR 104, 30427-30444, 1999

Tromp et al, *Potential Environmental Impact of a Hydrogen Economy on the Stratosphere,* Science 300, 1740-1742, 2003

Schultz et al., *Air pollution and Climate-Forcing Impacts of a Global Hydrogen Economy,* Science 302, 624-627, 2003

Rhee et al, *The overwhelming role of soils in the global atmospheric hydrogen cycle,* Atmos. Chem. Phys 6, 1611-1625, 2006