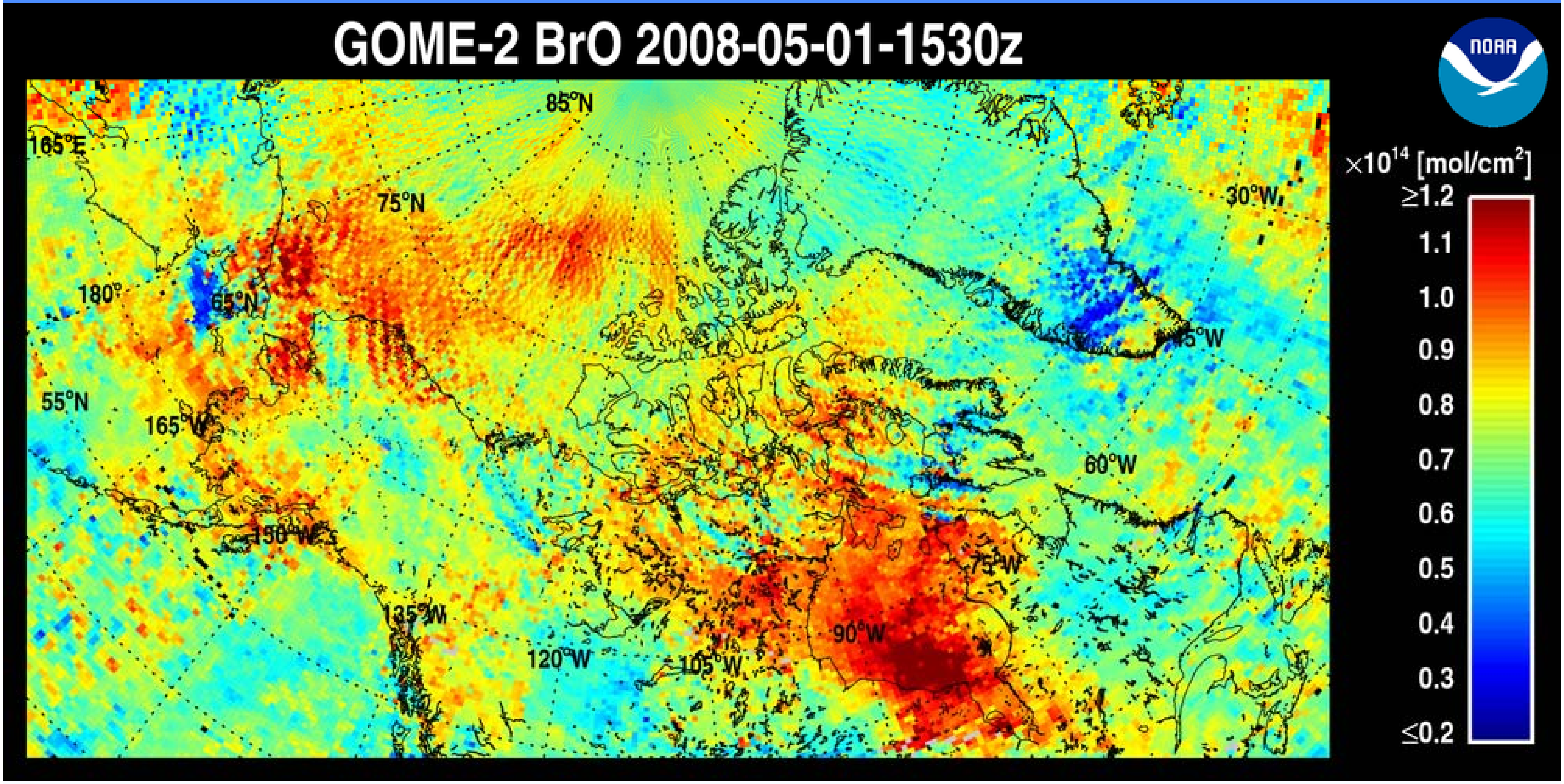
Arctic Tropospheric Ozone



David W. Tarasick, **Air Quality Research Division**

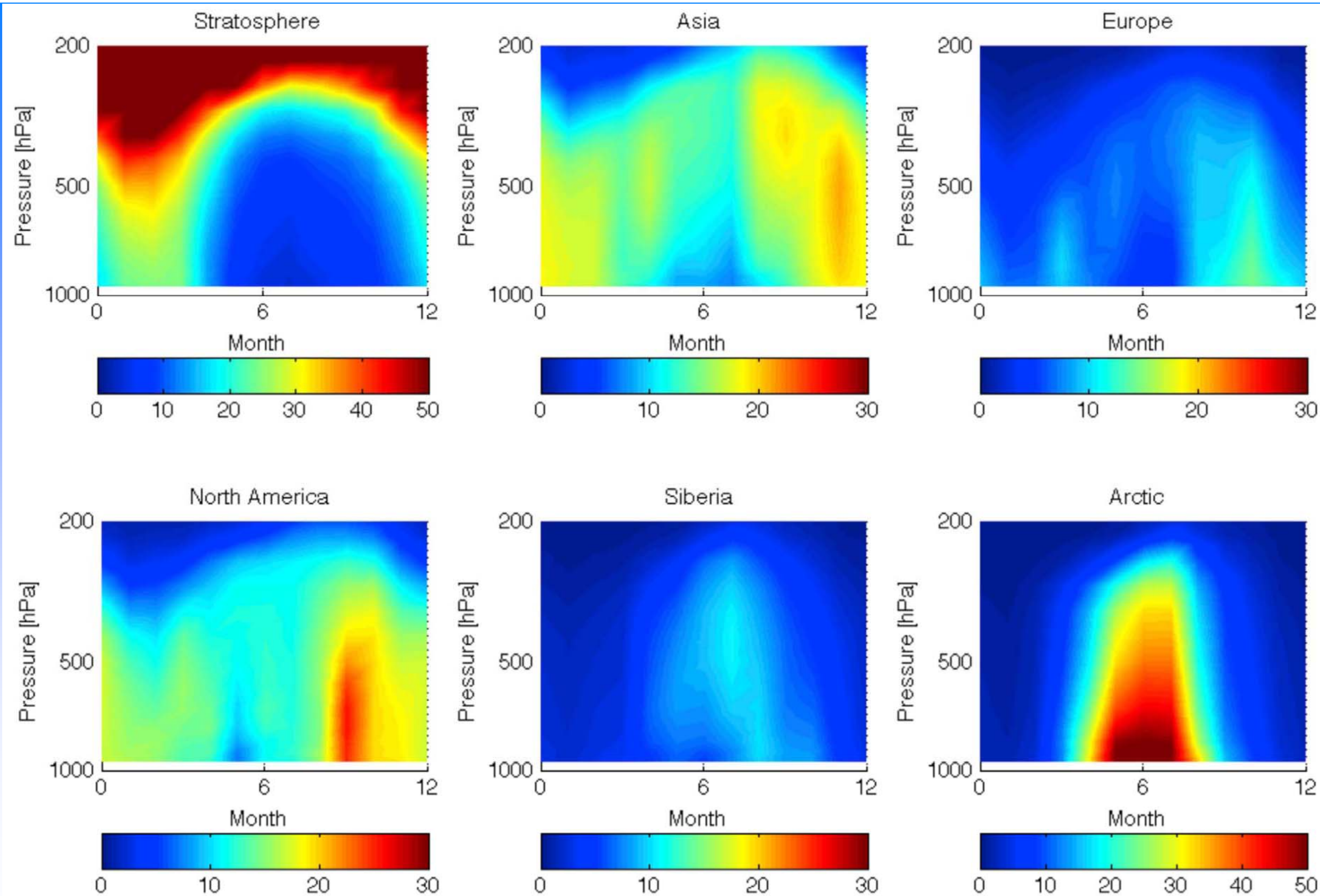
Environment Canada: http://exp-studies.tor.ec.gc.ca/

What's different about the Arctic?

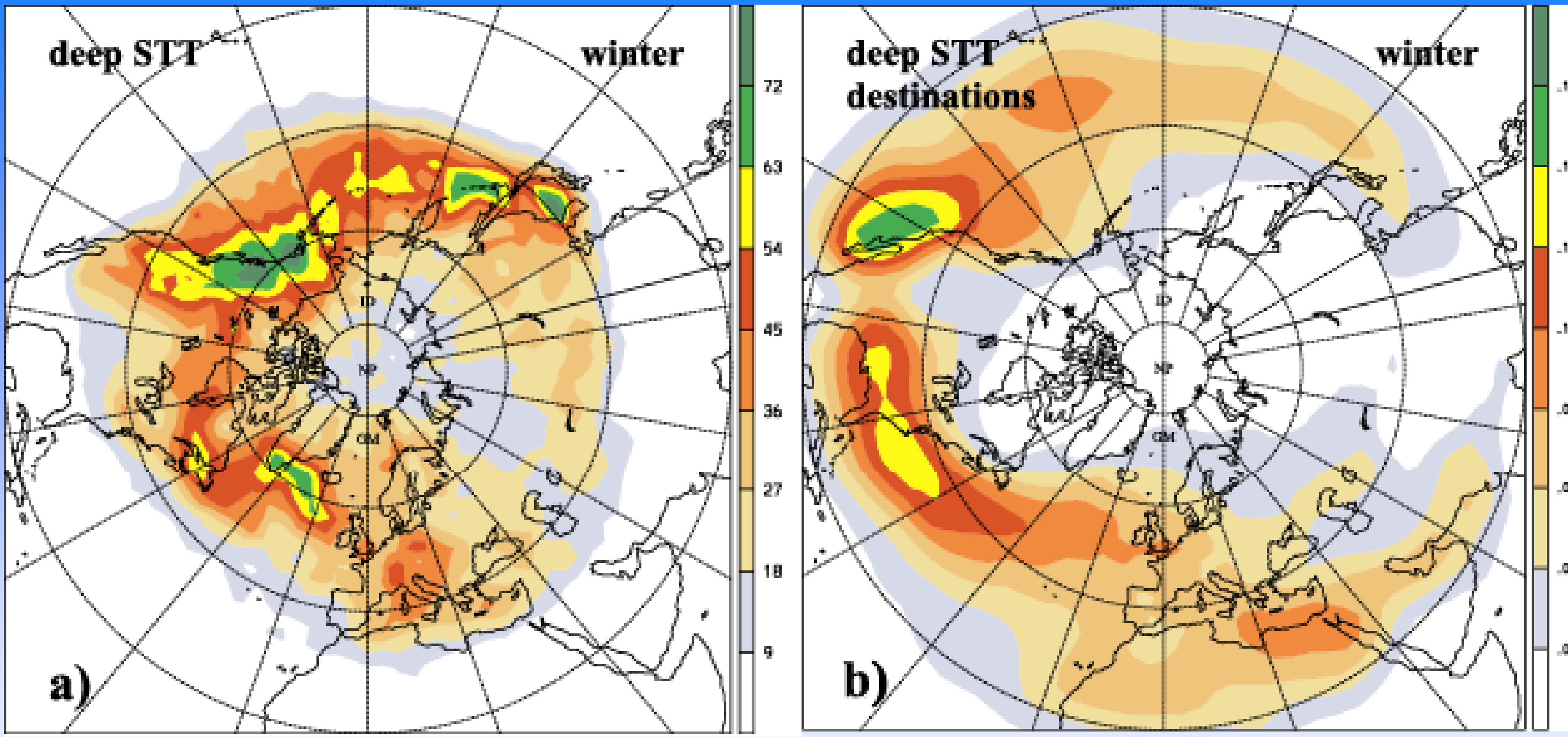
- There's hardly any data… (except ozonesondes)

Some similarities, some differences…

- Transport of ozone from lower latitudes very important (~25%?)
- Local production still dominant source (~50% in PBL; 30-40% in middle trop)
- Long-range transport of PAN important source of NO_x
- Stratospheric source less important than at mid-latitudes
- Fires?
- Br chemistry



Ozone transport: % contribution to the ozone profile above Eureka (*Walker et al.*, 2012)



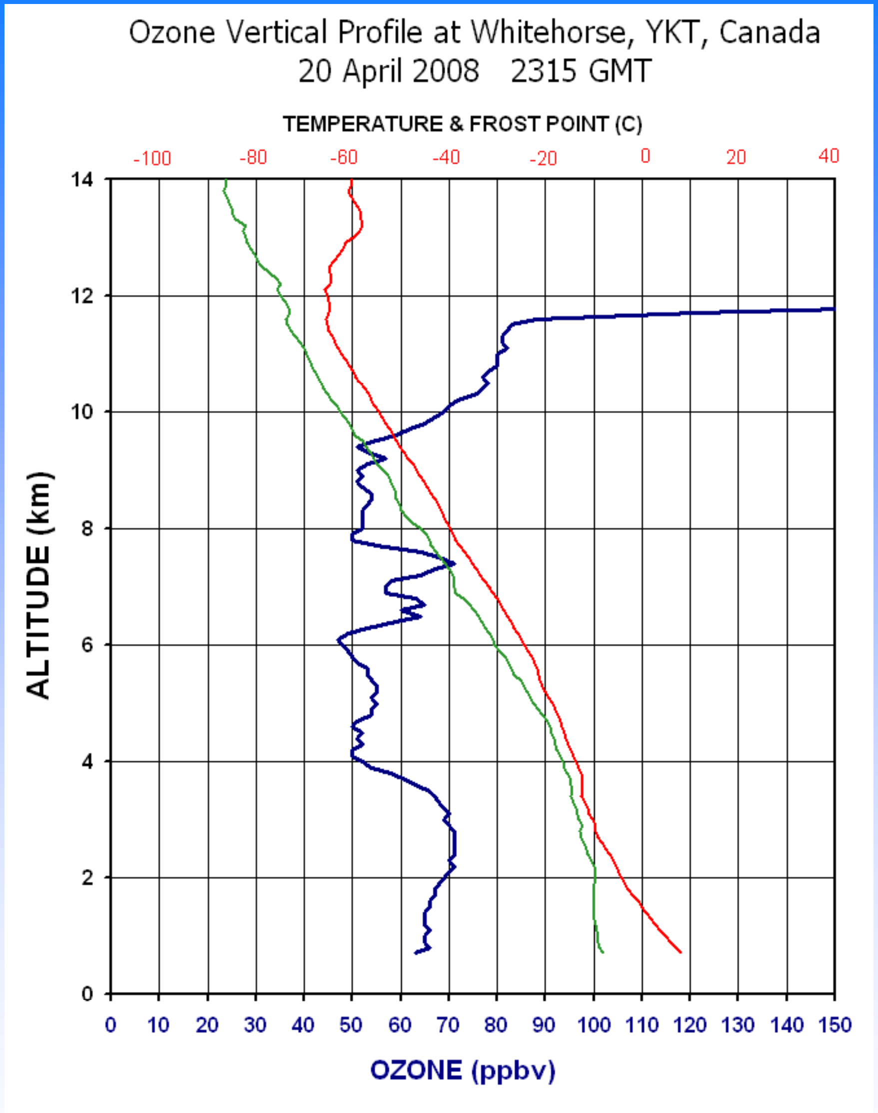
a) Cross-tropopause mass flux in kg km^{-2} s^{-1} of rapid exchange, deep STT events during Winter (DJF)

b) probability that a parcel in the boundary layer came from the lower stratosphere in the last four days. Estimates from an objective analysis of trajectories driven by the ERA-15 data set [*Sprenger and Wernli,* 2003]

Does the stratosphere control tropospheric variability?

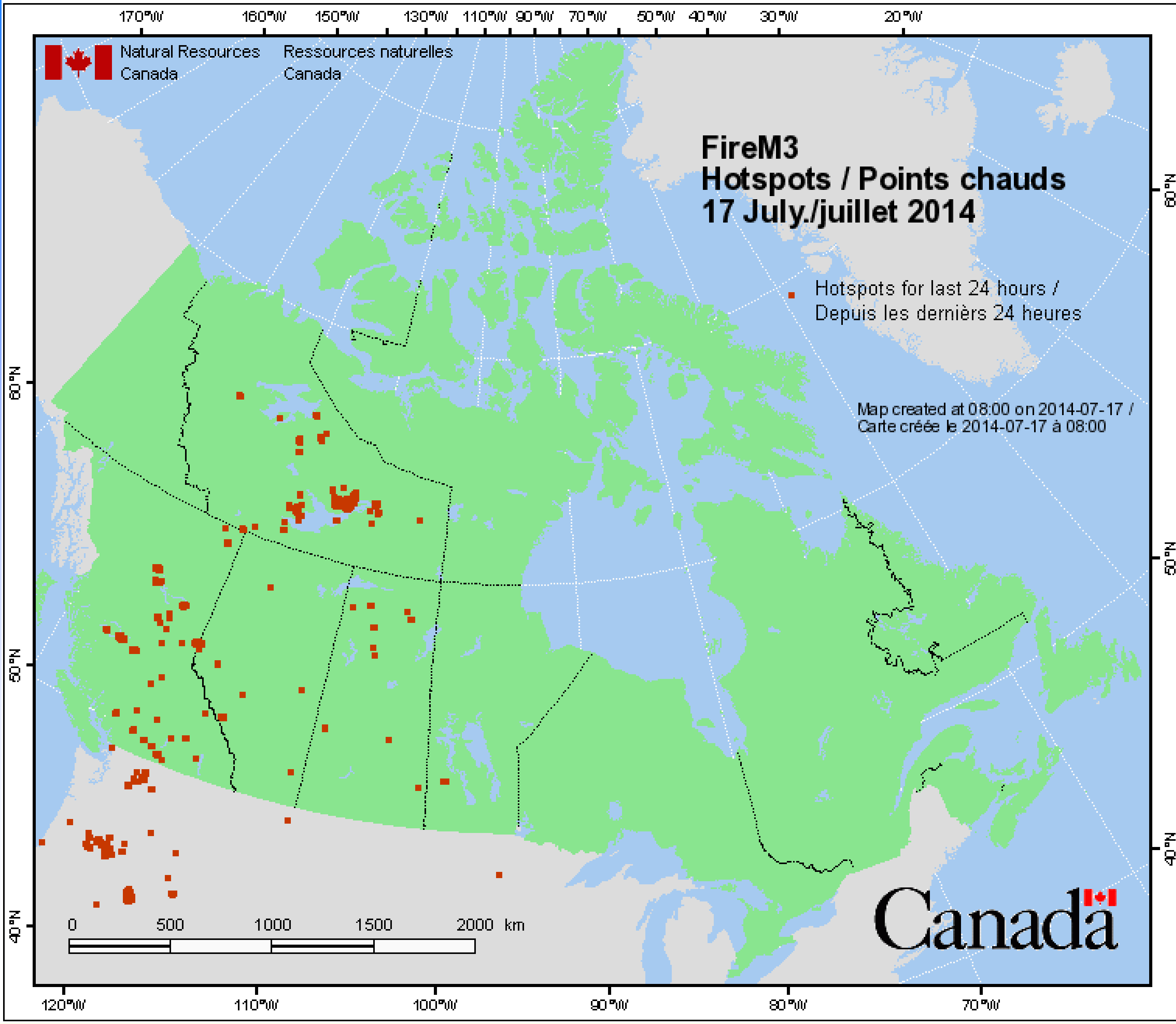
	Northern midlatitudes				Arctic			
	Ground	Gnd-630	630-400	400-250	Ground	Gnd-630	630-400	400-250
250-158 hPa	0.62	0.68	0.73	0.64	0.45	0.58	0.65	0.57
158-100 hPa	0.48	0.60	0.69	0.59	0.38	0.58	0.54	0.32
100- 63 hPa	0.34	0.57	0.71	0.56	0.34	0.55	0.52	0.19
63 - 40 hPa	0.37	0.61	0.73	0.58	0.19	0.35	0.40	0.11

Correlations between annual average ozone mixing ratio anomalies in the troposphere and in the lower stratosphere, for northern midlatitude and Arctic stations, 1980-2010. Statistically significant (95% confidence) correlations are indicated by shading. Stratosphere and troposphere are explicitly separated.



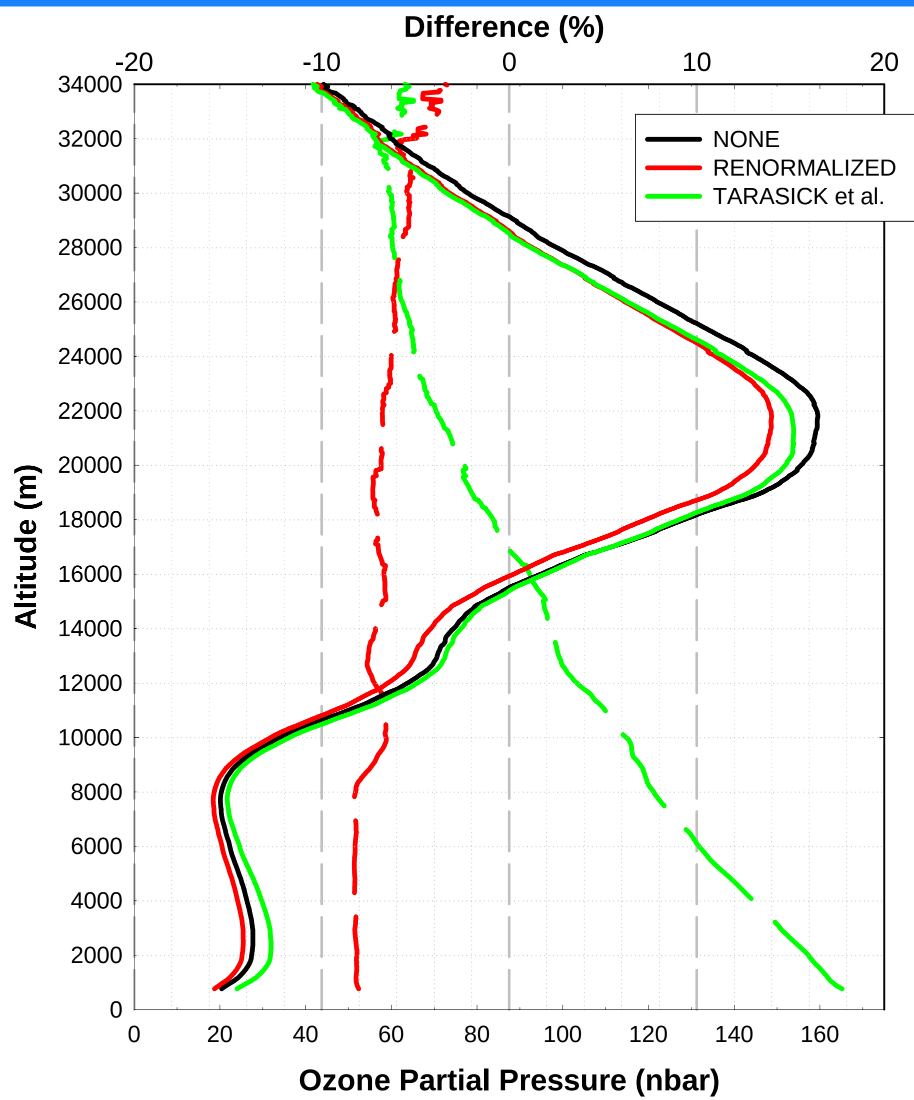
On April 19, 2008 at Barrow, the highest April ozone readings in 37 years of surface observations at the surface (hourly average values >55 ppbv) were recorded. At Denali National Park in central Alaska, an hourly average of 79 ppbv was observed. These were also traceable to biomass burning in Siberia and Kazakhstan. (*Oltmans et al., Atmospheric Environment,* 2010).

Ozone sounding at Whitehorse, YK (April 20, 2008) The layer of enhanced ozone near 3 km is traceable to biomass burning in Siberia and Kazakhstan.

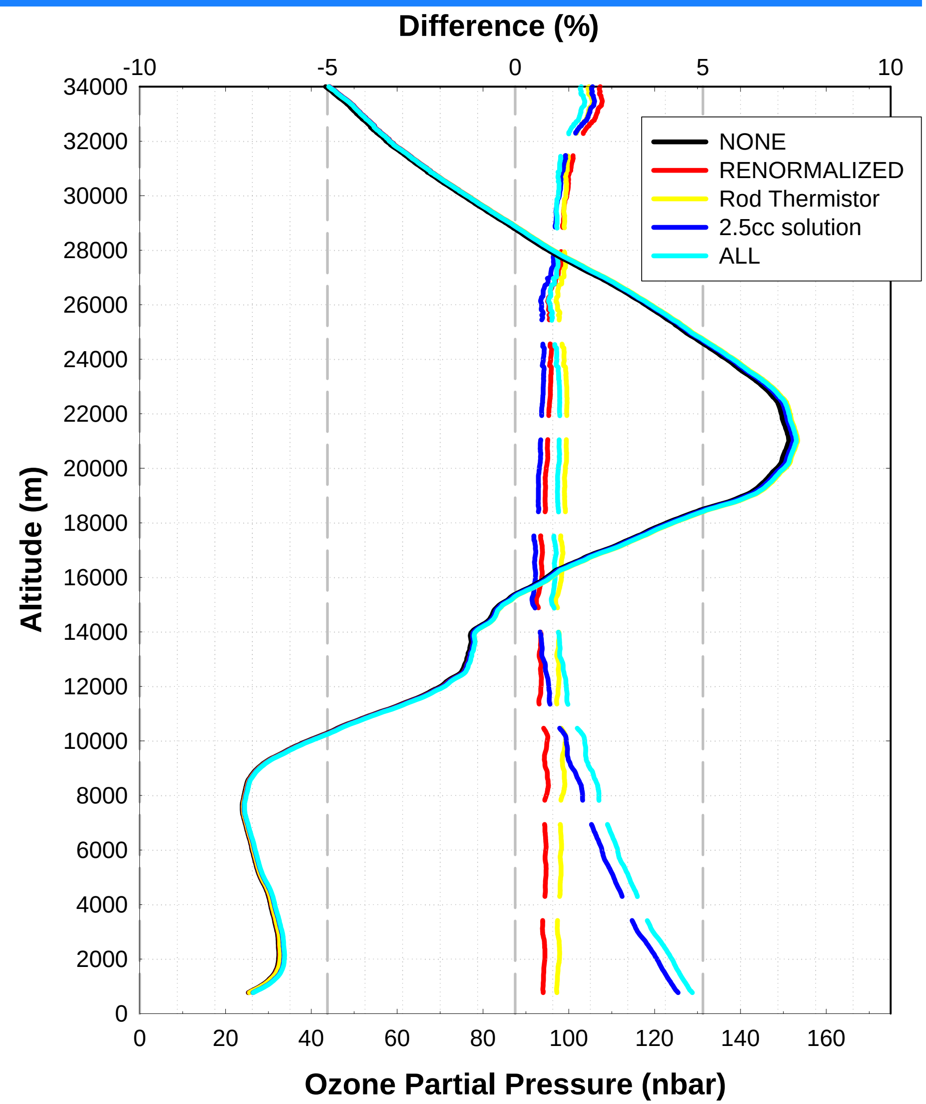

Natural Resources Canada
Ressources naturelles Canada
FireM3
Hotspots / Points chauds
17 July./juillet 2014
Hotspots for last 24 hours /
Depuis les dernièrs 24 heures
Map created at 08:00 on 2014-07-17 /
Carte créée le 2014-07-17 à 08:00
0 500 1000 1500 2000 km
Canada

Canadian ozonesonde network – changes in ozonesondes and associated radiosondes

Year	Change	Possible Effect
1979	ECC 3A introduced	~15% increase in tropospheric response response relative to BM sondes. Sonde T measured via rod thermistor.
1984	ECC 4A introduced	redesigned pump; maximum change <1%, at 50-20 hPa. Sonde "box" T measured; new rod thermistor.
1993	ECC 5A introduced	New pump correction; maximum change ~1%, at 100 hPa.
1993	Vaisala RS-80, RSA-11 introduced	Older VIZ sonde: warm bias in daytime; pressure errors. May introduce altitude shifts in profile; ozone increases of up to ~2% at 20 hPa.
1996	ECC 6A	No differences below about 20-25 km [*Smit et al*., 2000].
2000	ENSCI 1Z design change	High bias with 1% KI solution [*Smit et al*., 2007].
2004	3cc solution (new sites)	Better ozone capture in troposphere
2006	Vaisala RS-92 introduced	RS80s low by ~20m in the troposphere, high by 100m at 10hPa (Steinbrecht et al., 2008)
2007	Thermistor in ECC pump	More accurate measurement of air volume

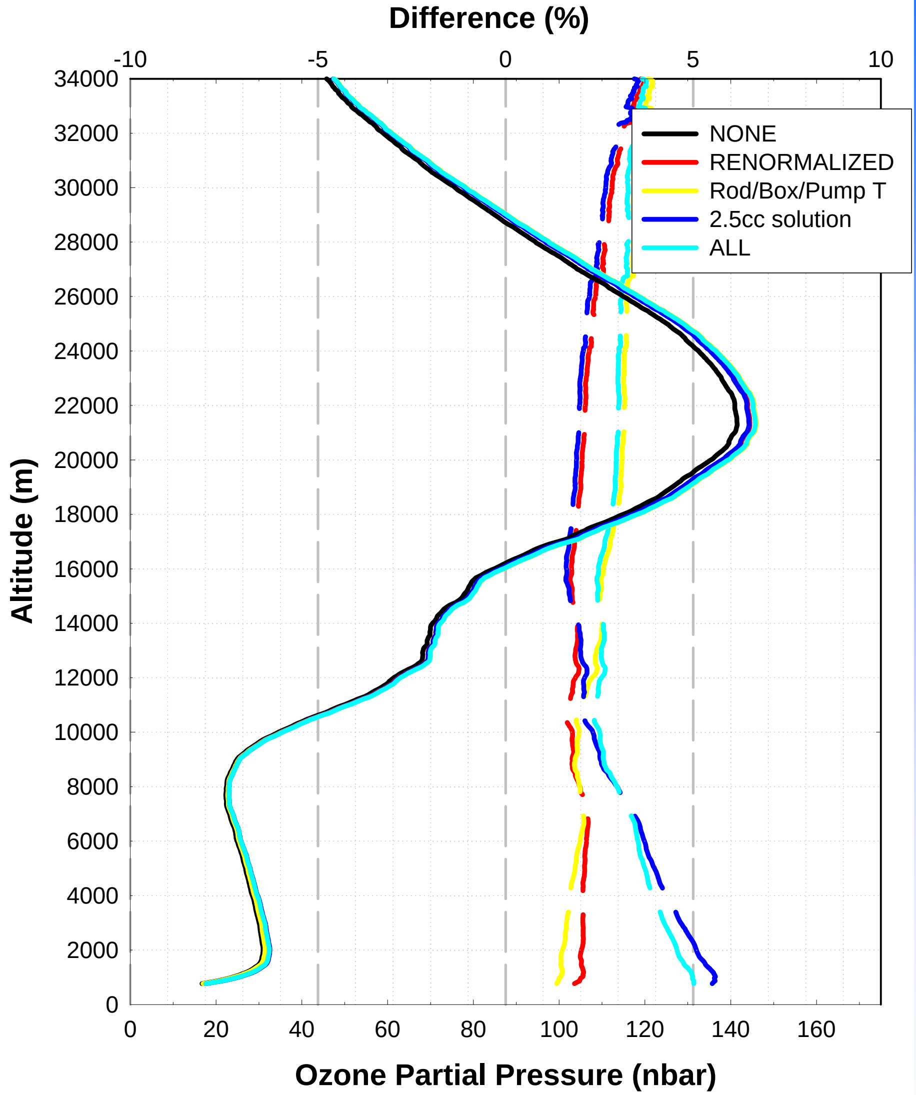


Edmonton: Reprocessed 1972-1978

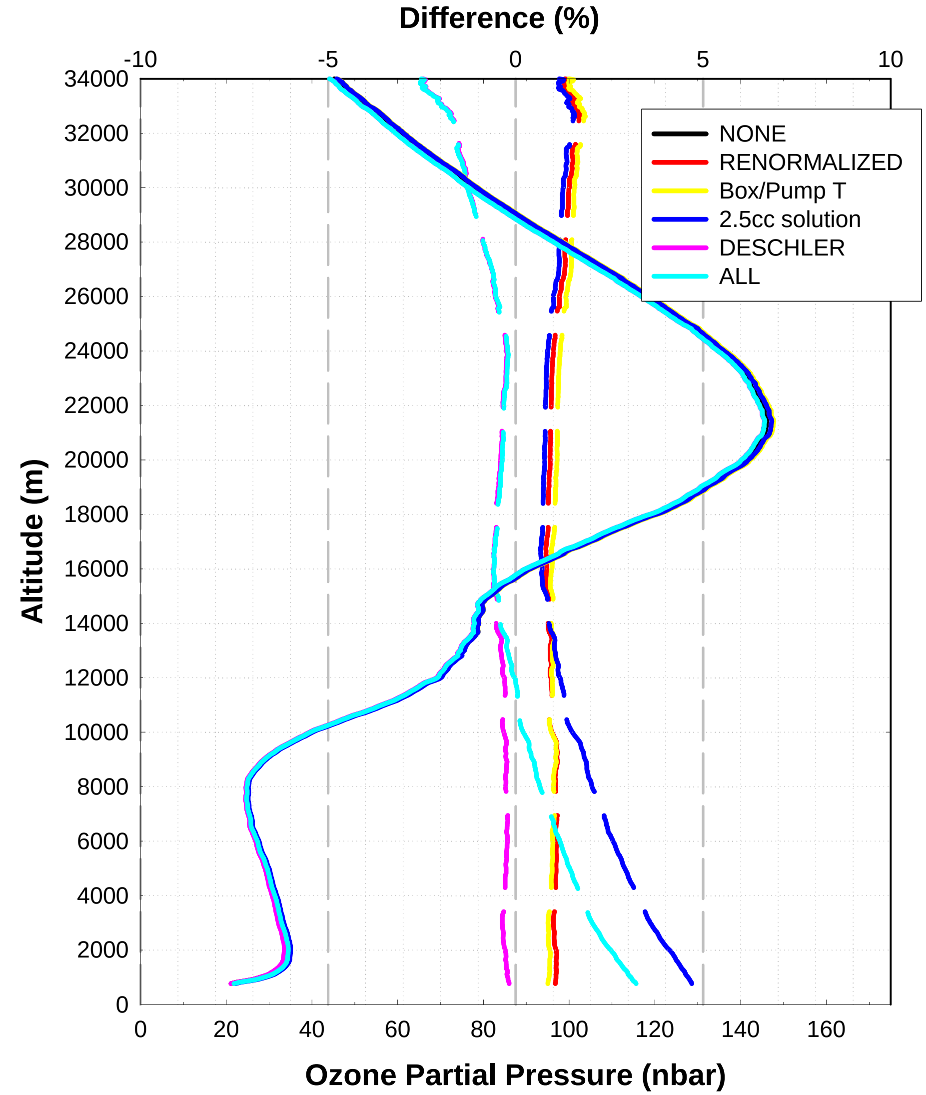


Edmonton: Reprocessed 1980-1989

Renormalized = New ozone residual calculation: now interpolated from 2011 MLS climatology (McPeters and Labow).



Edmonton: Reprocessed 1990-1999



Edmonton: Reprocessed 2000-2009

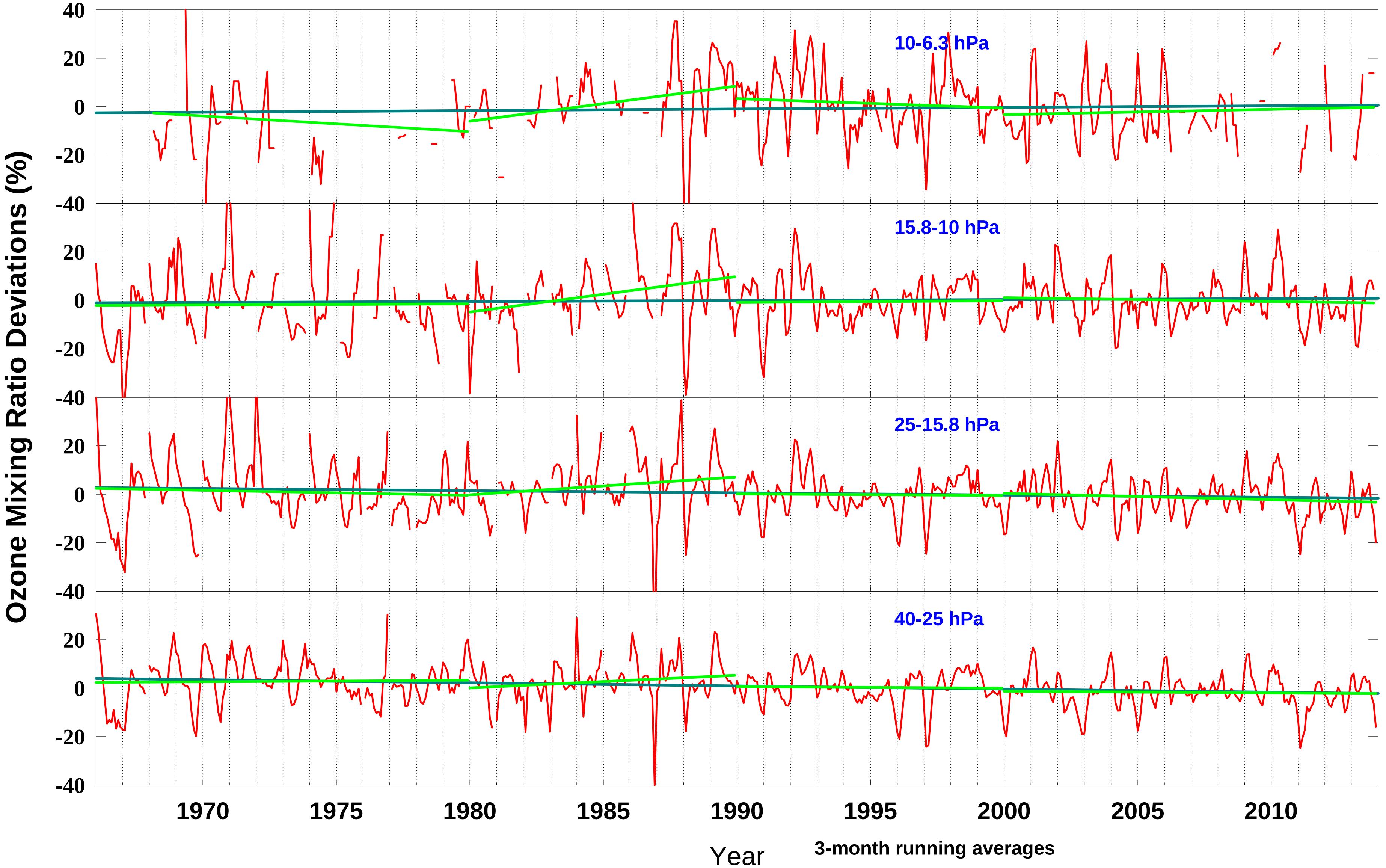
Deschler = correction for change from Science Pump to EN-SCI sondes

Results: reduced uncertainty

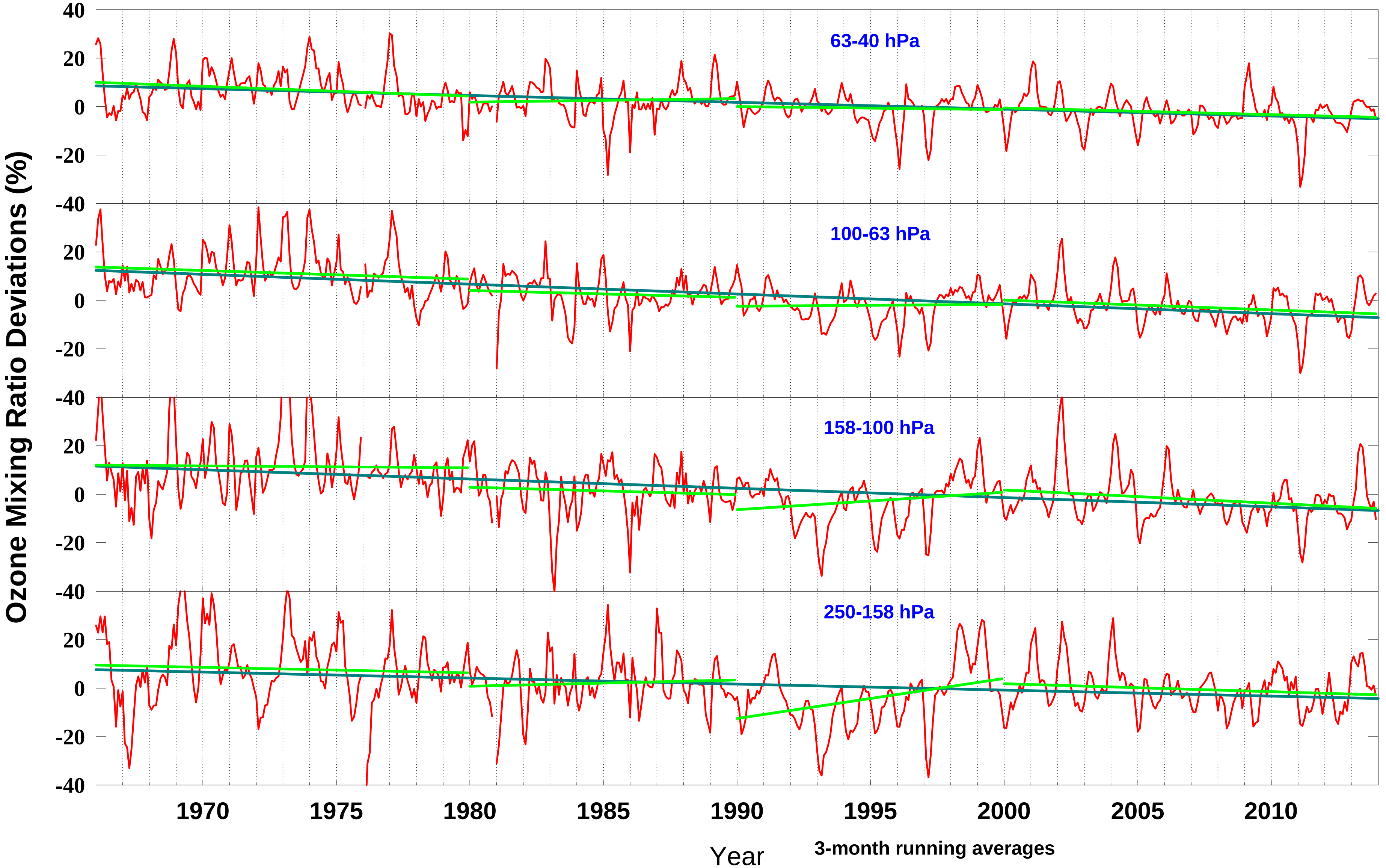
- **Tropospheric changes:** increases of up to 5% after 1979; up to 20% before 1980 (Brewer-Mast sondes), reducing with altitude.
- **Stratospheric changes:** decreases of up to 6% before 1980, less below 25km. Increases of ~1% in 1980s, ~2-3% in 1990s; little change in 2000s.
-

	Mean K	Std Dev	Trend
BM data			
Original	1.27	0.303	2.7%/decade
Renormalized	1.20	0.198	
Response correction	1.03	0.179	2.2%/decade
ECC data			
Original	0.97	0.101	-2.6 +/- 0.6 %/decade
All corrections	0.99	0.087	0.6 +/- 0.5 %/decade

Arctic (Resolute, Alert, Eureka)

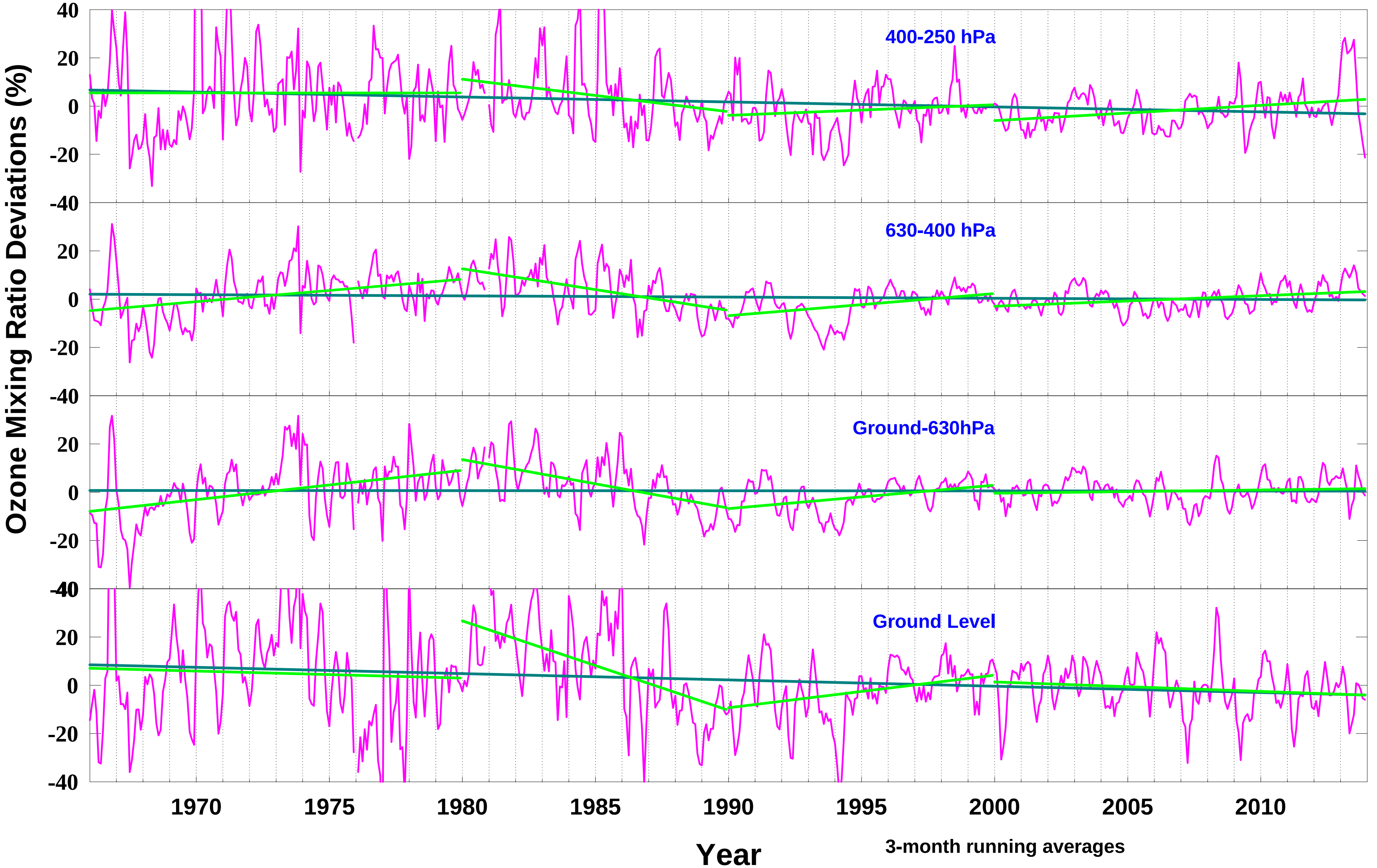


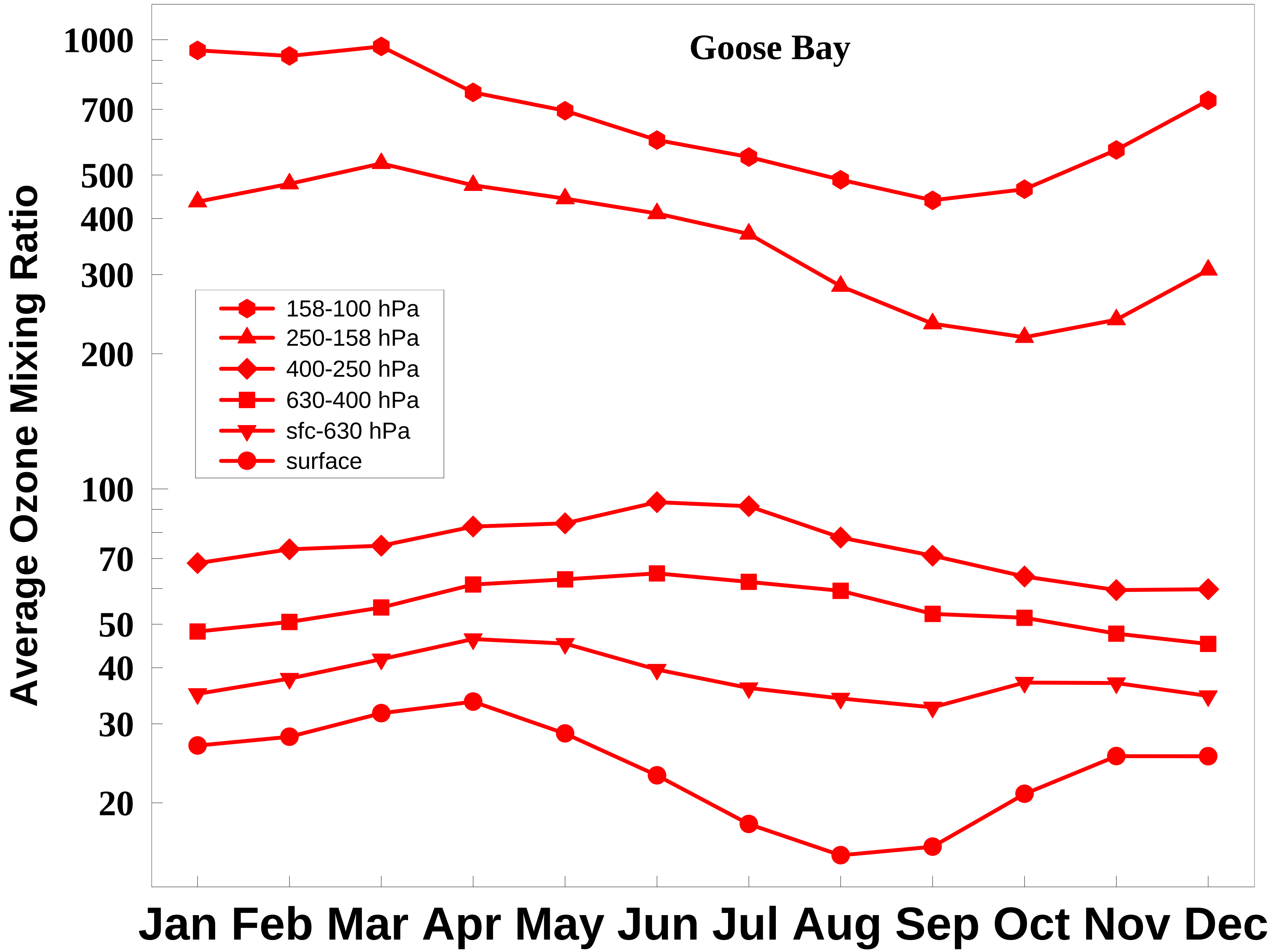
Arctic (Resolute, Alert, Eureka)

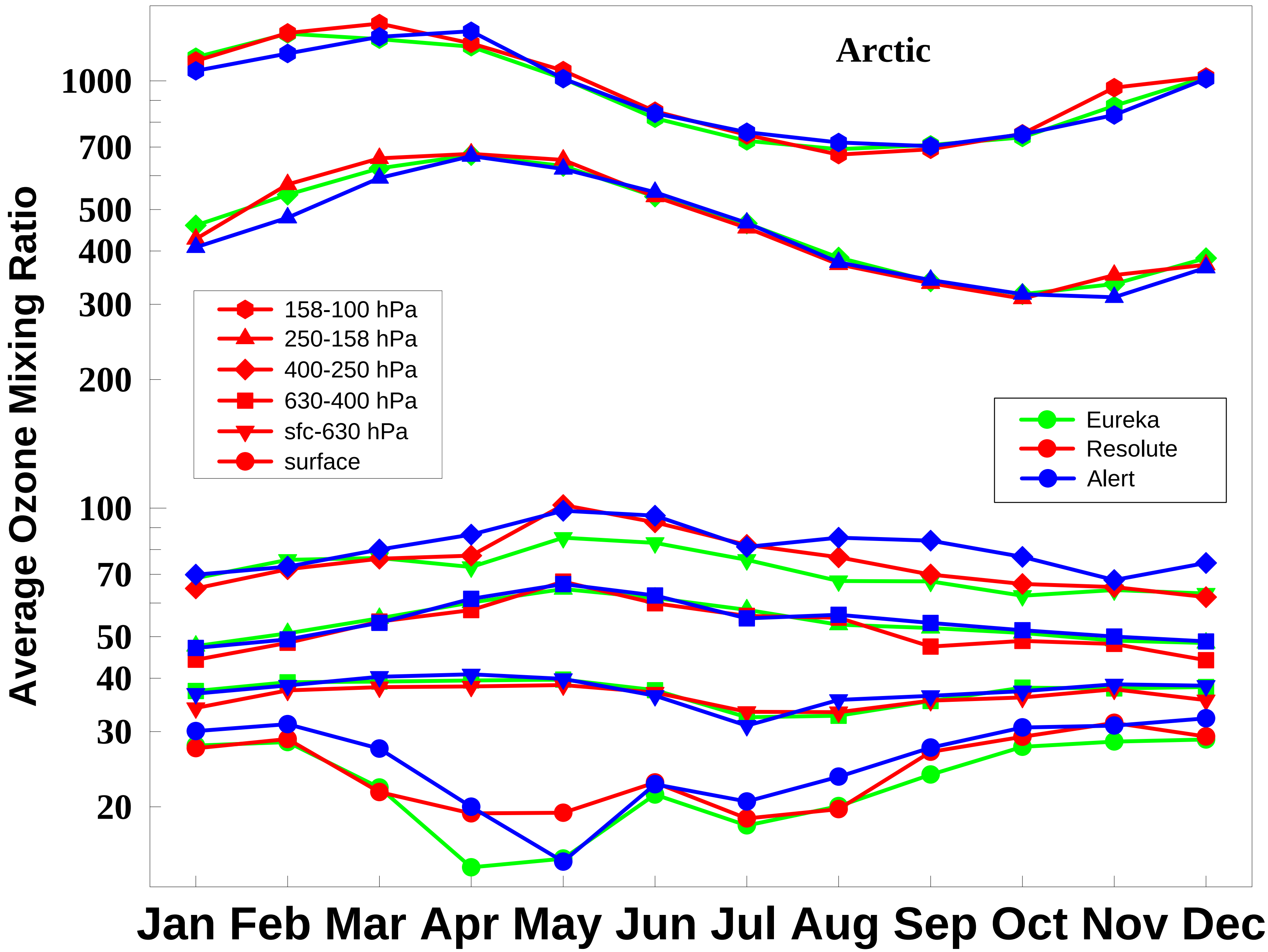


Environment Canada Environnement Canada

Arctic (Resolute, Alert, Eureka)




Goose Bay
Average Ozone Mixing Ratio
1000
700
500
400
300
200
100
70
50
40
30
20
158-100 hPa
250-158 hPa
400-250 hPa
630-400 hPa
sfc-630 hPa
surface
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec


Arctic
Average Ozone Mixing Ratio
1000
700
500
400
300
200
100
70
50
40
30
20
158-100 hPa
250-158 hPa
400-250 hPa
630-400 hPa
sfc-630 hPa
surface
Eureka
Resolute
Alert
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

a. gas phase:

$$Br + O_3 \longrightarrow BrO + O_2 \qquad (1)$$

$$BrO + BrO \longrightarrow Br_2 + O_2 \qquad (2)$$

$$BrO + HO_2 \longrightarrow HOBr + O_2 \qquad (3)$$

$$Br_2 + h\nu \longrightarrow 2Br \qquad (4)$$

$$Br + RH \longrightarrow HBr + R \qquad (5)$$

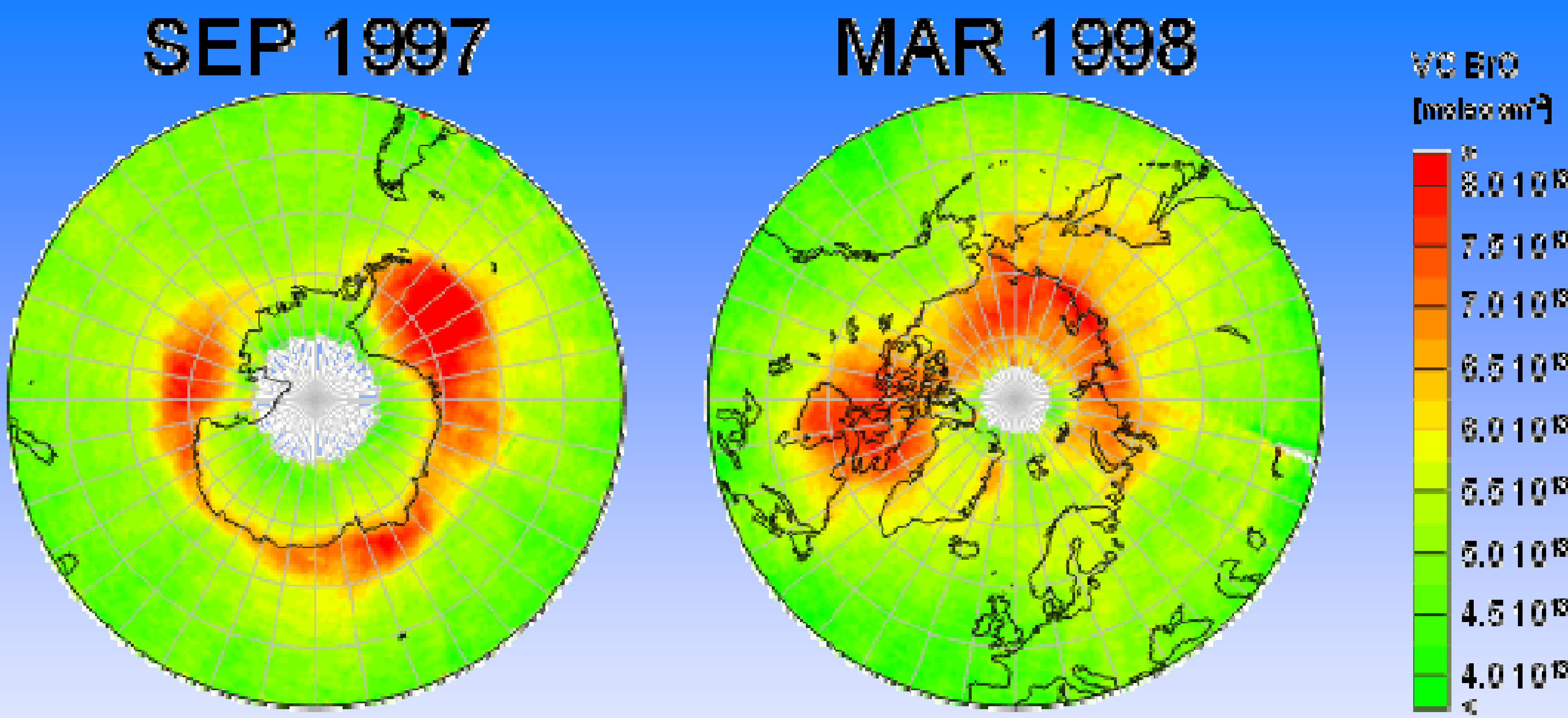
b. condensed phase:

$$HOBr + Br^- + H^+ \longrightarrow Br_2 + H_2O \qquad (6)$$

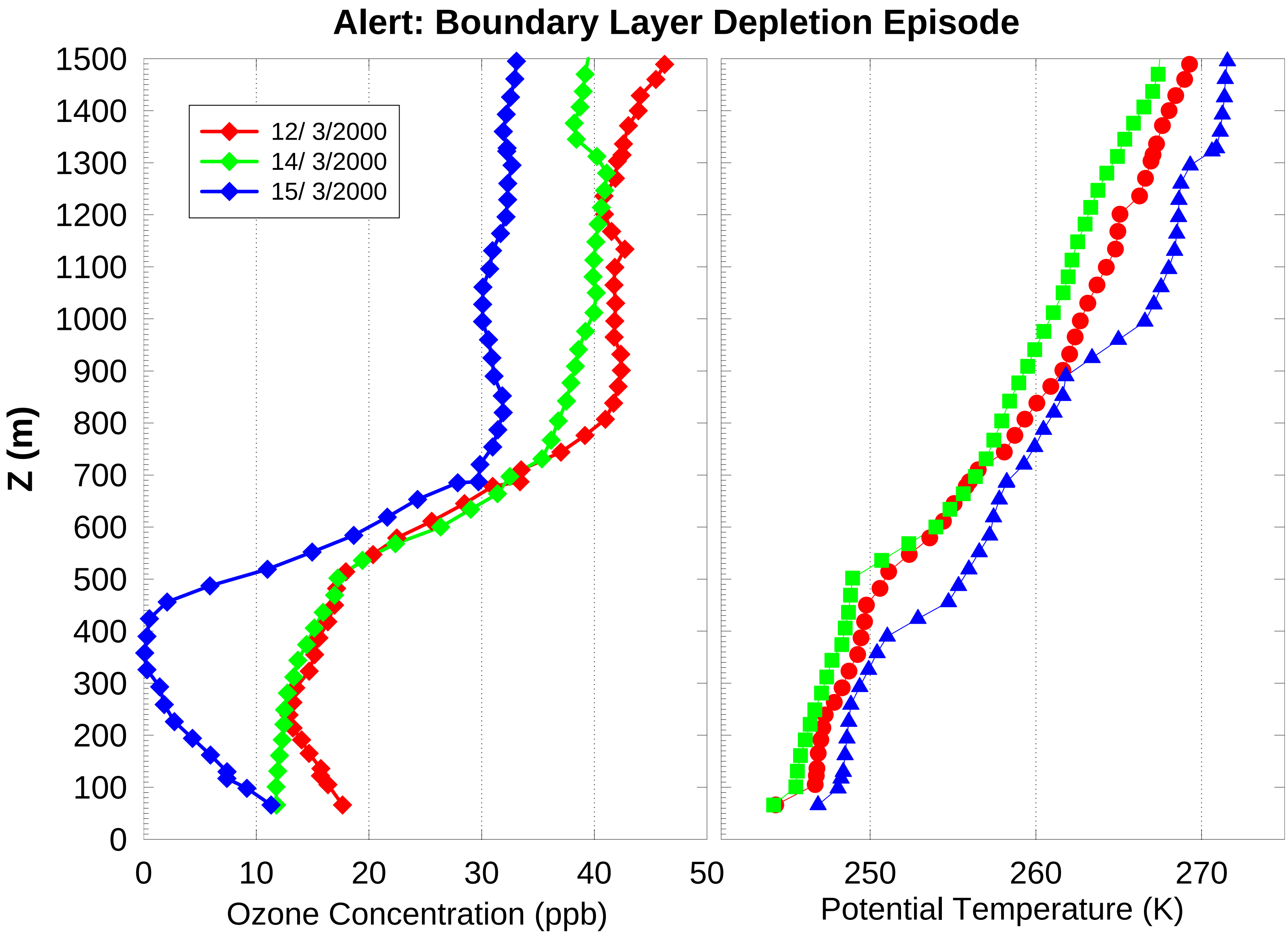
also:

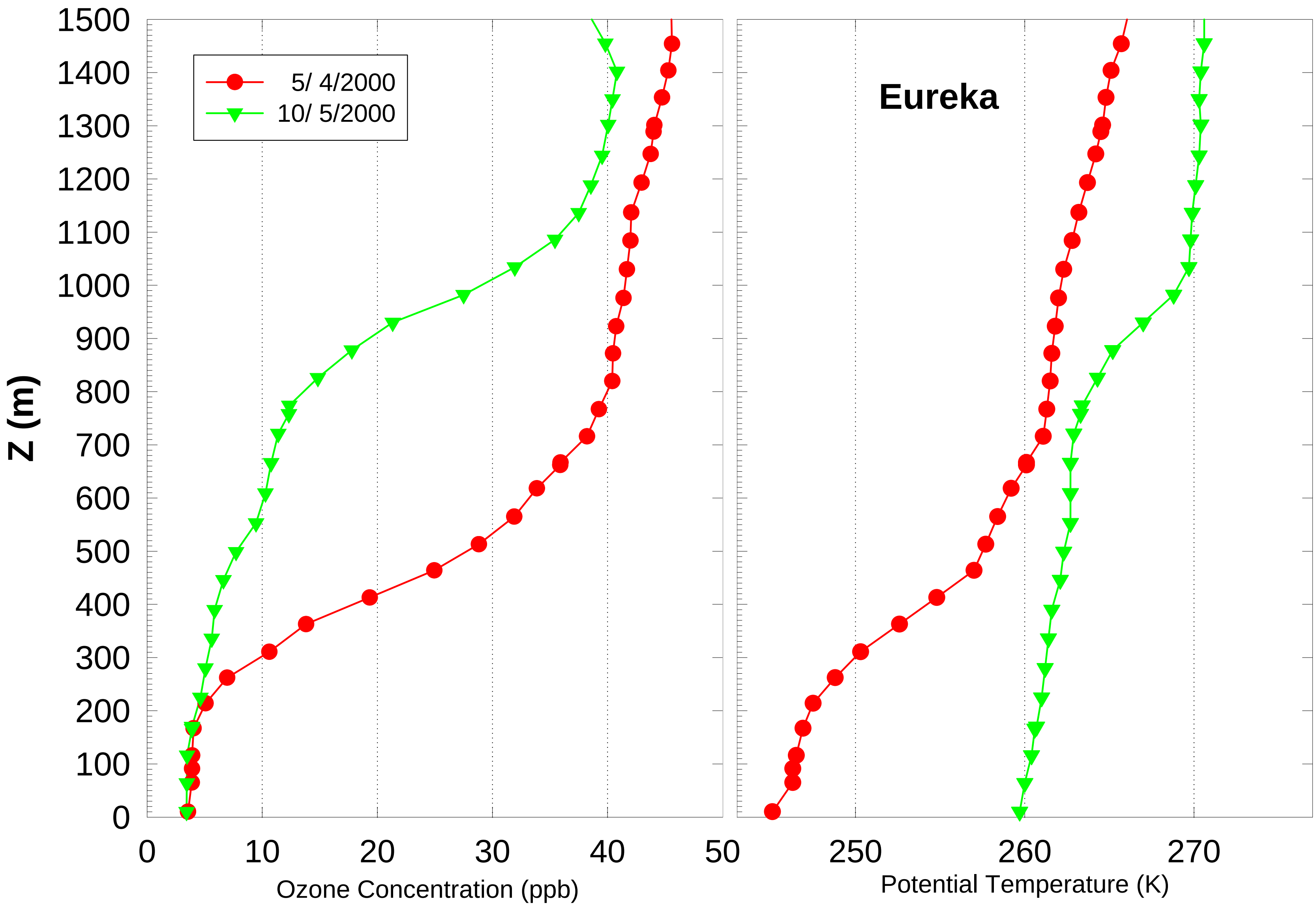
$$2Br + Hg(0) \longrightarrow HgBr_2 \qquad (a)$$

$$BrO + Hg(0) \longrightarrow Br + HgO \qquad (b)$$

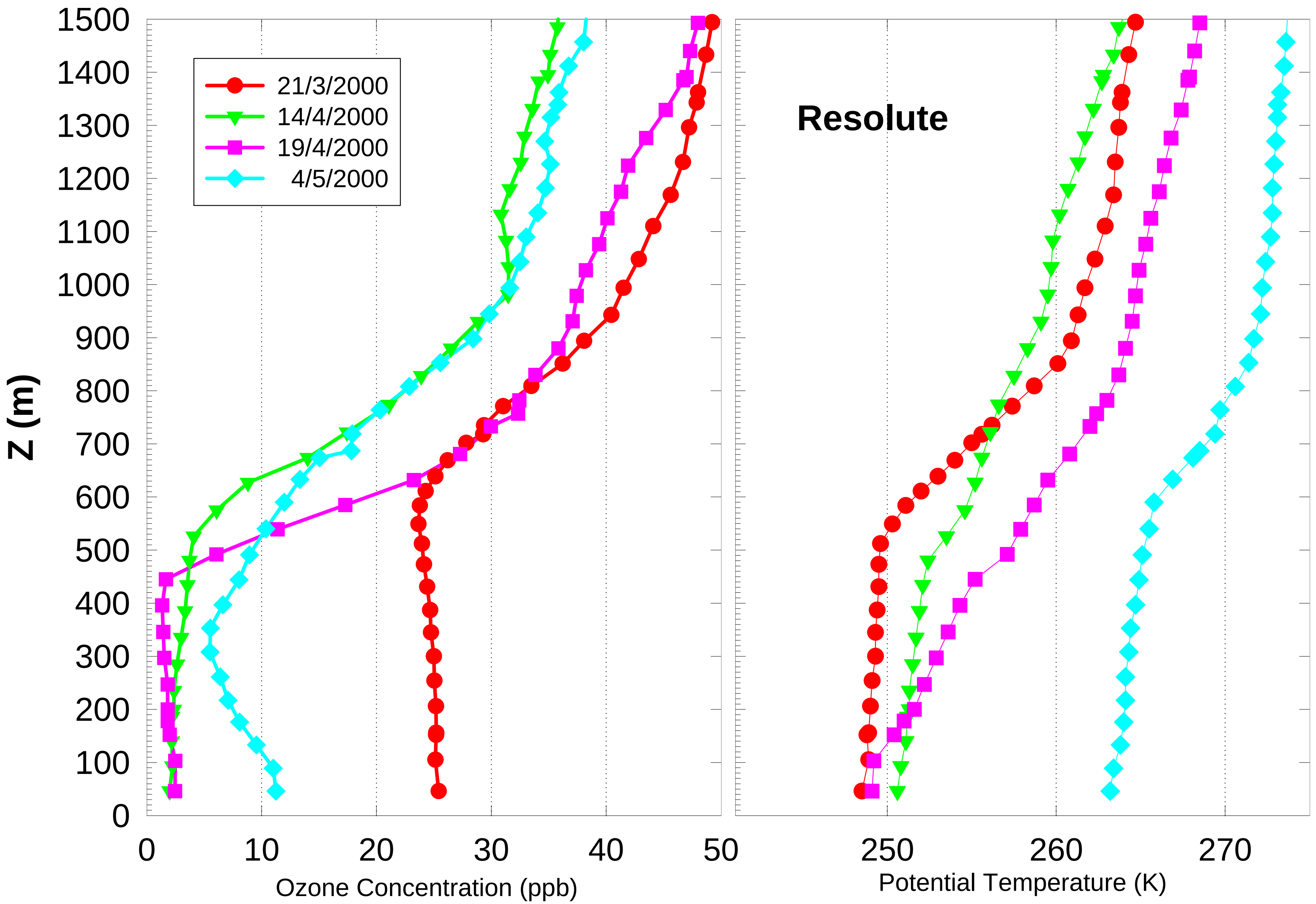


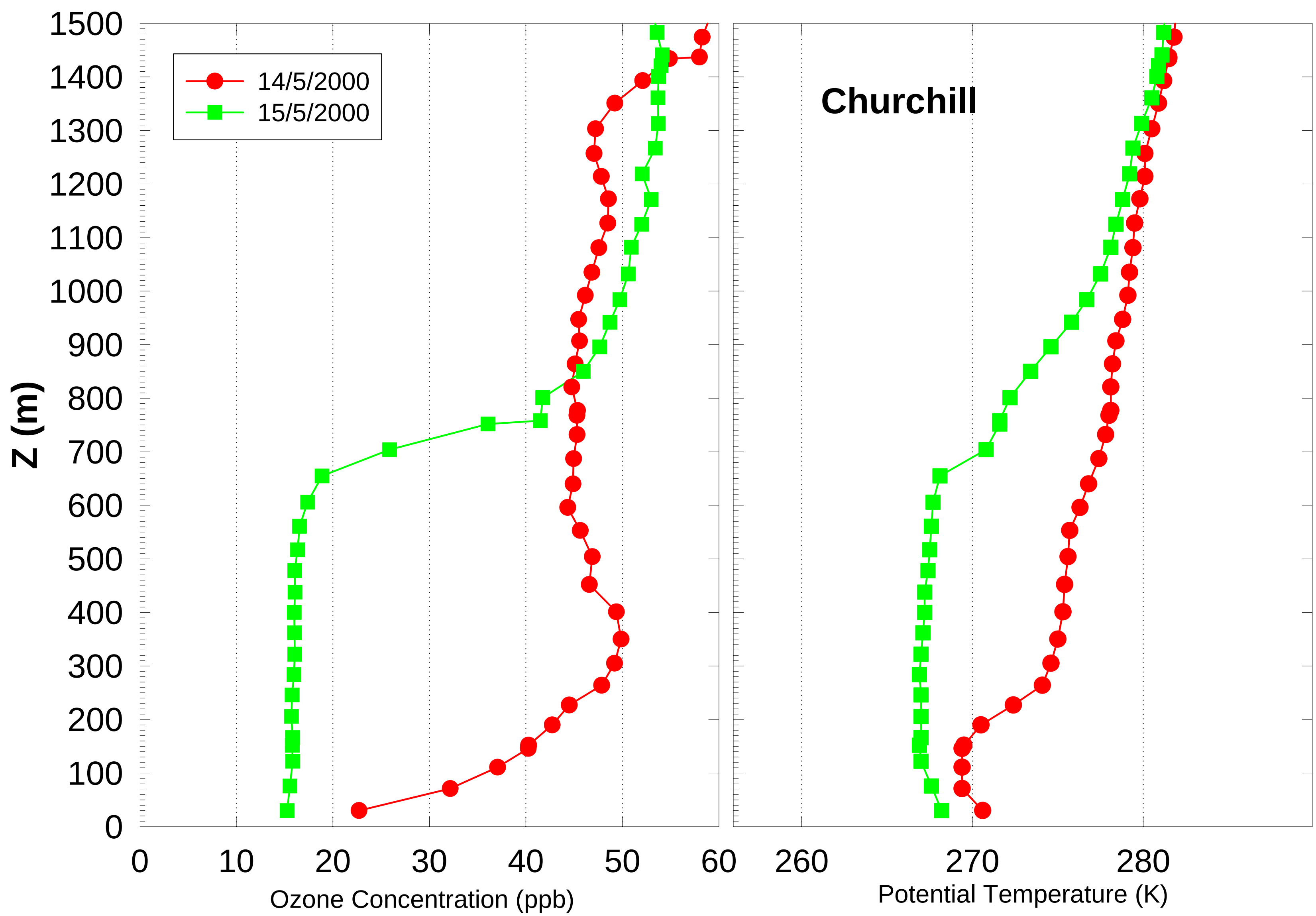
- Observations of anomalously low ozone at the surface in the Arctic spring reported at Alert (Bottenheim et al., 1986) and at Barrow (*Oltmans and Kohmyr,* 1986).
- High concentrations of tropospheric BrO over large areas of the Arctic and Antarctic seen by satellites


Alert: Boundary Layer Depletion Episode
12/ 3/2000
14/ 3/2000
15/ 3/2000
Z (m)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
Ozone Concentration (ppb)
250
260
270
Potential Temperature (K)

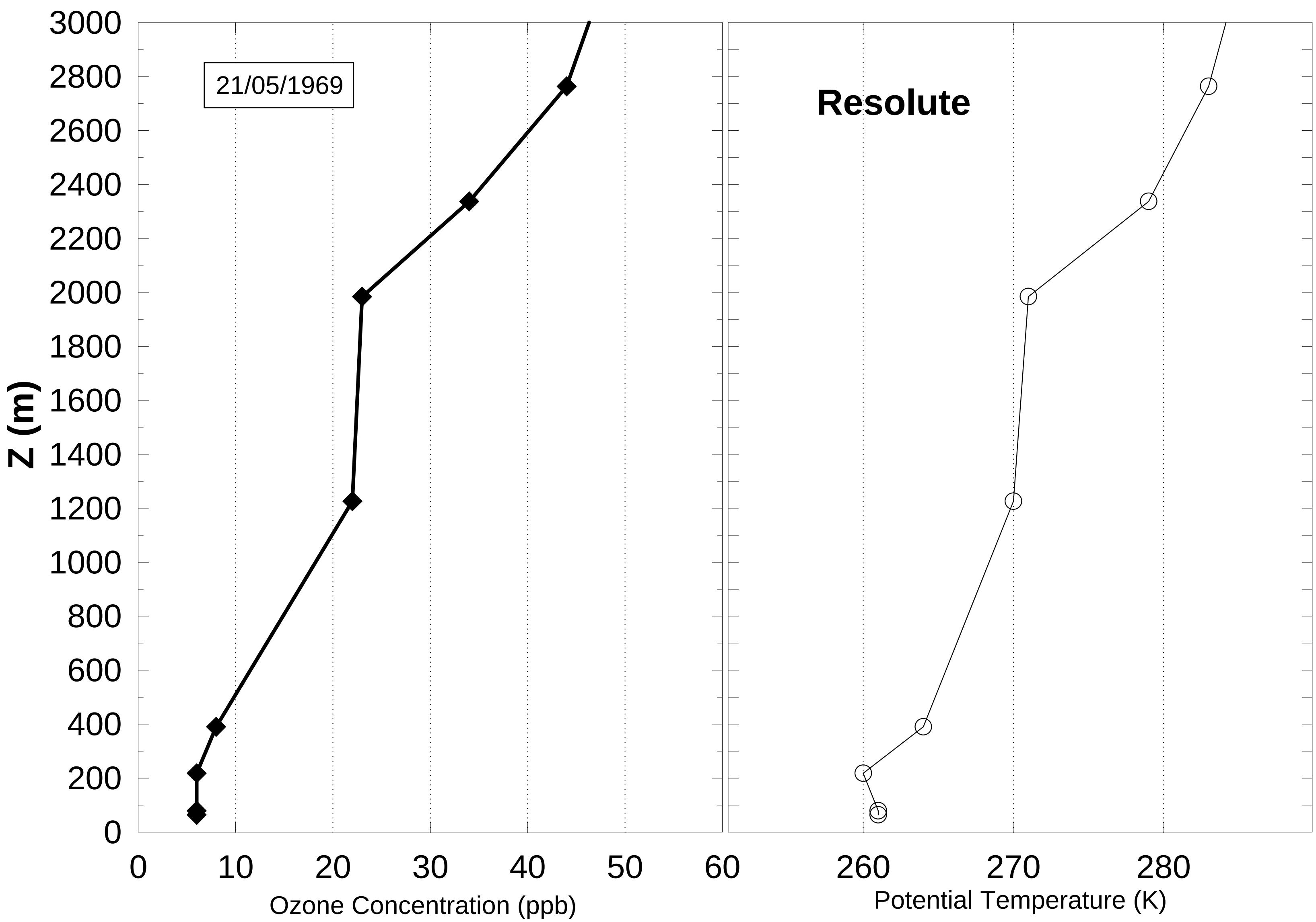


Z (m)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
5/ 4/2000
10/ 5/2000
0
10
20
30
40
50
Ozone Concentration (ppb)
Eureka
250
260
270
Potential Temperature (K)


Resolute
21/3/2000
14/4/2000
19/4/2000
4/5/2000
Z (m)
Ozone Concentration (ppb)
Potential Temperature (K)
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
0
10
20
30
40
50
250
260
270

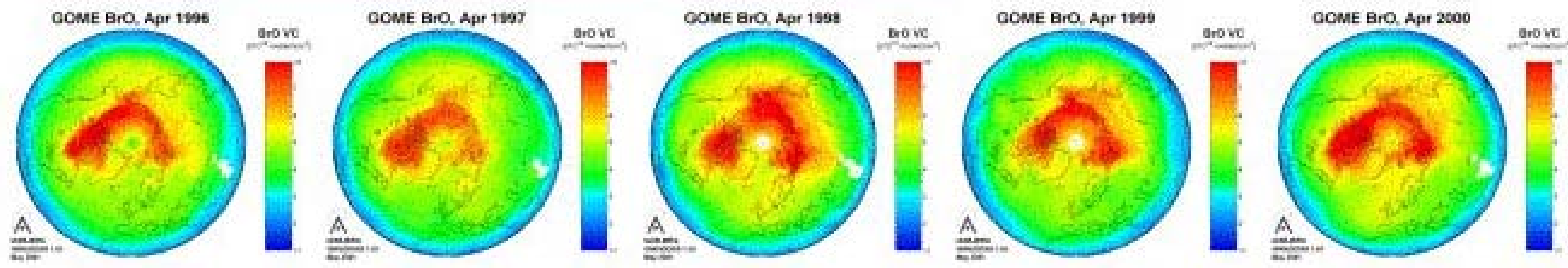

Churchill
14/5/2000
15/5/2000
Z (m)
Ozone Concentration (ppb)
Potential Temperature (K)
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
0
10
20
30
40
50
60
260
270
280

Depletion Event at Resolute 1969



Polar spring boundary layer BrO

Monthly-averaged BrO over Arctic, April, 1996-2000



Monthly-averaged BrO over Antarctic, October, 1996-2000

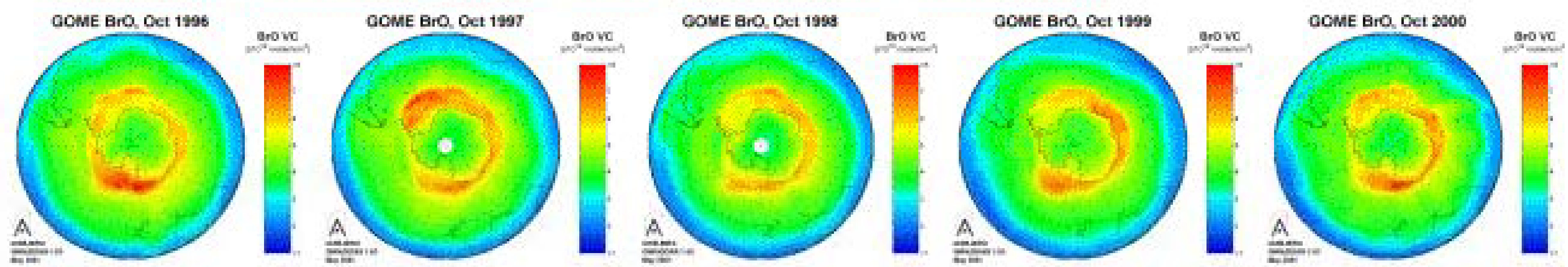


Table 1. Number of soundings indicating surface depletion (<10 ppbv) events in the historical ozonesonde record, grouped by season. The number in brackets is the total number of soundings in each period. Data up to the end of 2000 have been included. Canadian data are shown separately for the pre-1980 (BM) period and for the last two decades (ECC).

Station	ECC				Brewer-Mast			
	DJF	MAM	JJA	SON	DJF	MAM	JJA	SON
	0 (250)	**64** (207)	**5** (146)	**1** (150)	--	--	--	--
Resolute	**6** (246)	**61** (225)	**7** (190)	**3** (189)	**1** (142)	**22** (166)	**9** (150)	**1** (141)
Eureka	**1** (264)	**28** (139)	**1** (96)	**0** (105)	--	--	--	--
Churchill	**2** (222)	**8** (240)	**3** (218)	**1** (194)	**1** (62)	**1** (57)	**12** (69)	**5** (62)
Goose Bay	**2** (237)	**2** (239)	**19** (226)	**20** (221)	**4** (134)	**1** (117)	**16** (123)	**15** (122)
Edmonton	**24** (222)	**6** (239)	**9** (225)	**15** (203)	7 (86)	**1** (83)	**2** (81)	4 (82)
Ny-Ålesund	**0** (370)	**11** (305)	**1** (136)	**0** (149)	--	--	--	--
Neumayer	**7** (163)	**1** (126)	**1** (170)	**7** (246)	--	--	--	--
Marambio	**7** (48)	**0** (23)	**1** (92)	**5** (167)	--	--	--	--

Comparison with hourly surface data

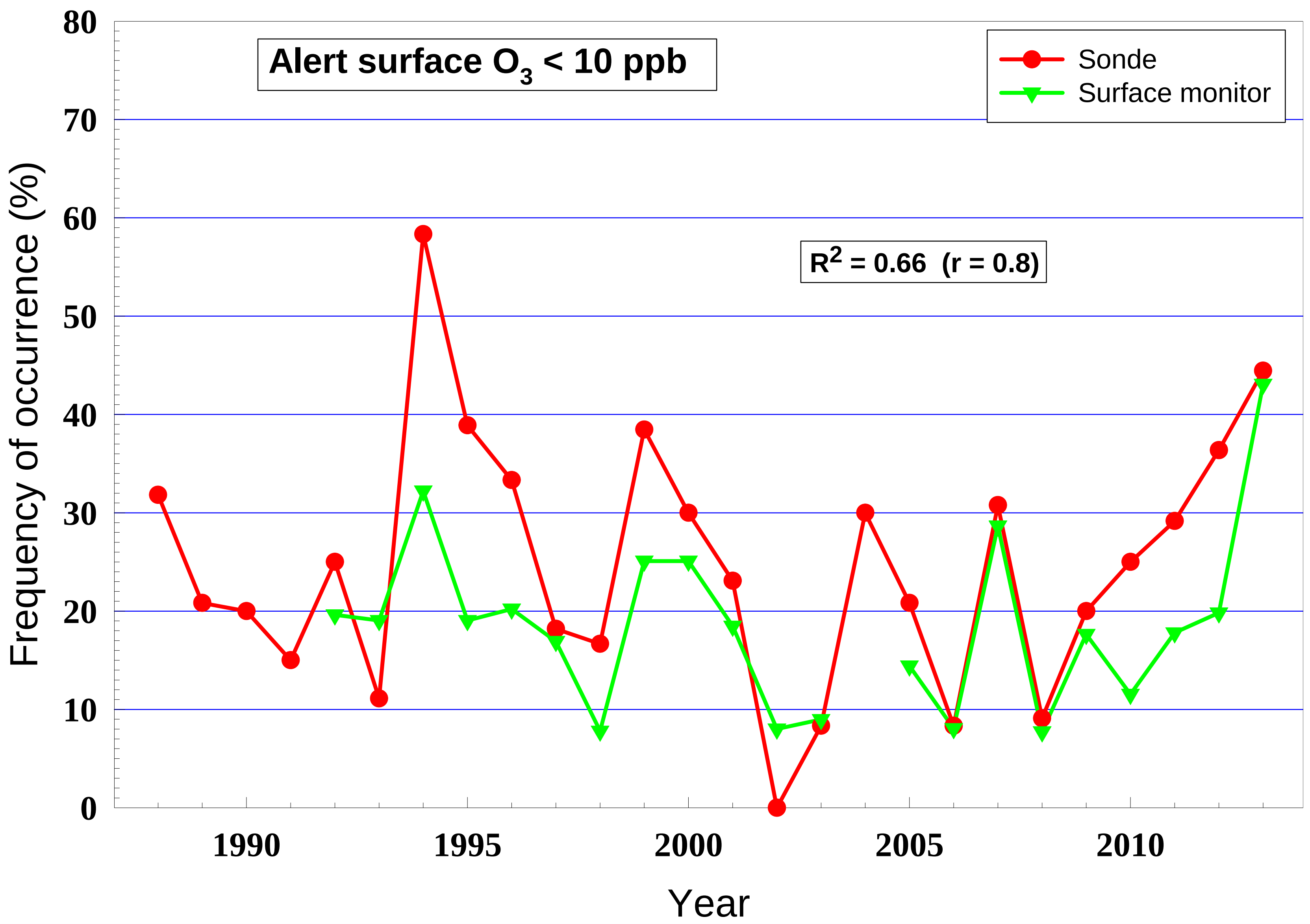


Table 2. Columns 3 & 4: Average frequency of occurrence of surface ozone depletion events at polar stations over the period 1991-2000. Column 5: Average springtime surface temperatures ($\overline{T}$). Column 6: Average surface temperatures ($\overline{T}$) during depletion episodes. Column 7: Difference between springtime surface temperature and that at 1000m ($\overline{T_{1000} - T_s}$). Data have been adjusted for the effects of occasional irregular sampling. Temperature averages are for the entire record in each case.

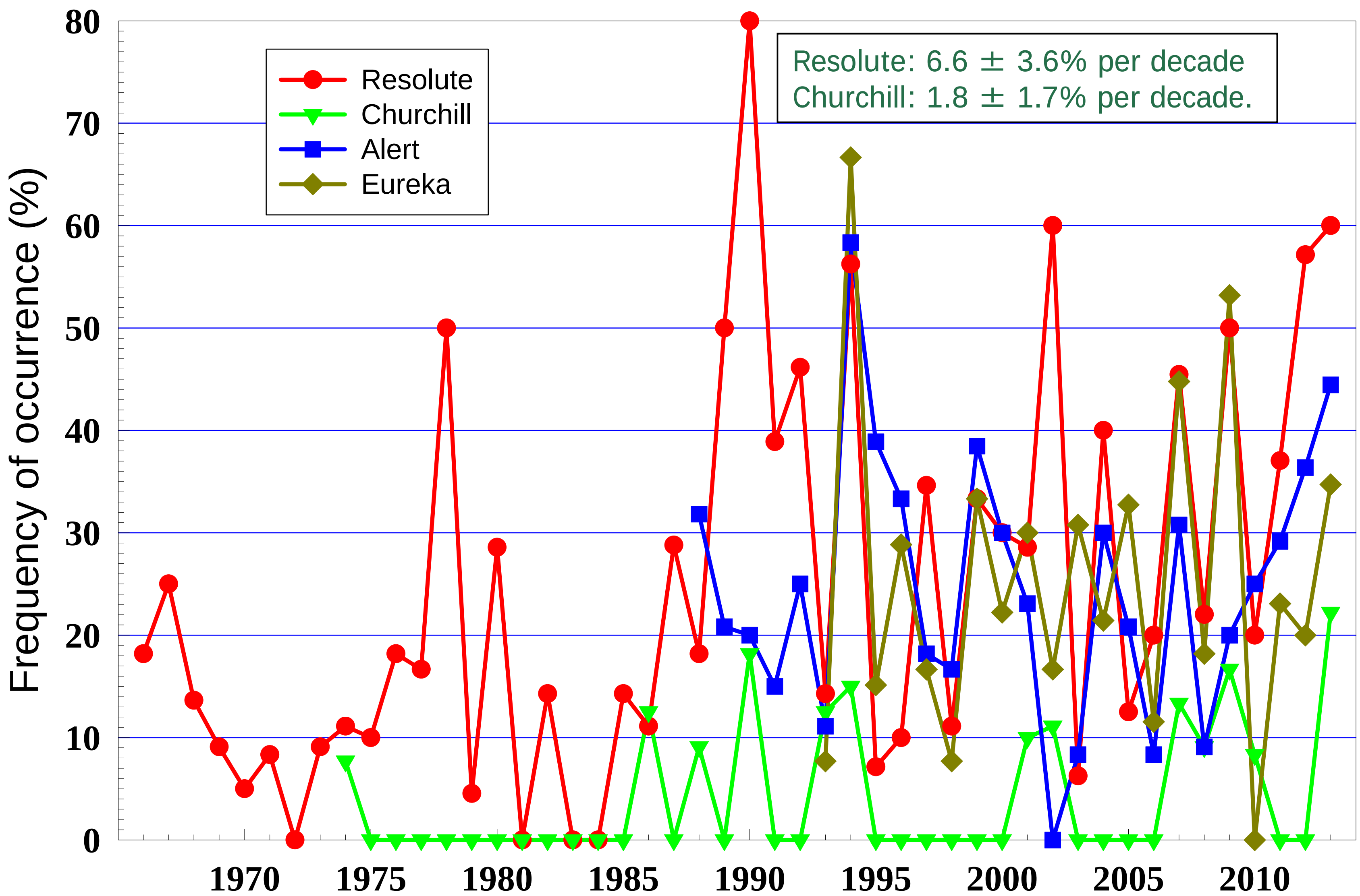
Station	Latitude	Adjusted frequency (%)		$\overline{T}$ (°C)	$\overline{T}$ (DE) (°C)	$\overline{T_{1000} - T_s}$ (°C)
		<10 ppbv	<20 ppbv			
Alert	83 N	27.3	41.1	-21.9	-19.6	3.9
Resolute	75 N	29.6	51.5	-21.9	-23.5	4.0
Eureka	80 N	26.4	41.7	-24.3	-24.4	6.4
Churchill	59 N	3.4	16.6	-11.5	-17.1	3.0
Ny-Ålesund	79 N	3.2	12.0	-7.8	-9.9	-3.8
Neumayer	71 S	2.8	32.5	-17.4	-18.8	1.3
Marambio	64 S	3.3	28.9	-6.3	-9.2	-2.8

Conclusions

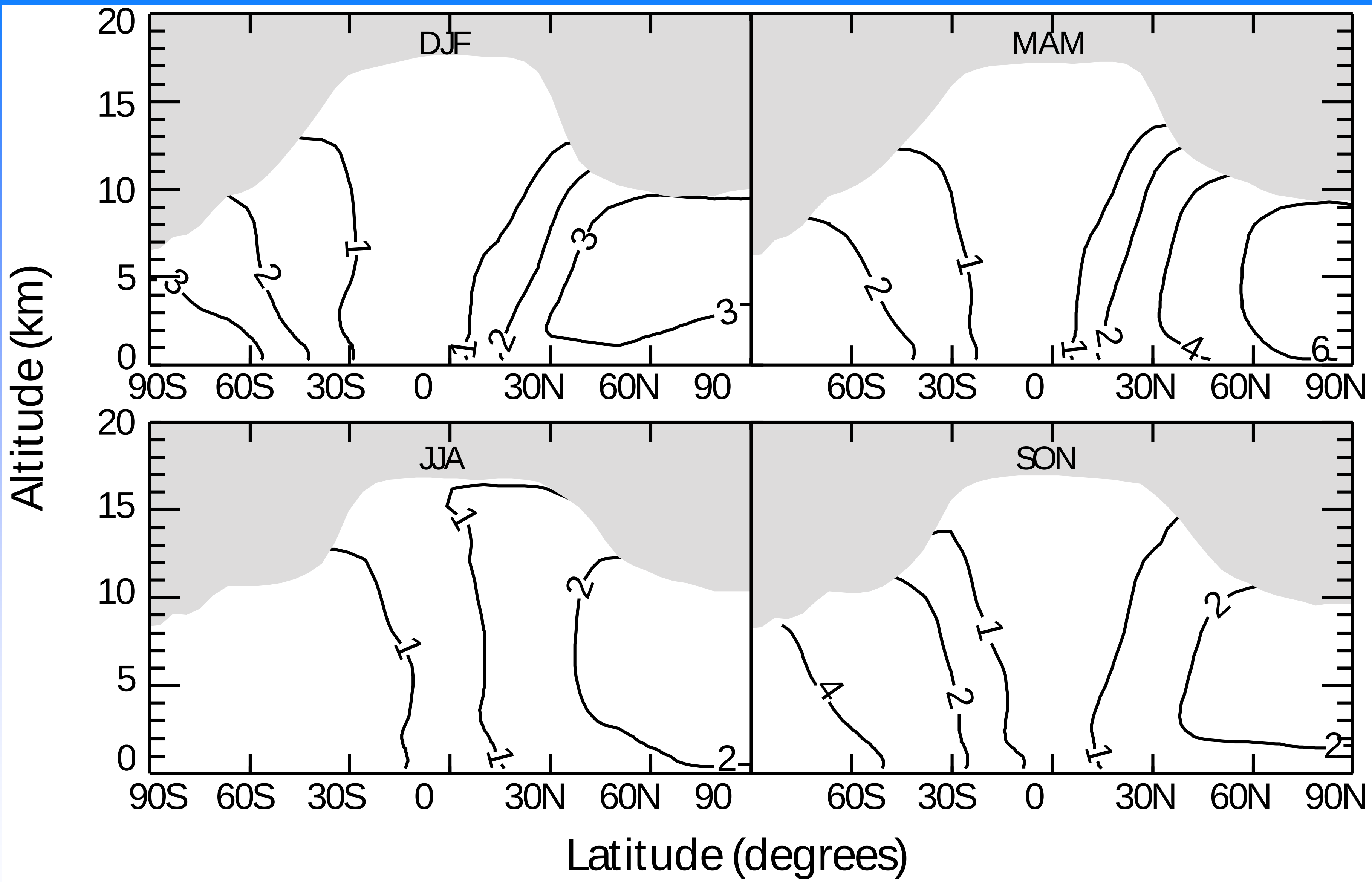
- Severe boundary-layer depletion events occur frequently at Alert, Eureka and Resolute in Canada, but infrequently at Churchill, and at other stations in the Arctic and Antarctic.
- Temperature profiles near polar sunrise at the three Canadian high Arctic stations are characterized by strong surface temperature inversions and cold (below -20 °C) surface temperatures.
- The frequency of occurrence of boundary-layer ozone depletion episodes is increasing, explaining the increase in mercury levels in Arctic biota over the last few decades.
- We speculate that the requirement for cold (~ -20 °C) surface temperatures is related to a more efficient heterogeneous reaction converting bromide to bromine on saline ice crystals. We also propose that "frost flowers" on new sea ice, which are known to form more efficiently at lower temperatures, may provide the required saline ice surfaces. The increase in frequency of boundary layer ozone depletion events can then be understood in light of the increase in open leads in the Arctic ice cover due to the increase in greenhouse gas levels.

Frost flowers on new ice in the Beaufort Sea. The red object is a 6-inch ruler.

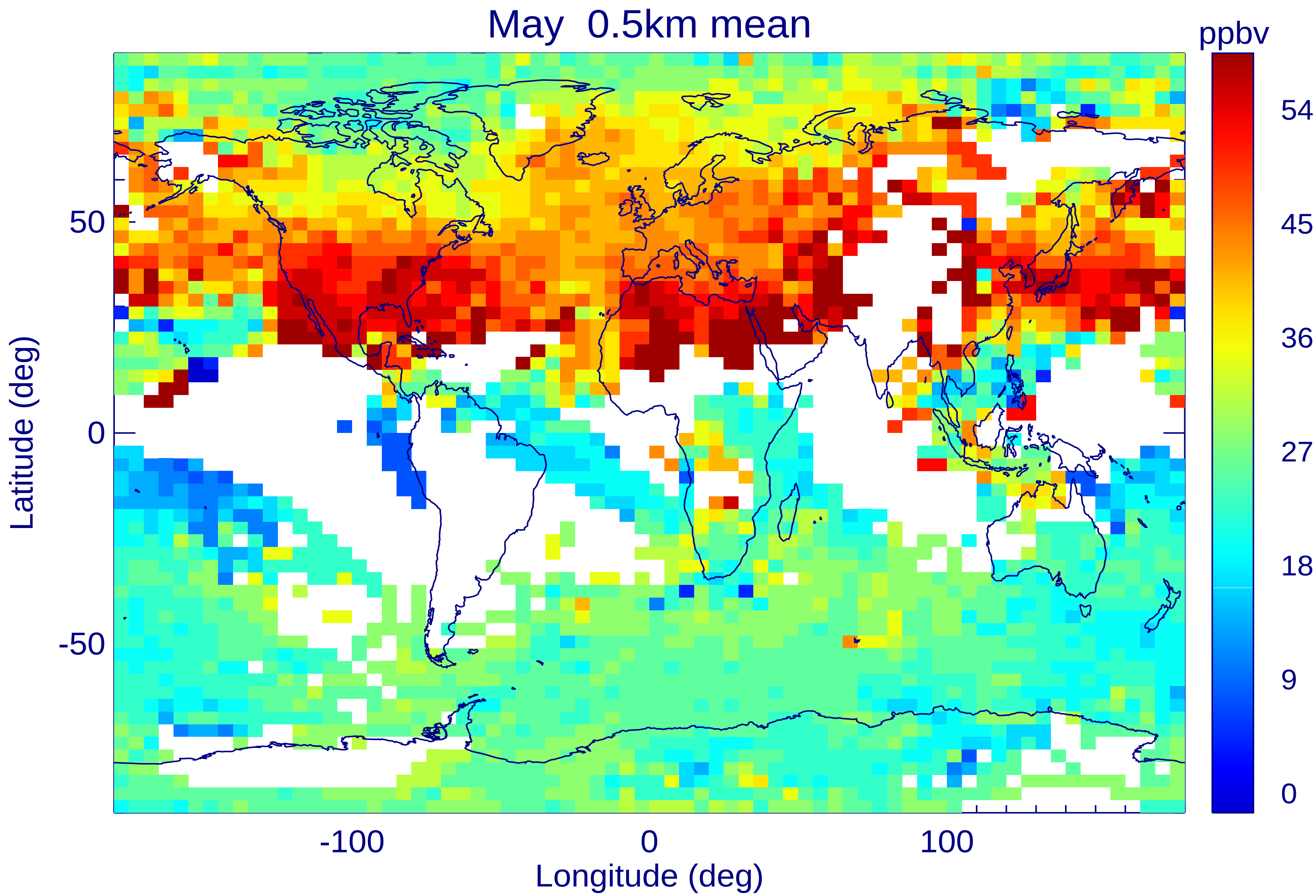
Trends in frequency of depletions



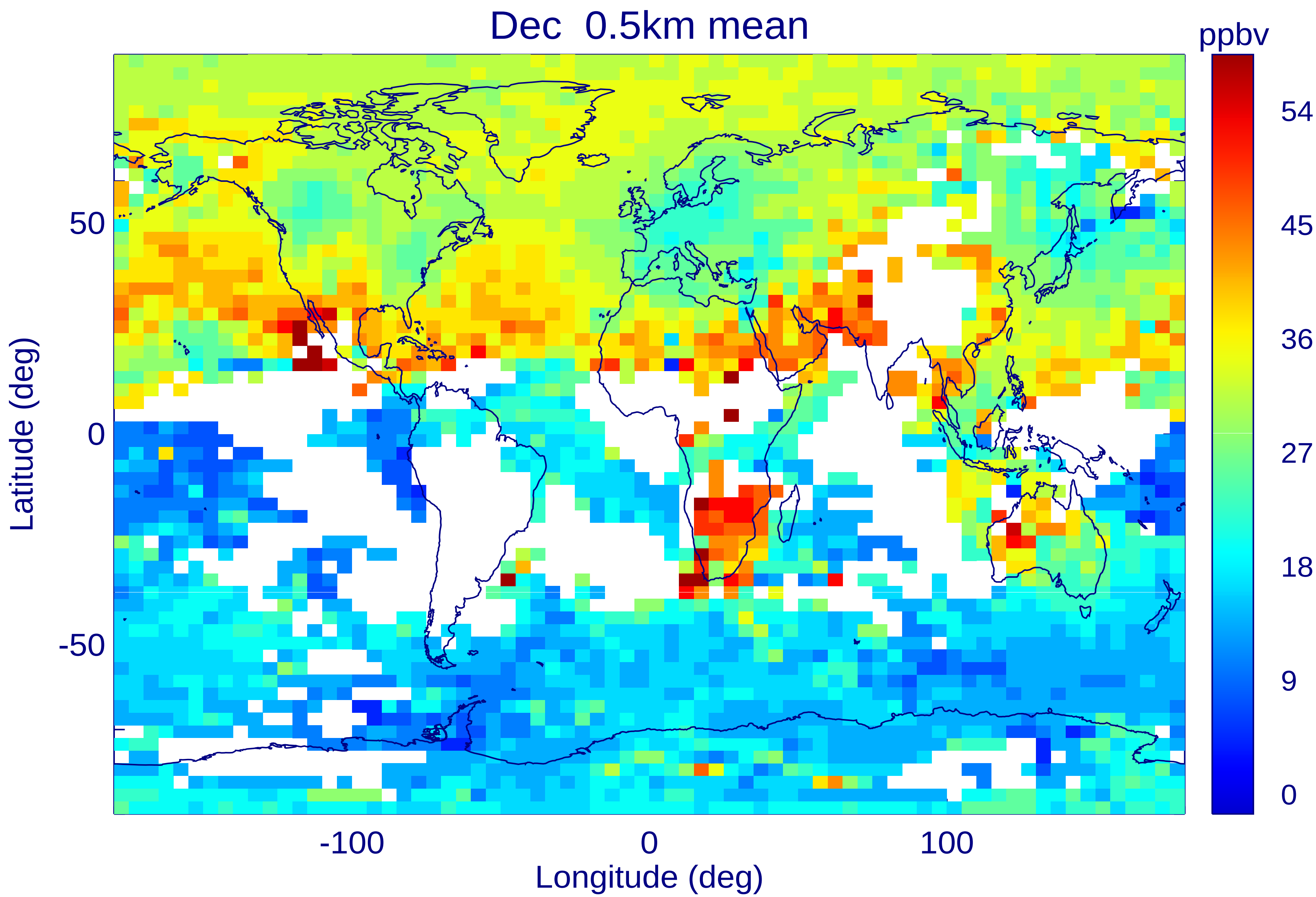
-- Trends at Alert & Eureka are ~0, but positive after 1994



Decrease in tropospheric ozone (ppb) from bromine chemistry.
Parrella et al., ACP, 2012.



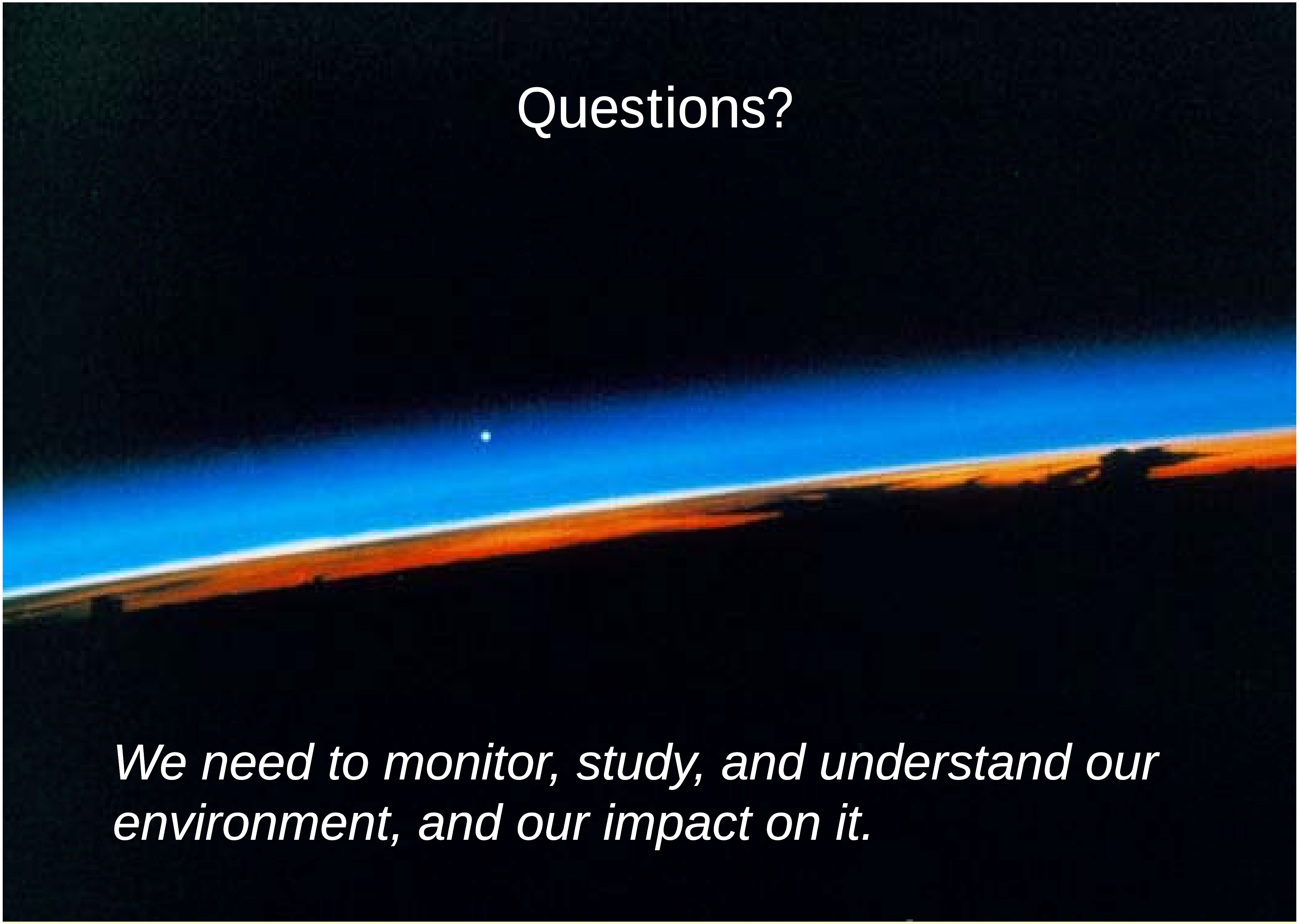
Data from a 3D global mapping of WOUDC ozonesonde data, using HYSPLIT trajectories driven by NCEP reanalysis data



Data from a 3D global mapping of WOUDC ozonesonde data, using HYSPLIT trajectories driven by NCEP reanalysis data

The future

- The success of the Montreal Protocol means that ODS will continue to decline and stratospheric ozone levels return to normal by mid-century. Climate change may accelerate this.
- Climate change may cause future Arctic ozone holes.
- Climate change is expected to produce significant increases in ozone in the upper troposphere:
  - more forest fires; aerosols & ozone, may affect STE
  - increases in stratospheric O_3 transport to the troposphere as a result of enhancement in the tropospheric and stratospheric circulation with climate change
  - increases in temperature lead to more photochemical production (offset in the lower troposphere by increased loss via reaction with water vapour)


Questions?
We need to monitor, study, and understand our environment, and our impact on it.