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Physics and Astronomy]

Modeling the global hydrogen isotope cycle

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M. C. Krol
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Contents

Background

- Potential advantages of H_2 economy
  - Reduced greenhouse gas emissions
  - Better urban air quality

- Potential disadvantages of H_2 economy
  - Slower methane removal (Schultz *et al.*, 2003)
  - Stratospheric ozone removal (Tromp *et al.*, 2003)

- Potential adverse effects on climate
- Determine baseline budget of H_2
  - Use concentration measurements (H_2)
  - Use stable hydrogen isotope measurements (H_2 and HD)
  - Use global models for interpretation

- Note: $\delta D(H2) = (2([HD]/[H2])/R_{VSMOV} - 1)*1000$ o/oo

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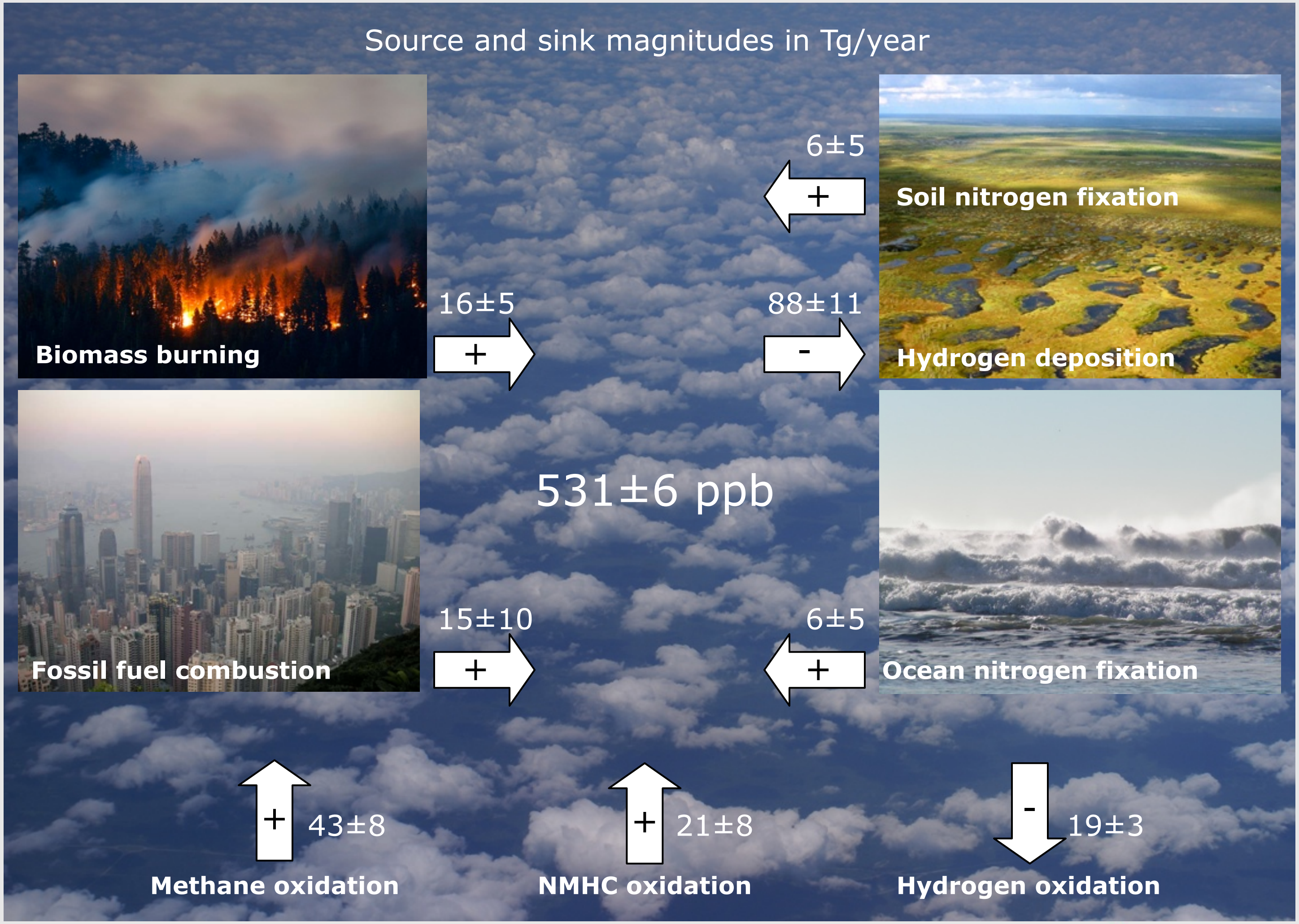
Atmospheric Budget of H_2



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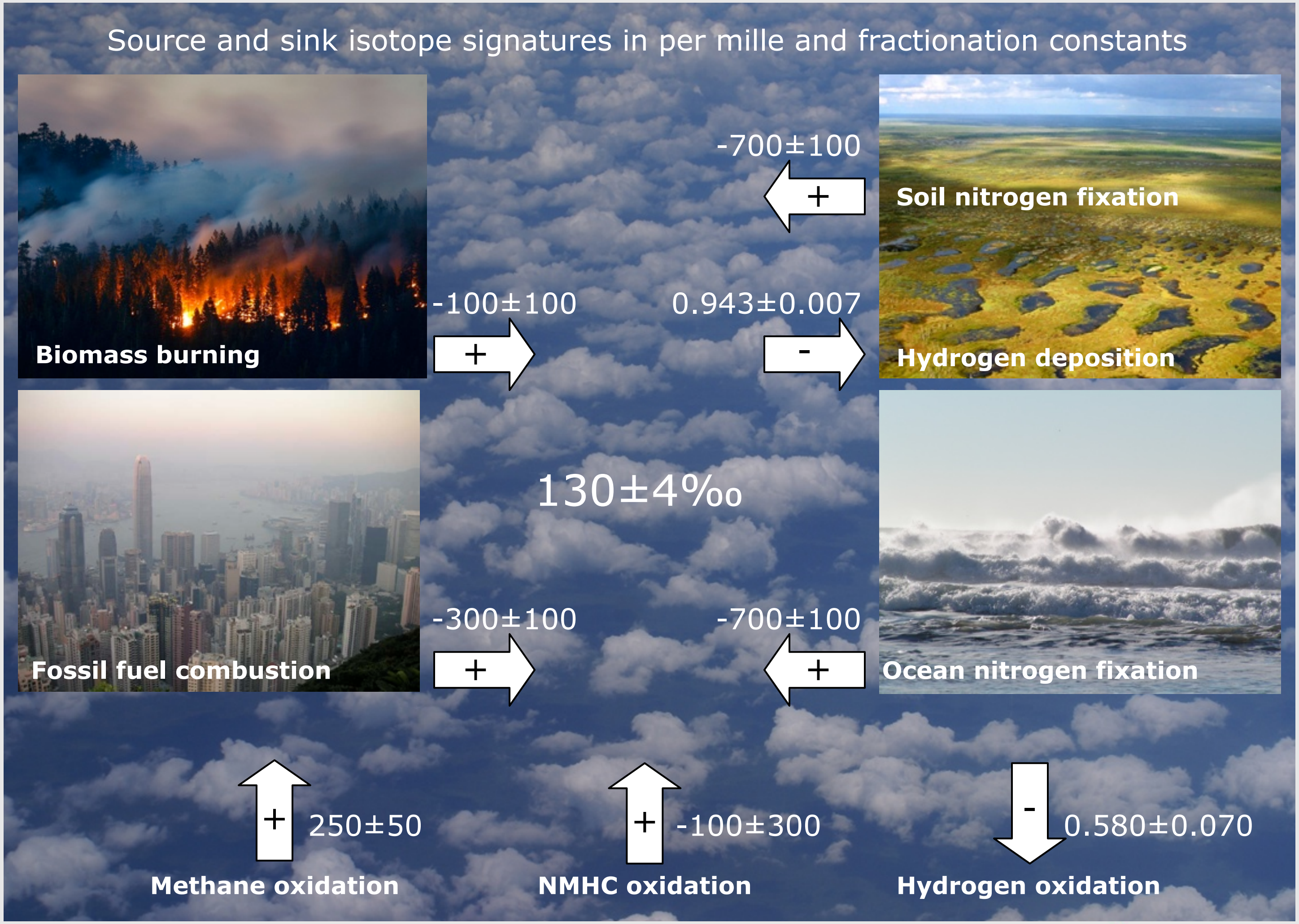
NMHC = Non Methane HydroCarbons

Atmospheric Budget of H_2



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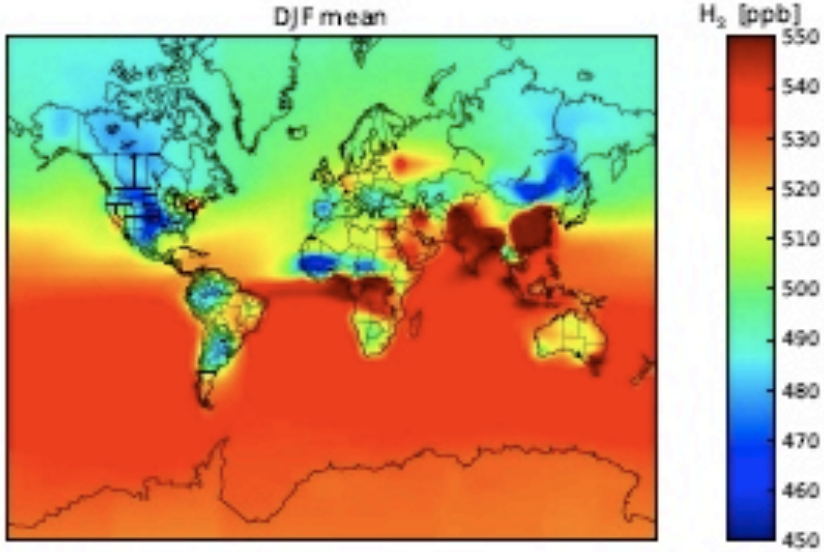
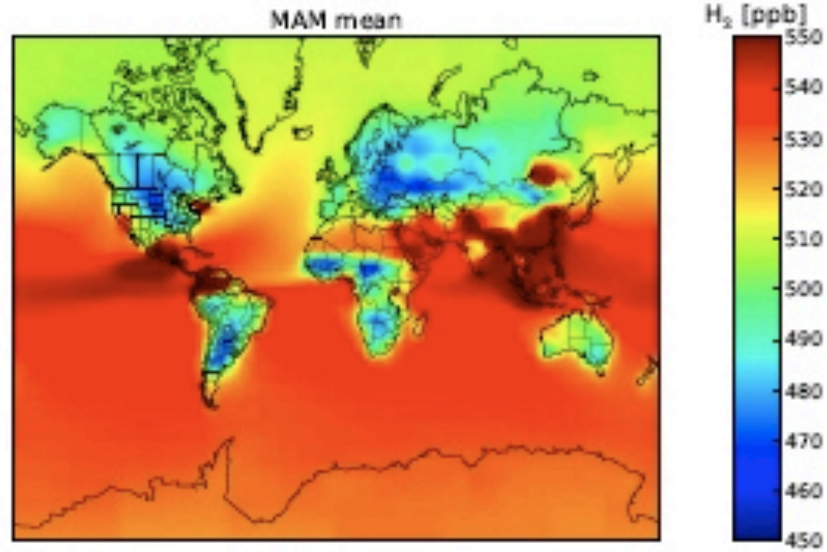
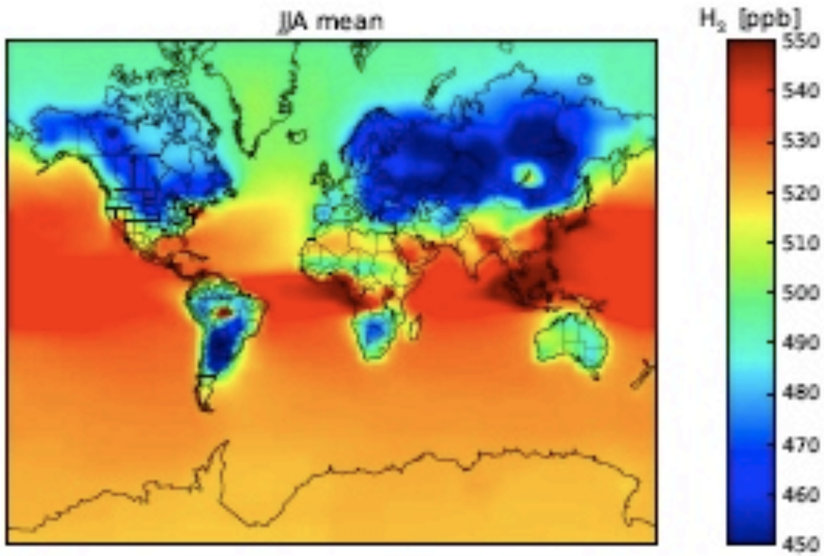
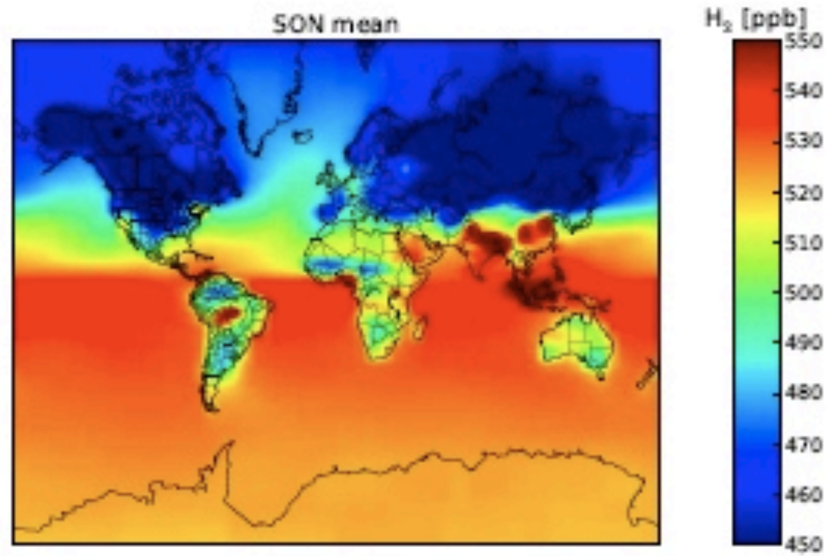

DJF mean
H$_s$ [ppb]
550
540
530
520
510
500
490
480
470
460
450

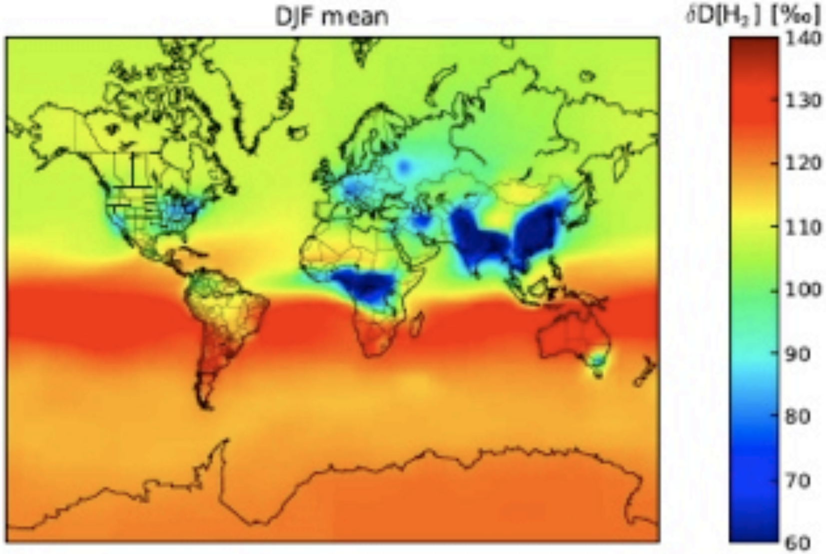
(a)


MAM mean
H$_s$ [ppb]
550
540
530
520
510
500
490
480
470
460
450

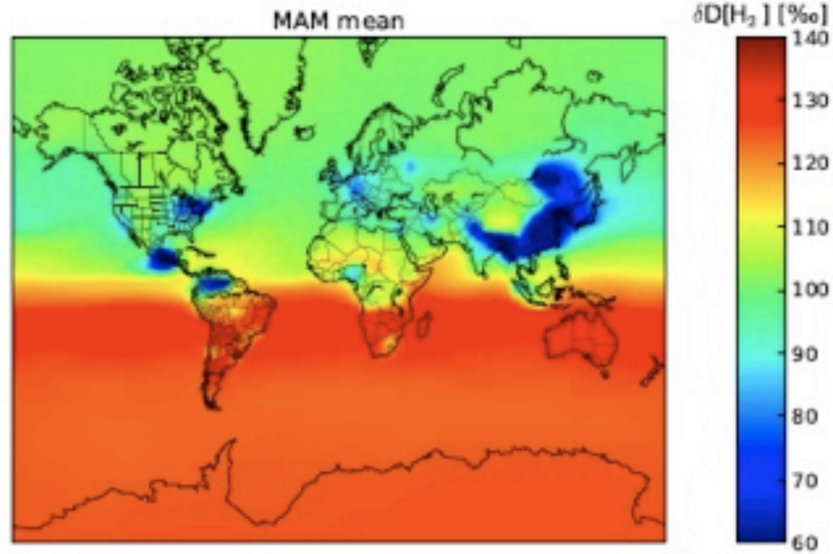
(b)


JJA mean
H$_s$ [ppb]
550
540
530
520
510
500
490
480
470
460
450

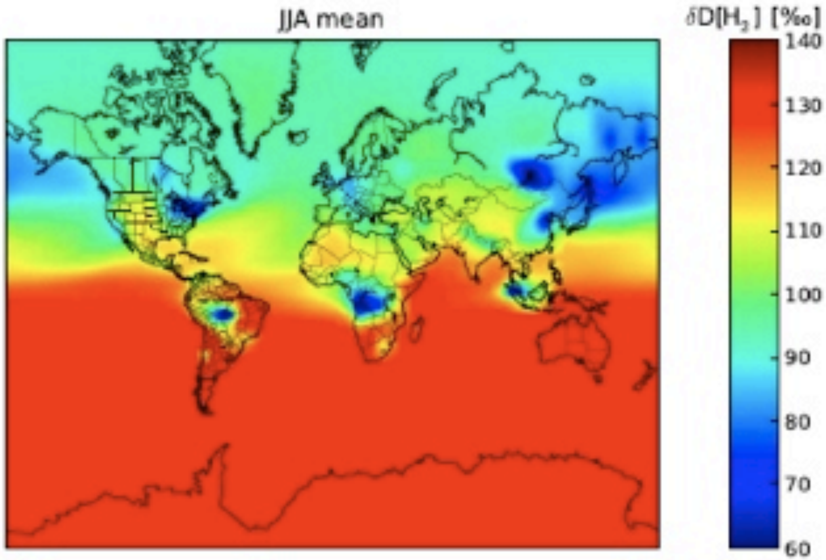

SON mean
H$_s$ [ppb]
550
540
530
520
510
500
490
480
470
460
450

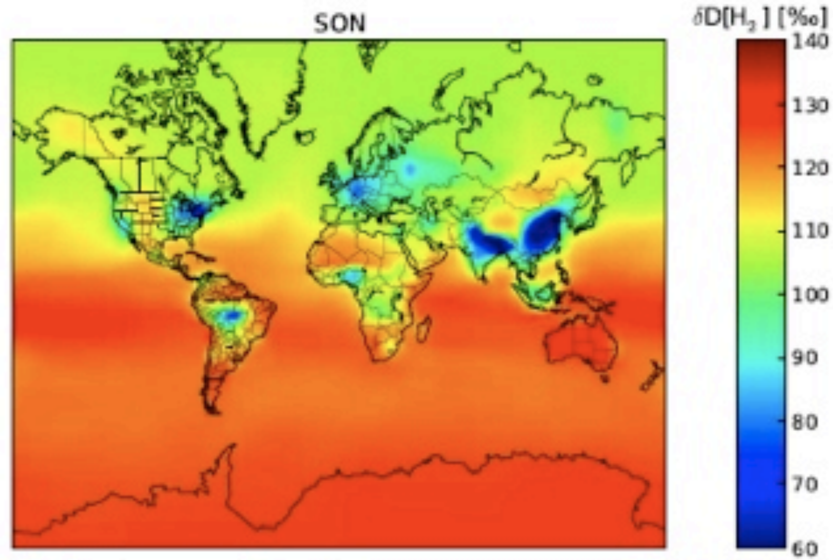

DJF mean
δD[H$_2$] [‰]
140
130
120
110
100
90
80
70
60

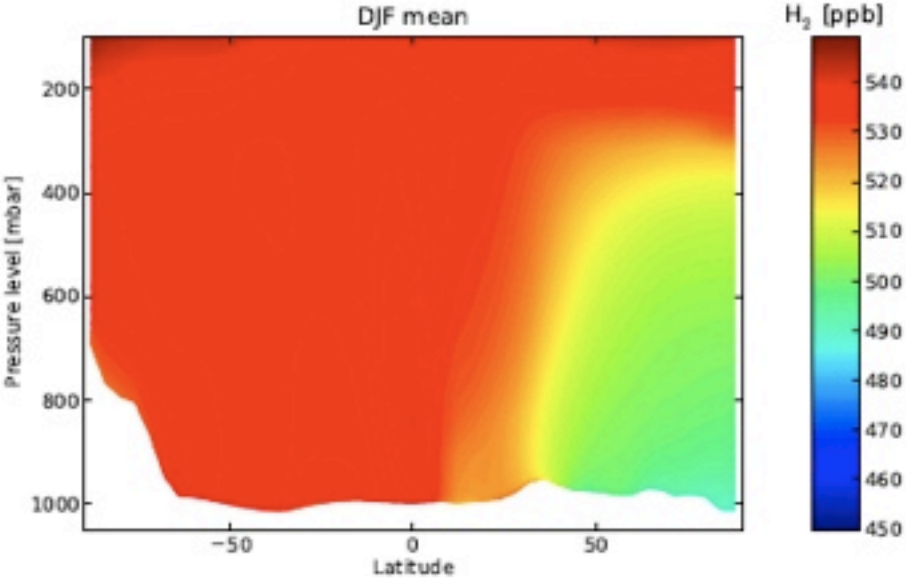
(a)


MAM mean
δD[H$_2$] [‰]
140
130
120
110
100
90
80
70
60

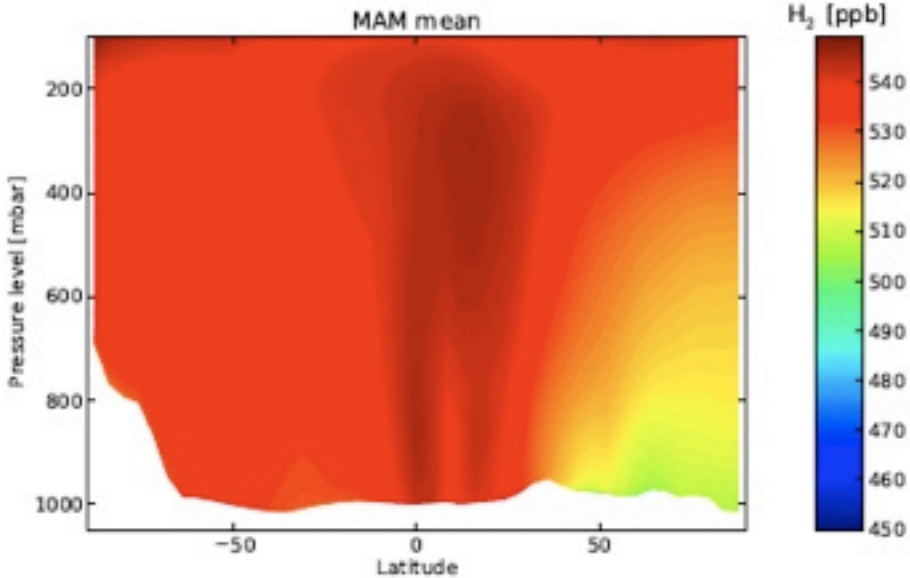
(b)


JJA mean
δD[H$_2$] [‰]
140
130
120
110
100
90
80
70
60

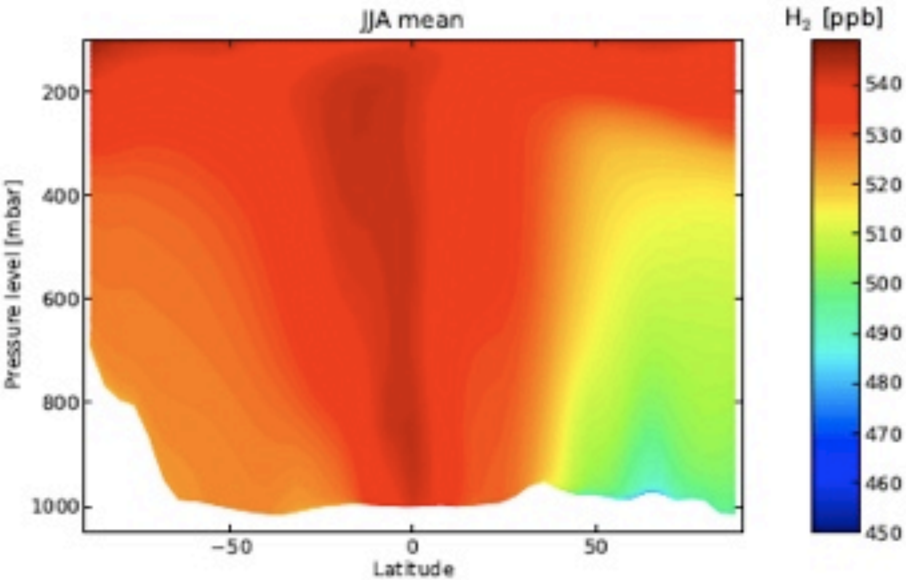

SON
δD[H$_2$] [‰]
140
130
120
110
100
90
80
70
60

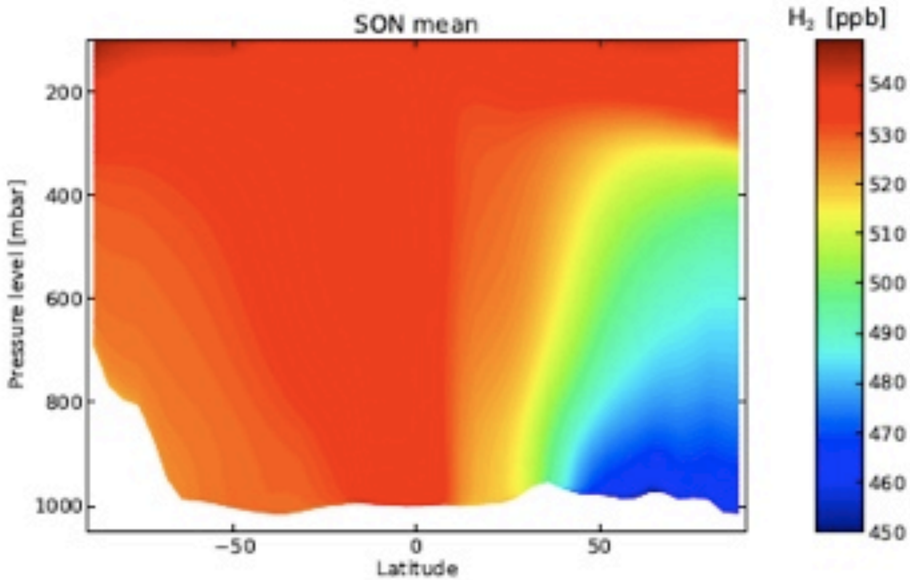

DJF mean
H2 [ppb]
Pressure level [mbar]
200
400
600
800
1000
−50
0
50
Latitude
540
530
520
510
500
490
480
470
460
450

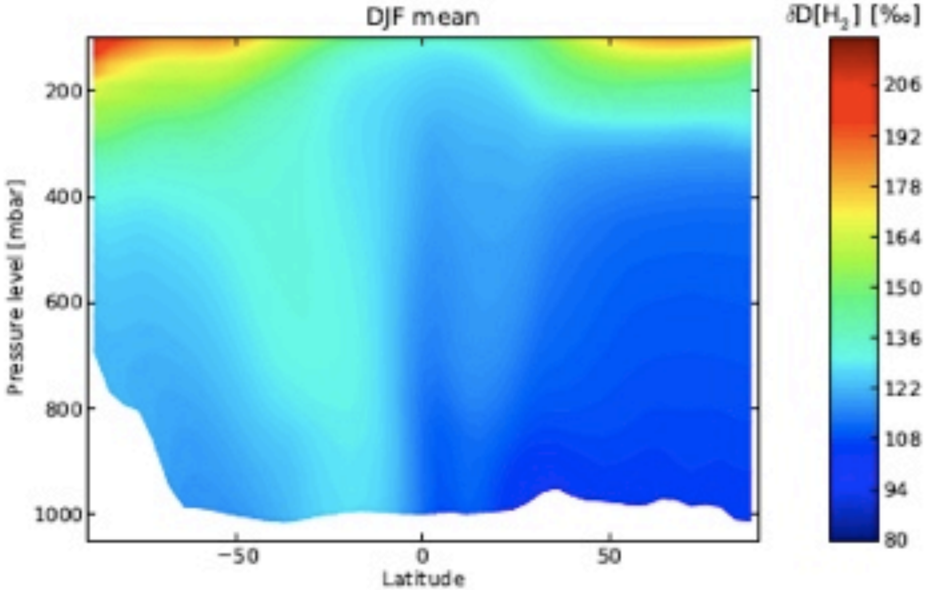
(a)


MAM mean
H2 [ppb]
Pressure level [mbar]
200
400
600
800
1000
−50
0
50
Latitude
540
530
520
510
500
490
480
470
460
450

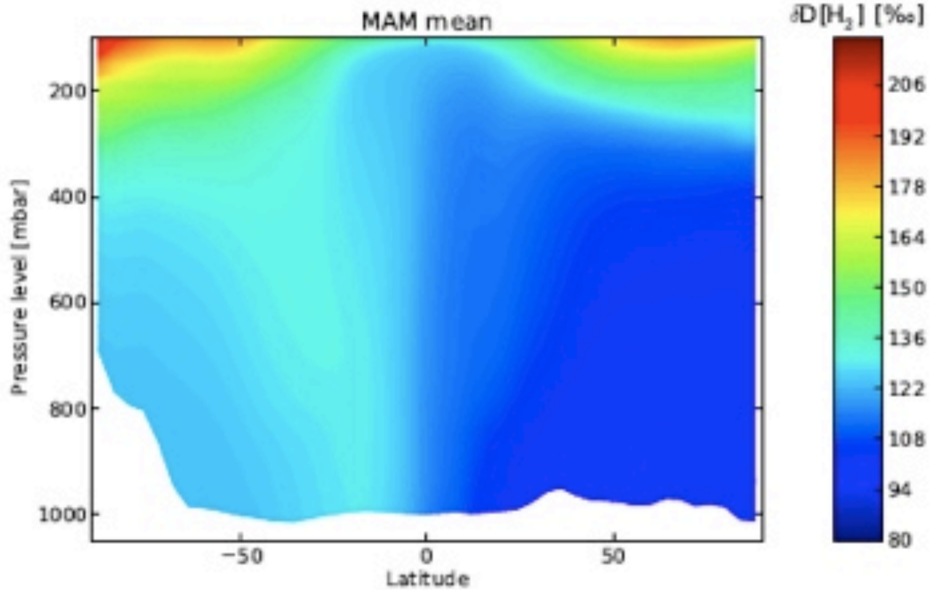
(b)


JJA mean
H2 [ppb]
Pressure level [mbar]
200
400
600
800
1000
−50
0
50
Latitude
540
530
520
510
500
490
480
470
460
450

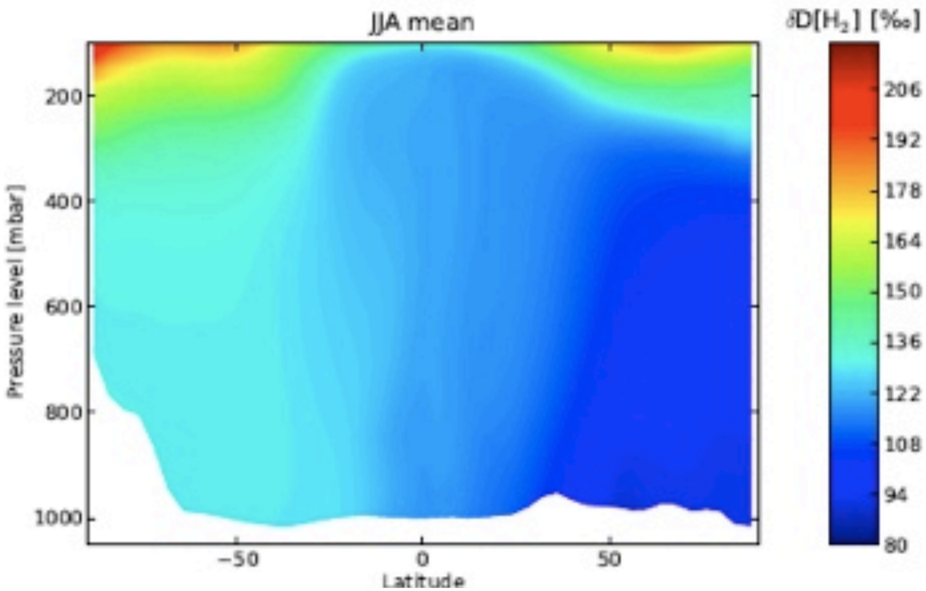

SON mean
H2 [ppb]
Pressure level [mbar]
200
400
600
800
1000
−50
0
50
Latitude
540
530
520
510
500
490
480
470
460
450

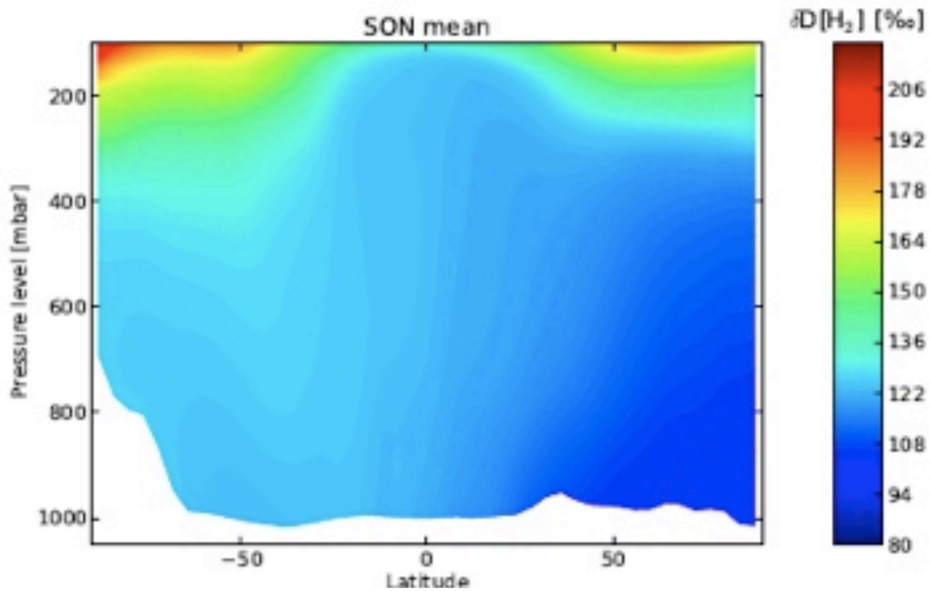

DJF mean
δD[H$_2$] [‰]
Pressure level [mbar]
Latitude
200
400
600
800
1000
−50
0
50
206
192
178
164
150
136
122
108
94
80

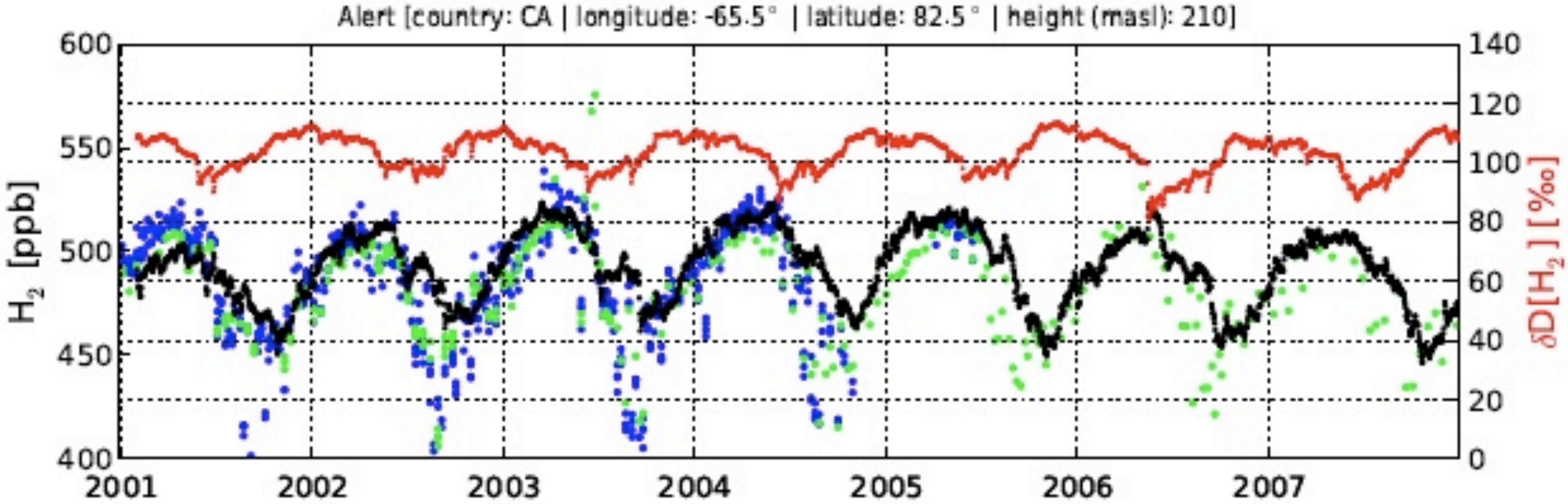
(a)


MAM mean
δD[H$_2$] [‰]
Pressure level [mbar]
Latitude
200
400
600
800
1000
−50
0
50
206
192
178
164
150
136
122
108
94
80

(b)

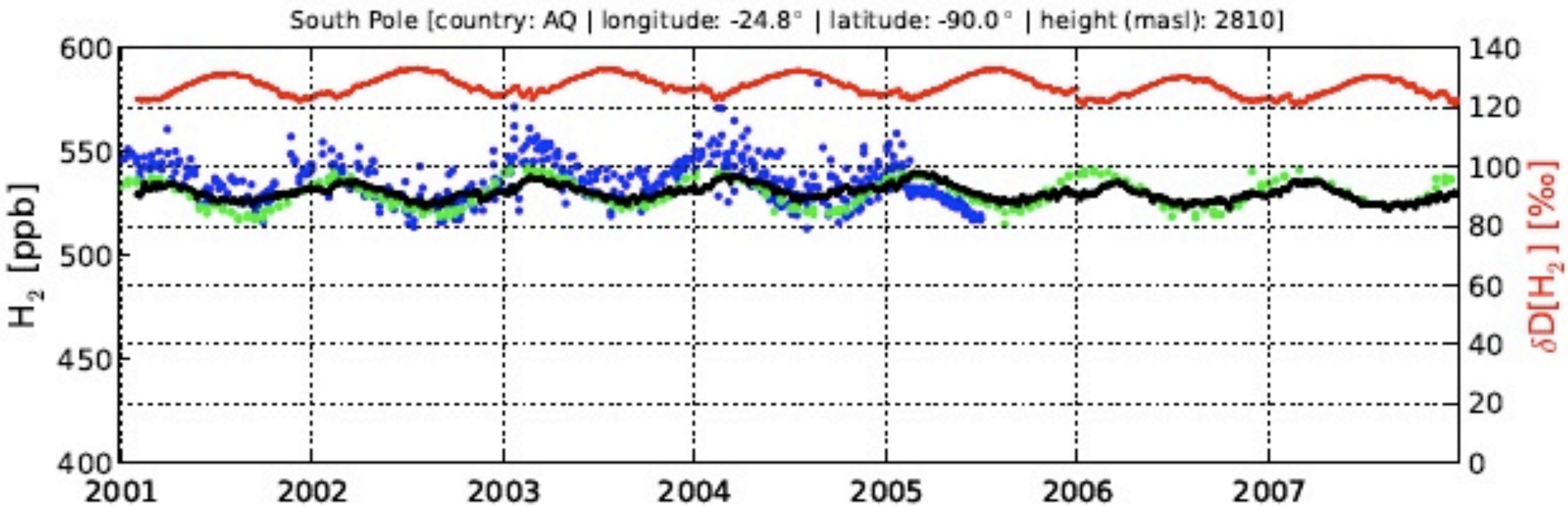

JJA mean
δD[H$_2$] [‰]
Pressure level [mbar]
Latitude
200
400
600
800
1000
−50
0
50
206
192
178
164
150
136
122
108
94
80


SON mean
δD[H$_2$] [‰]
Pressure level [mbar]
Latitude
200
400
600
800
1000
−50
0
50
206
192
178
164
150
136
122
108
94
80

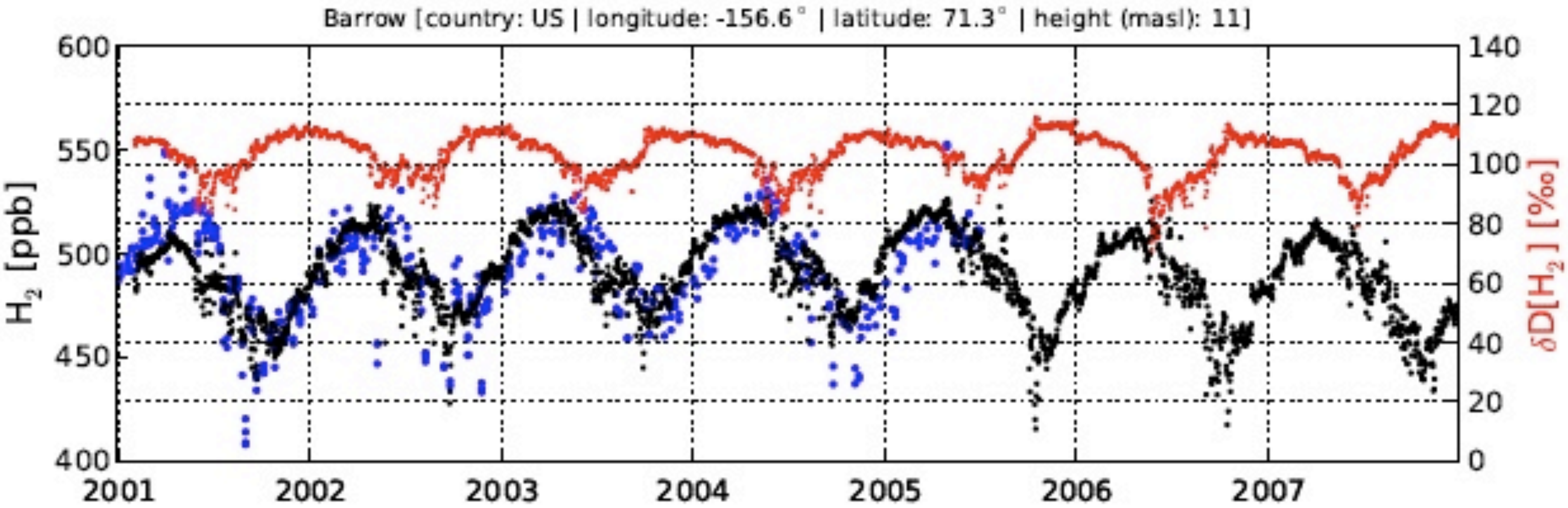


Alert [country: CA | longitude: -65.5° | latitude: 82.5° | height (masl): 210]
600
550
500
450
400
H_2 [ppb]
140
120
100
80
60
40
20
0
$\delta D[H_2]$ [‰]
2001
2002
2003
2004
2005
2006
2007

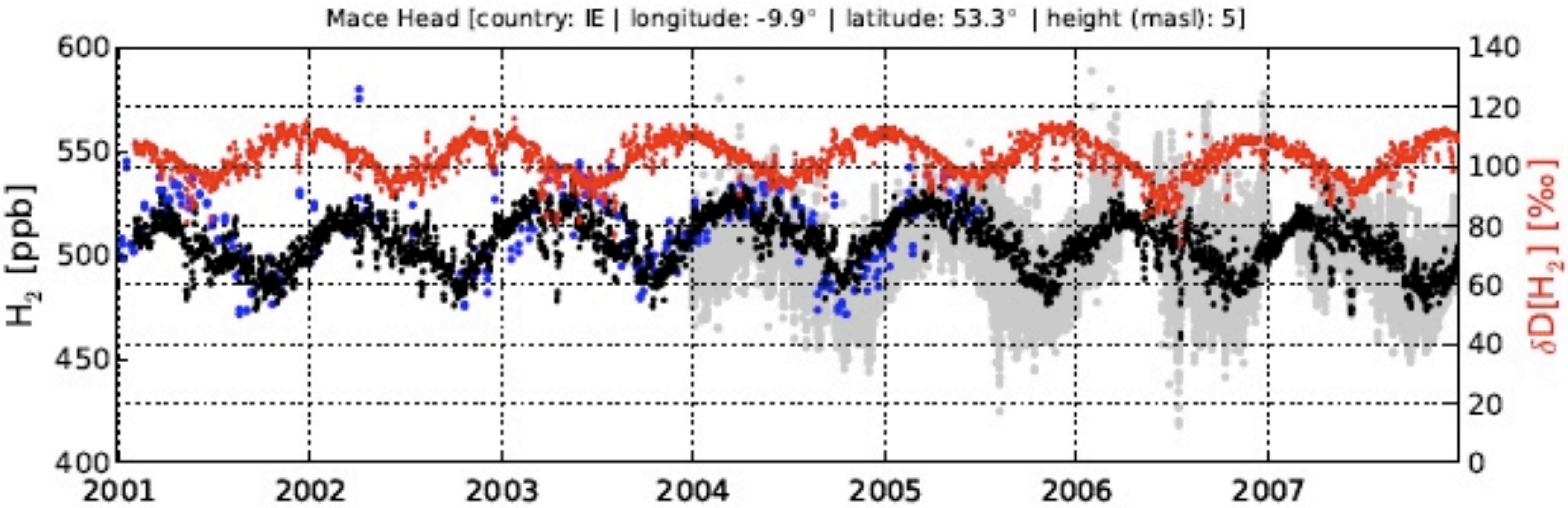
(a)

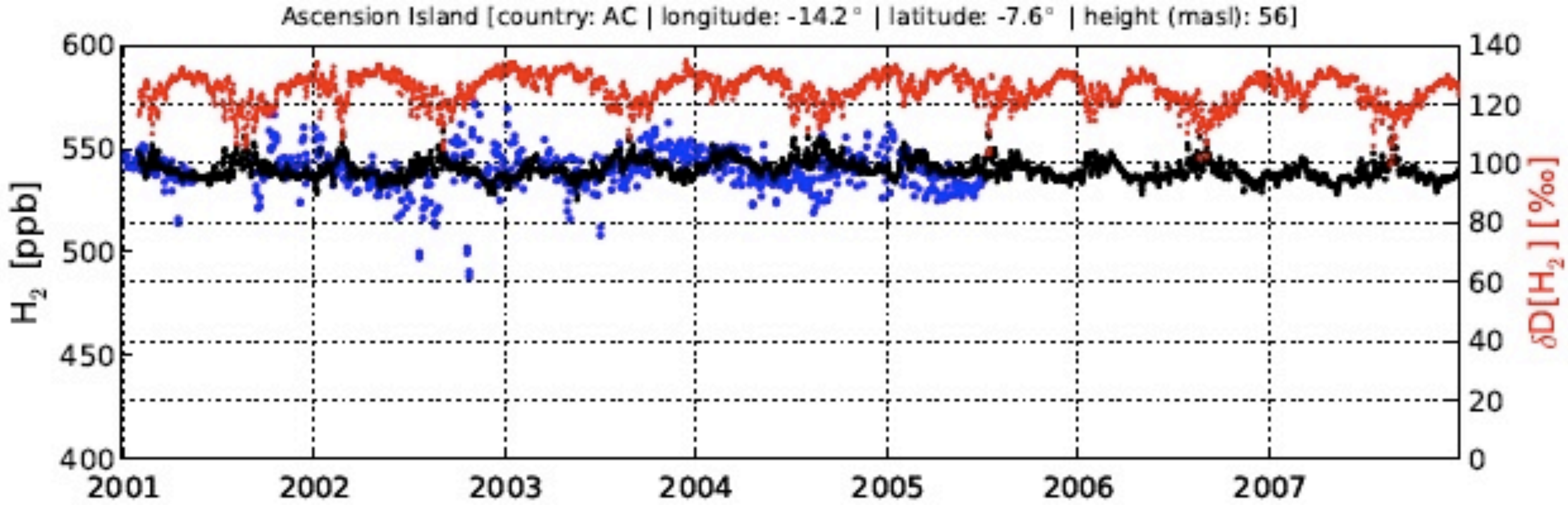


South Pole [country: AQ | longitude: -24.8° | latitude: -90.0° | height (masl): 2810]
600
550
500
450
400
H_2 [ppb]
140
120
100
80
60
40
20
0
$\delta D[H_2]$ [‰]
2001
2002
2003
2004
2005
2006
2007


Barrow [country: US | longitude: -156.6° | latitude: 71.3° | height (masl): 11]
H2 [ppb]
δD[H2] [‰]
600
550
500
450
400
140
120
100
80
60
40
20
0
2001
2002
2003
2004
2005
2006
2007

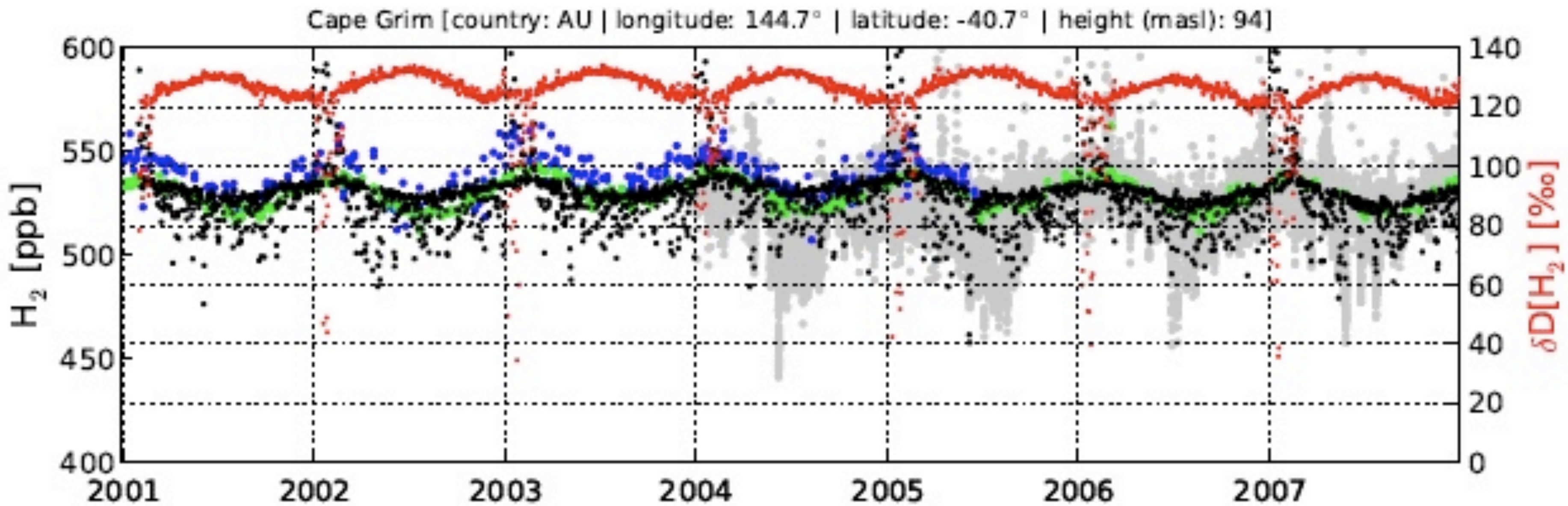
(c)


Mace Head [country: IE | longitude: -9.9° | latitude: 53.3° | height (masl): 5]
H2 [ppb]
δD[H2] [‰]
600
550
500
450
400
140
120
100
80
60
40
20
0
2001
2002
2003
2004
2005
2006
2007

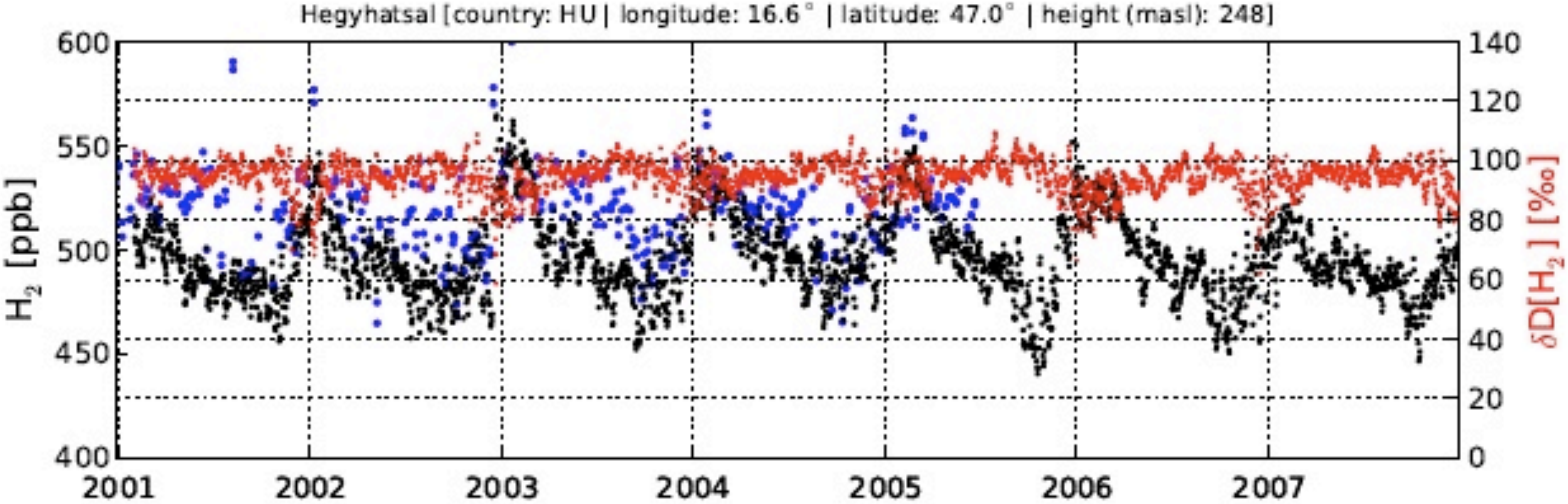


Ascension Island [country: AC | longitude: -14.2° | latitude: -7.6° | height (masl): 56]
600
550
500
450
400
H_2 [ppb]
140
120
100
80
60
40
20
0
$\delta D[H_2]$ [‰]
2001
2002
2003
2004
2005
2006
2007

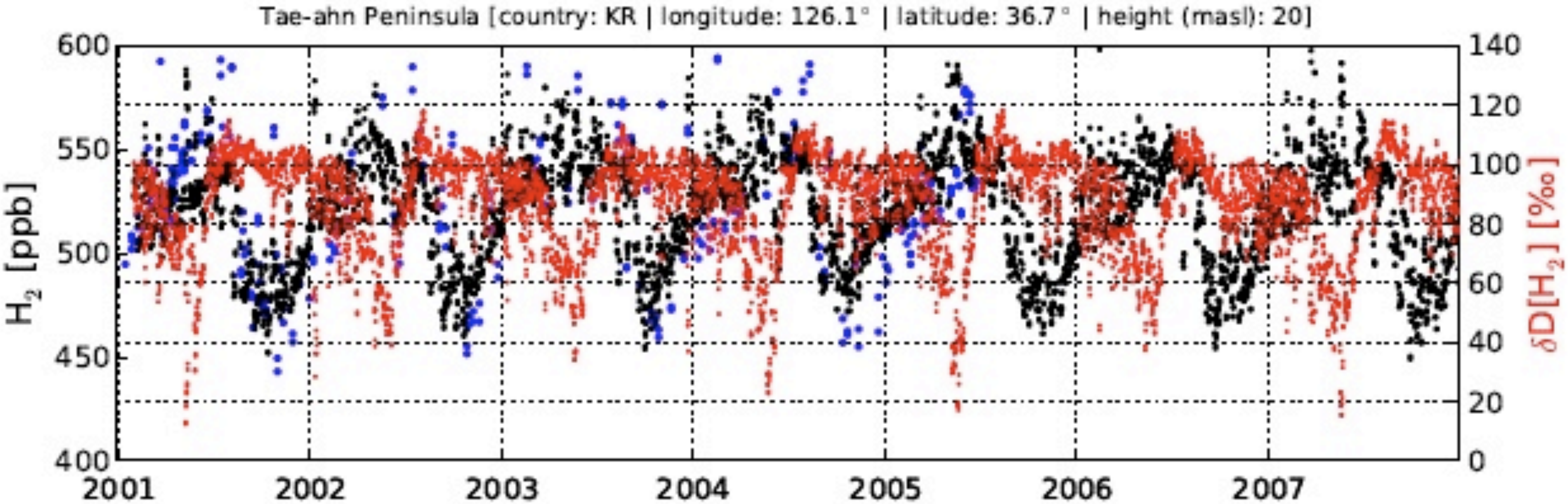
(a)

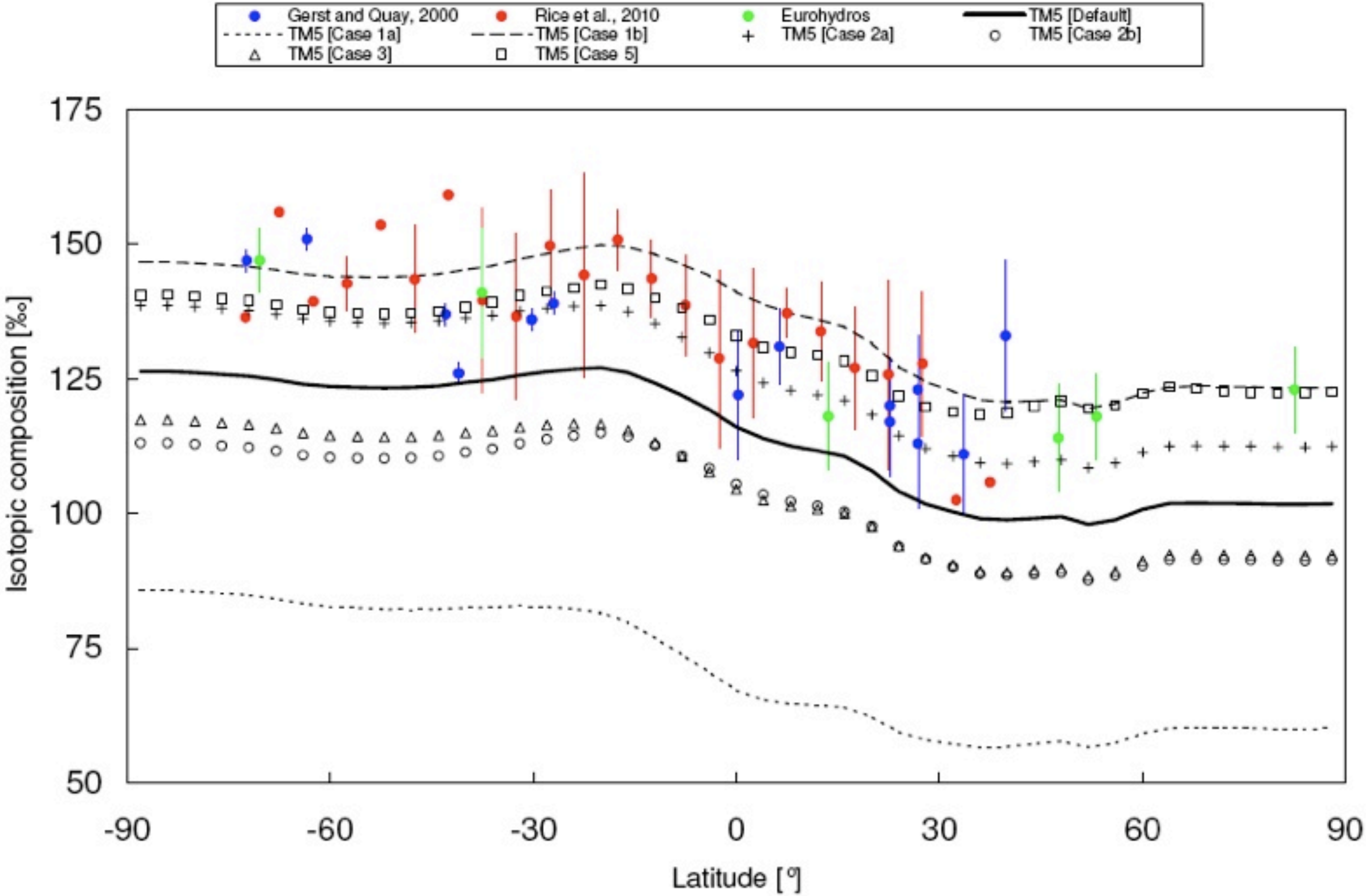


Cape Grim [country: AU | longitude: 144.7° | latitude: -40.7° | height (masl): 94]
600
550
500
450
400
H_2 [ppb]
140
120
100
80
60
40
20
0
$\delta D[H_2]$ [‰]
2001
2002
2003
2004
2005
2006
2007


Hegyhatsal [country: HU | longitude: 16.6° | latitude: 47.0° | height (masl): 248]
H2 [ppb]
δD[H2] [‰]
600
550
500
450
400
140
120
100
80
60
40
20
0
2001
2002
2003
2004
2005
2006
2007

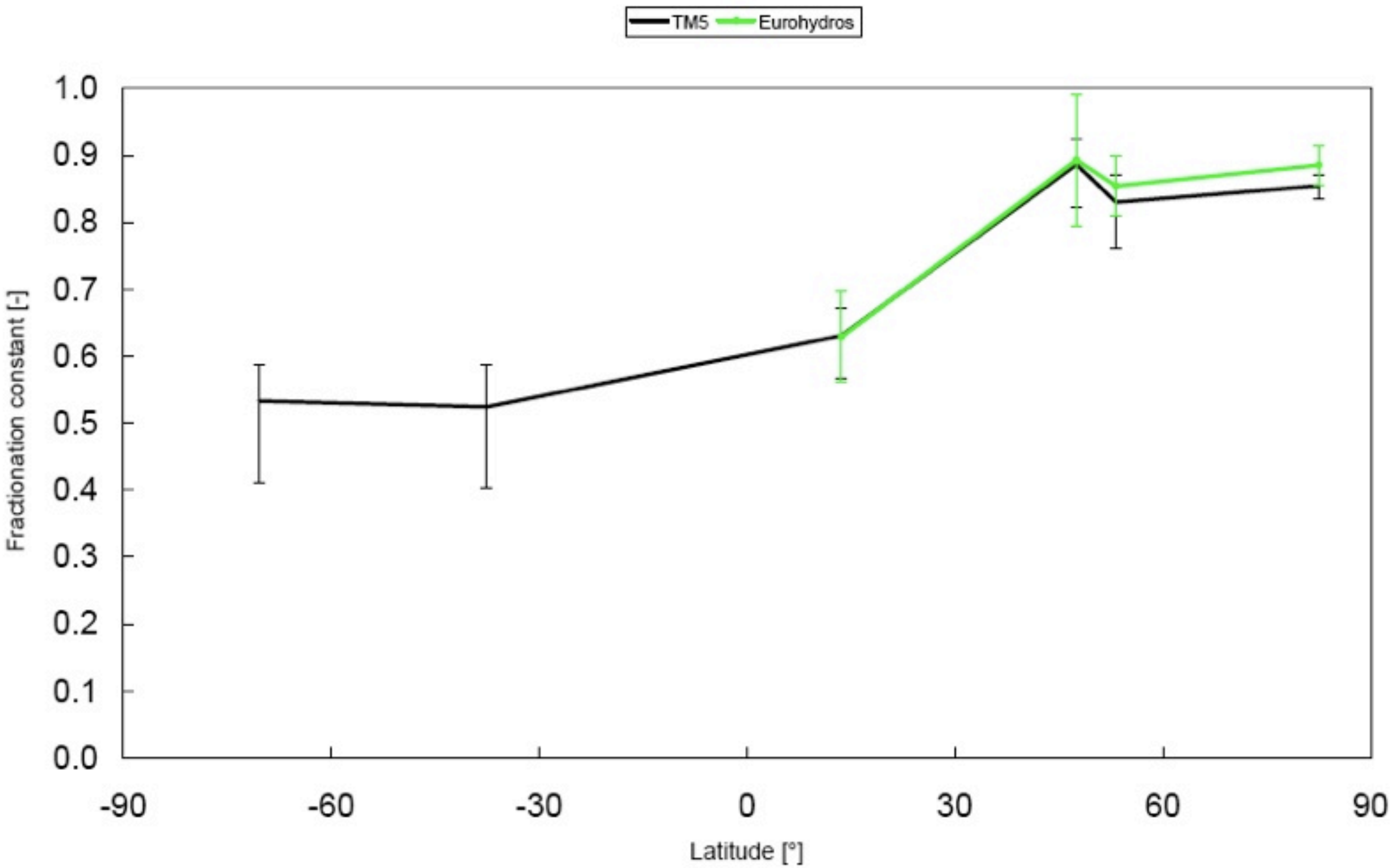
(c)


Tae-ahn Peninsula [country: KR | longitude: 126.1° | latitude: 36.7° | height (masl): 20]
H2 [ppb]
δD[H2] [‰]
600
550
500
450
400
140
120
100
80
60
40
20
0
2001
2002
2003
2004
2005
2006
2007



Gerst and Quay, 2000
Rice et al., 2010
Eurohydros
TM5 [Default]
TM5 [Case 1a]
TM5 [Case 1b]
TM5 [Case 2a]
TM5 [Case 2b]
TM5 [Case 3]
TM5 [Case 5]
175
150
125
100
75
50
Isotopic composition [‰]
-90
-60
-30
0
30
60
90
Latitude [°]

Scenario	Perturbed variables	Composition [‰]
Default		+125
1a	KIE[R32b]=1.100, KIE[R33b]=1.820	+82
1b	KIE[R33b]=$(500.00 + 2.50 \cdot 10^{-2}p)/(500.00 + 1.60 \cdot 10^{-2}p)$	+146
2a	Stratospheric composition increased by 20‰	+137
2b	Tropopause boundary defined by $p_s = 2.10 \cdot 10^4 - 1.65 \cdot 10^4 cos\,(\theta)$	+113
2c	Tropopause boundary defined by $p_s = 2.00 \cdot 10^4 - 1.15 \cdot 10^4 cos\,(\theta)$	+115
3	δD[NMHCs]=-200‰	+115
4a	δD[N_2 fixation emissions]=-700‰	+121
4b	δD[fossil fuel burning emissions]=-250‰	+120
4c	δD[biomass burning emissions]=-290‰	+122
5	Fractionation constant deposition changed to 0.900	+139



$$\frac{R_f}{R_i} = \left(\frac{[C]_f}{[C]_i}\right)^{\alpha-1}$$

	Rhee *et al.* (2006b)	Price *et al.* (2007)	Xiao *et al.* (2007)	Ehhalt and Rohrer (2009)	This work
Sources					
Fossil fuel	15	18.3	15	11	17.0^{+3}_{-6}
Biomass burning	16	10.1	13	15	15.0^{+5}_{-5}
Biofuel		4.4			
Ocean N_2 fixation	6	6.0		6	5.0^{+1}_{-2}
Land N_2 fixation	6	0.0		3	3.0^{+3}_{-3}
Photochemical production	64	34.3	77	41	37.3
Total	107	73.1	105	76	77.3
Sinks					
Photochemical removal	19	18.0	18	19	22.1
Deposition	88	55.0	85	60	55.7
Total	107	73.0	105[a]	79	77.8
Tropospheric burden [TgH_2]	150[c]	141	149	155[d]	169[e]
Tropospheric lifetime [year]	1.4	1.9	1.4	2.0	2.2[e]

	Magnitude [TgH_2/year]	Signature [a]	Relative signature	Composition [‰]
Sources				
Fossil fuel	17.0^{+3}_{-6}	-196	$2.754 \cdot 10^{-5}$	
Biomass burning	15.0^{+5}_{-5}	-260	$2.237 \cdot 10^{-5}$	
Ocean N_2 fixation	5.0^{+1}_{-2}	-628	$3.748 \cdot 10^{-6}$	
Land N_2 fixation	3.0^{+3}_{-3}	-628	$2.249 \cdot 10^{-6}$	
Photochemical production	37.3	103	$8.290 \cdot 10^{-5}$	
Total	77.3		$1.388 \cdot 10^{-4}$	
Sinks				
Photochemical removal	22.1	0.542[b]	0.154	
Deposition	55.7	0.925[b]	0.663	
Total	77.8		0.816	
Isotopic composition				
From budget				91
Modeled composition				125
Stratospheric contribution				34

Conclusions

- Excellent H_2 simulation, hardly biases
- $\delta D(H_2)$ about 15 ‰ too light
  - explained by
    - CH_2O photolysis
    - deposition
    - stratospheric input
- Stratospheric input largest unknown at the moment
- Paper in preparation
- Next: high resolution analysis, e.g. Mace Head data