Observations of Mercury Species and Halogens at Summit, Greenland

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G-SHO$_x$ Summer 2007
Greenland – Summit Halogens and HO$_x$

Species	Method	Research Group
Hg (GEM, RGM, FPM)	Tekran	NOAA - Brooks
OH, RO_2, H_2SO_4	CIMS	Ga. Tech
HCl, HO_2NO_2, BrO,SO_2, etc	CIMS	Ga. Tech
BrO, HCHO	DOAS	UCLA - Stutz
Soluble Gases Br^-, Cl^-, etc.	Mist Chamber	UNH - Dibb
Radiation, J-values	Spectrom.	UH - Lefer
Whole Air Samples	GC-MS	UCI – Blake
NO, O_3, Dewpoint, etc	commercial	

Polar Chemistry

- $Br_2 + h\nu \Rightarrow 2Br$

- $Br + O_3 \Rightarrow BrO + O_2$
- $BrO + h\nu \Rightarrow Br + O$ ‘very fast

- $Br + Hg \Rightarrow HgBr$ ‘ Hg(I) radical precursor to RGM Hg(II)
- $HgBr \Rightarrow Hg + Br$ ‘ Dominates at Temps. > 0 C
  or
- $HgBr + X \Rightarrow HgBrX$ ‘ X = Br, OH, …
- RGM Hg(II) formation mechanism rate doubles for every 6 degree C drop in temperature below 0°C (Goodsite et al., 2004; Holmes et al., 2006)
- Bromine is recycled in the surface snow

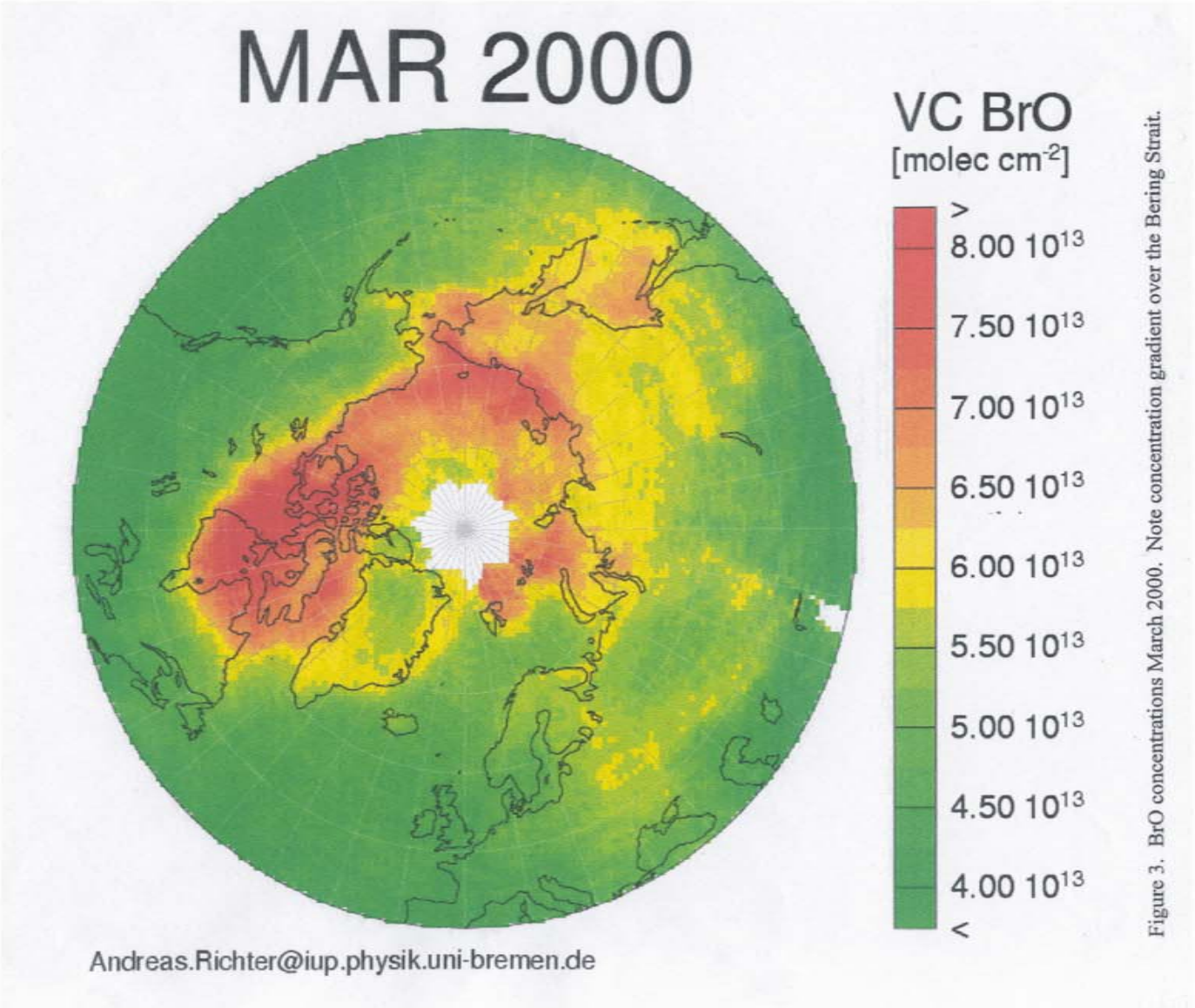


Figure 3. BrO concentrations March 2000. Note concentration gradient over the Bering Strait.

Determination of surface level concentrations of atmospheric mercury

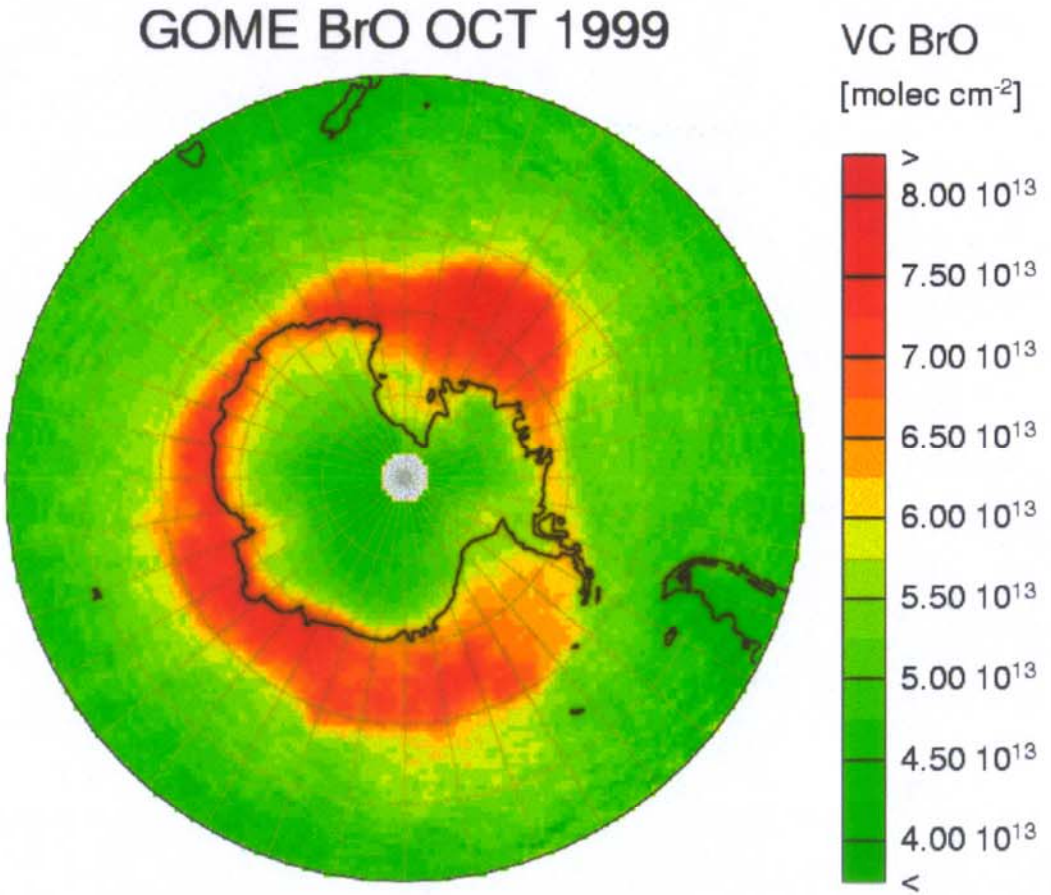
GKSS FORSCHUNGSZENTRUM

Global Ozone Monitoring Experiment-Instruments = GOME

Institute of Environmental Physics, University of Bremen

Institut für Umweltphysik (iup) Universität Bremen

BrO total columns were obtained during 1999 as part of the EU GODIVA project and were generated at the University of Bremen using the GDP Level-1 data (radiometrically calibrated sun and earthshine spectra).

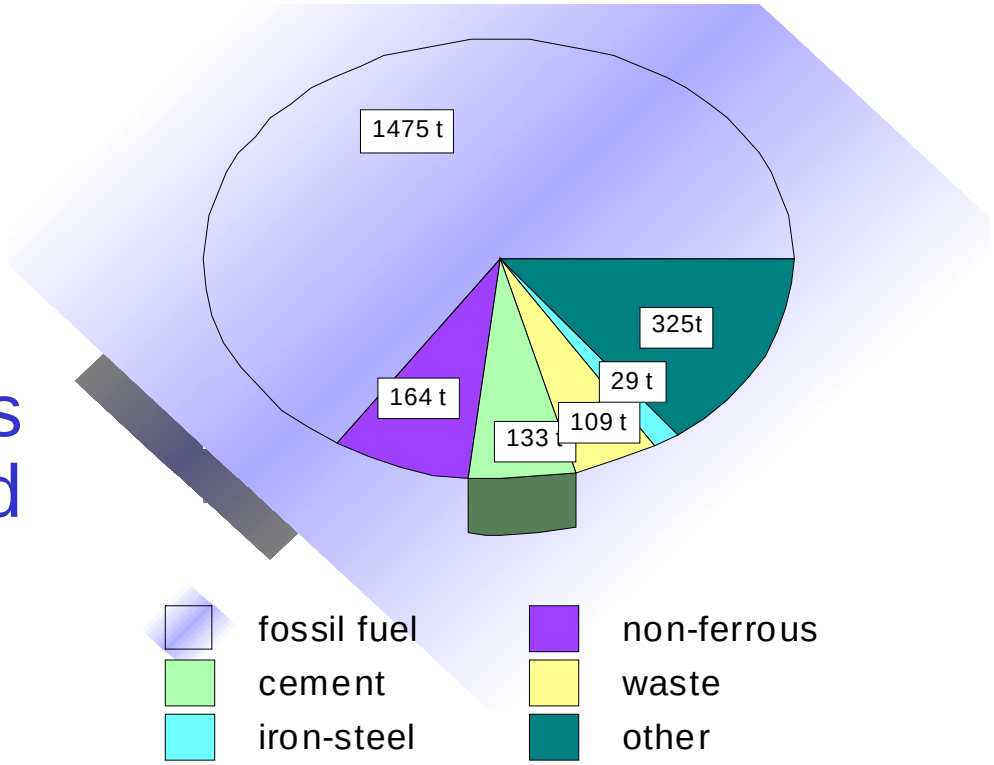


Christian Temme, GKSS Forschungszentrum (May 2000)

from S. Marcy

Mercury Emissions – 1995 (t/y)

- Hg is released through coal burning, waste incineration and industry
- Stationary fossil fuel combustion accounts for 66% of Hg emitted
- In addition, there are natural sources – Volcanoes, enriched soils



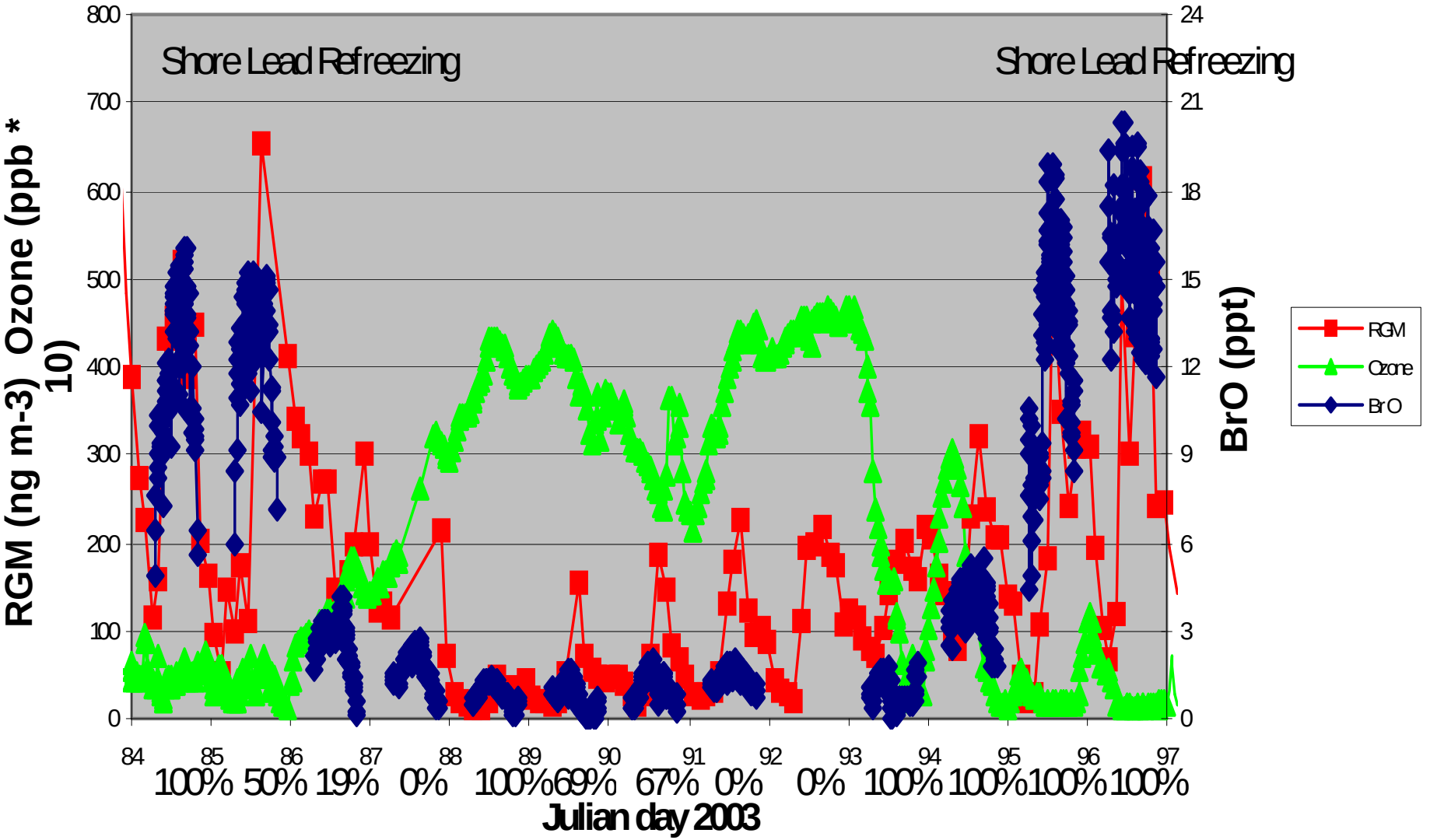
Gaseous Elemental Mercury

- Comprises ~95% of Atmospheric Mercury
- Atmospheric lifetime ~6 mo. -1 year
- Removed by direct deposition or oxidation
- Many natural and anthropogenic sources (volcanoes, enriched soils, coal combustion, etc.)

Reactive Gaseous Mercury

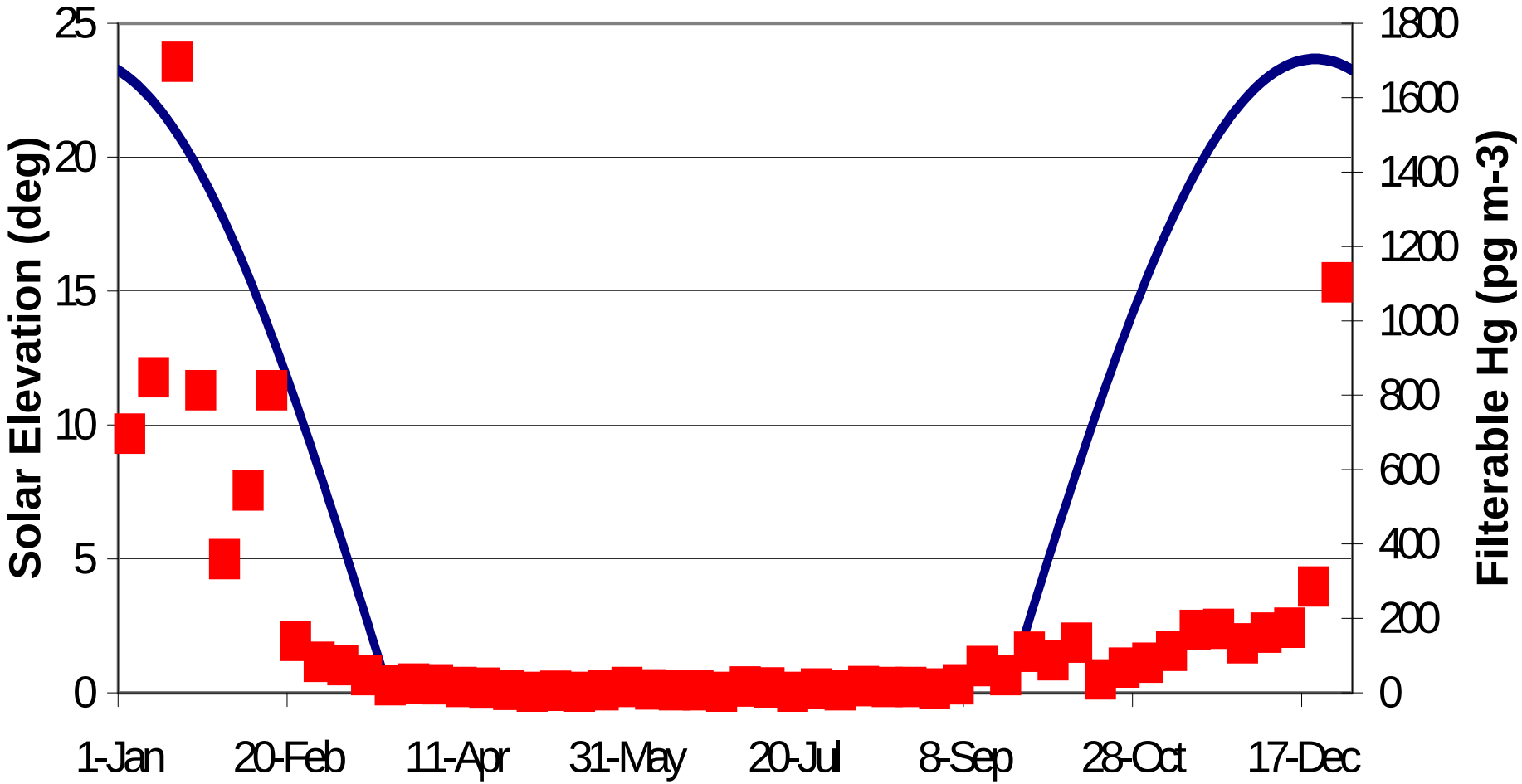
- Operational defined as mercury collected by a KCl coated denuder tube
- Typically believed to be dominated by Hg(II) such as $HgCl_2$, HgBrX
- Typically rare in the lower troposphere 1-2 pg/m^3 (sub-parts per trillion levels)
- Short lifetime (hours) in the near-surface air – dry deposits quickly (similar to nitric acid)
- Water soluble – wet deposits

BARROW Brooks et al GRL 2006



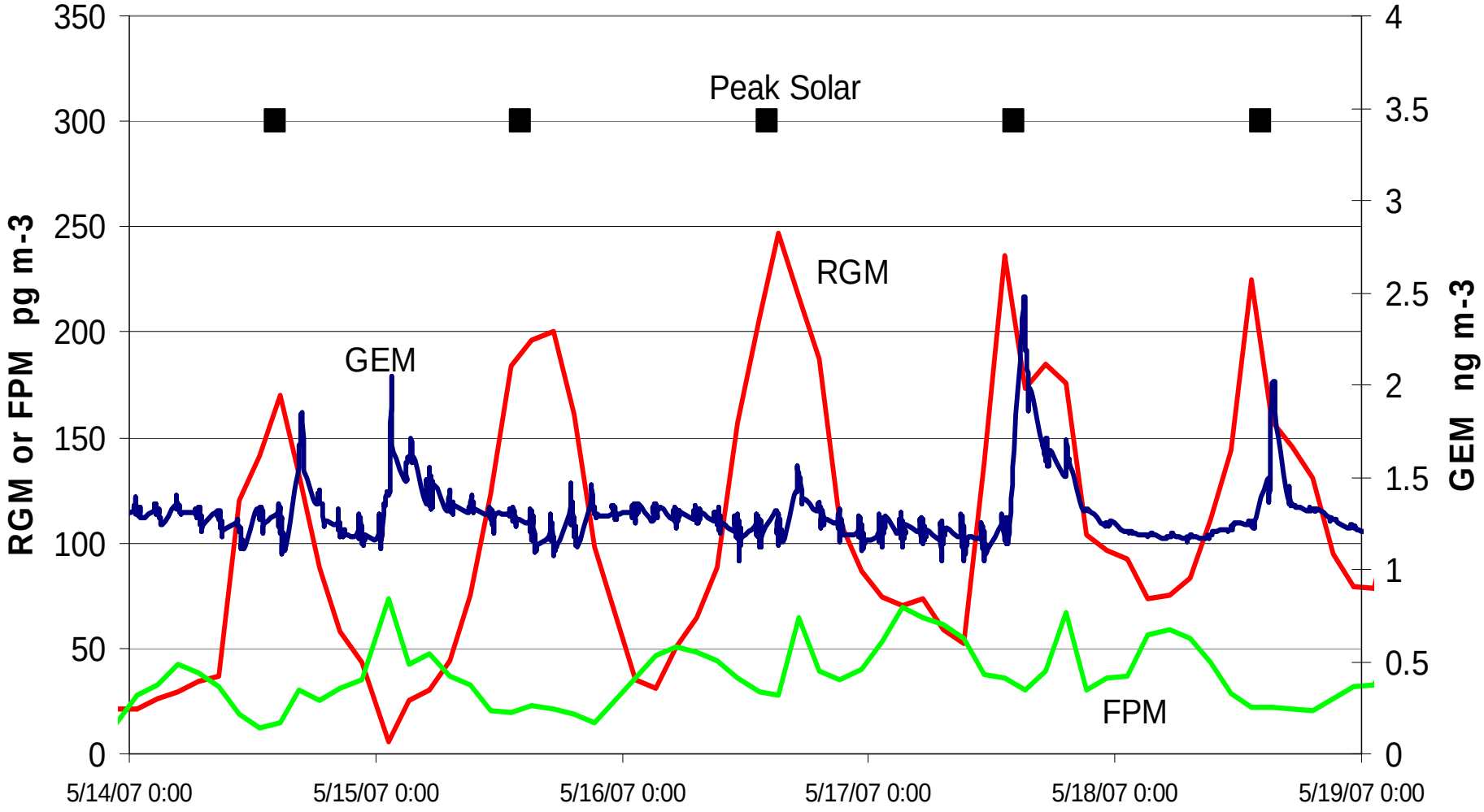
Percentage time 48-hour back trajectory was over sea ice

South Pole Averages of High Volume Filters,
Brooks et al. Atmos. Environ. 2008



Mercury speciation at Summit 2007

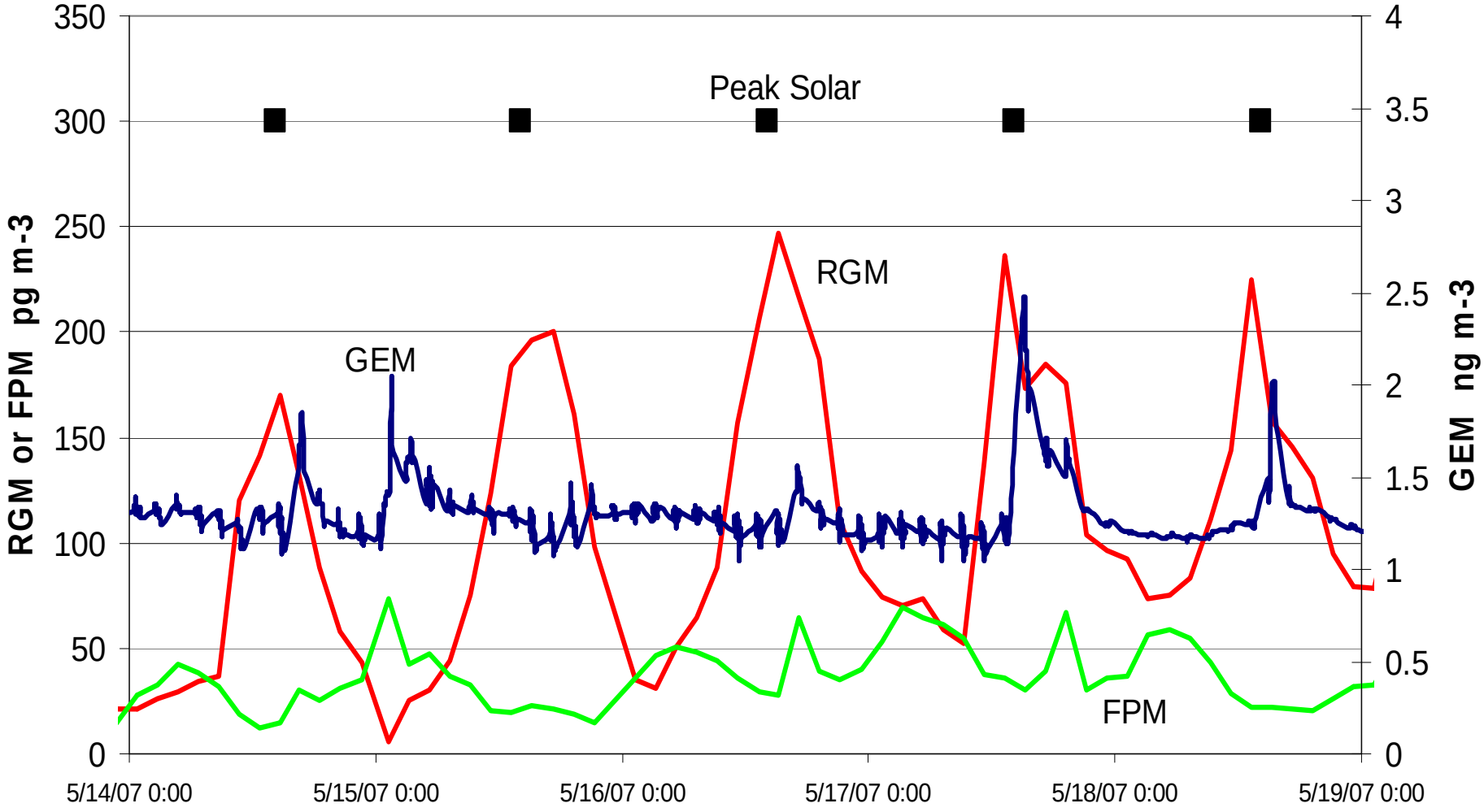
GEM – Gaseous Elem Hg, RGM – Reactive Gaseous Hg, FPM – Fine Particulate Hg

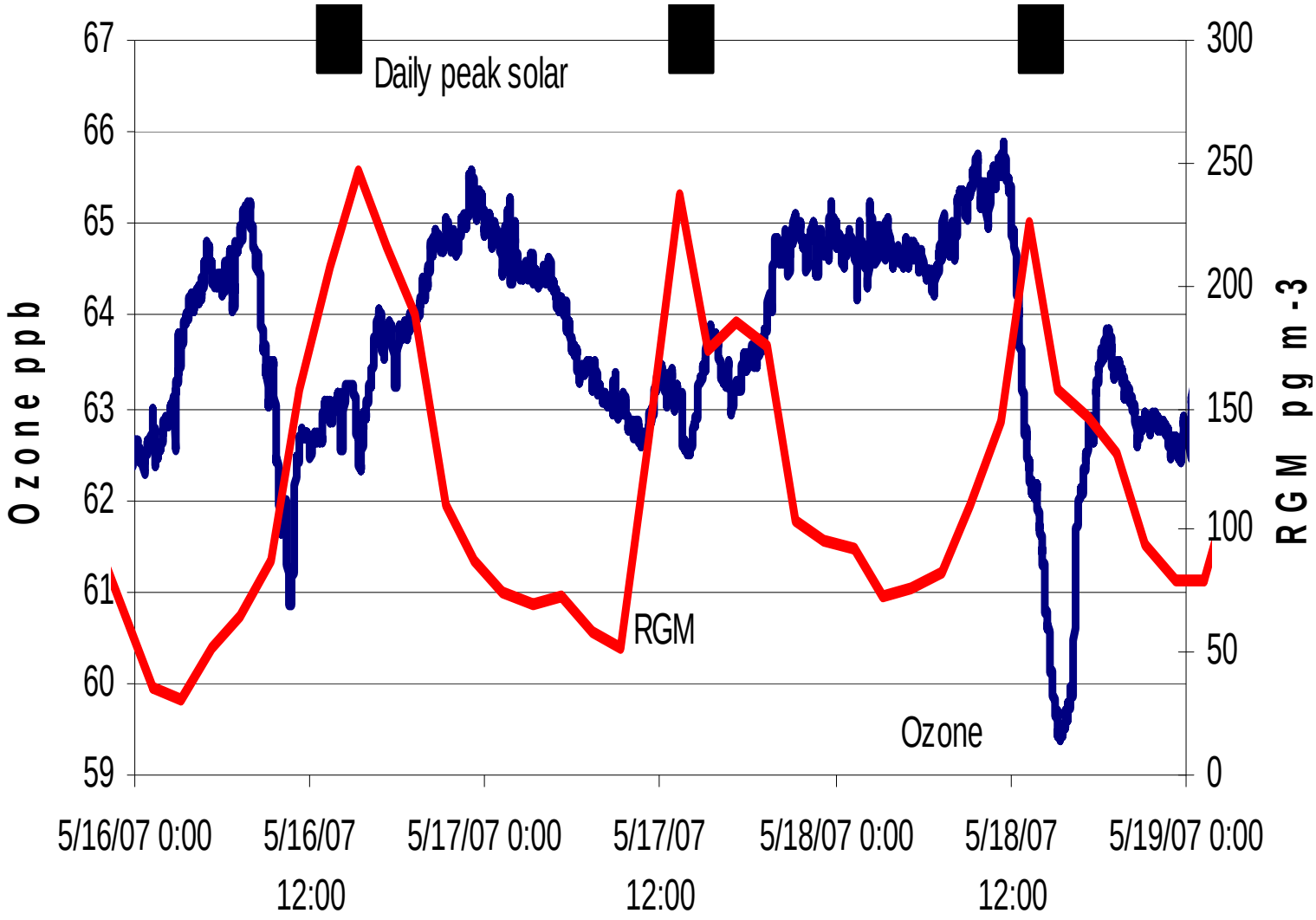



Coca-Cola

Mercury speciation at Summit 2007

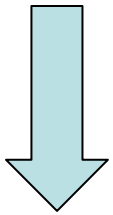
GEM – Gaseous Elem Hg, RGM – Reactive Gaseous Hg, FPM – Fine Particulate Hg

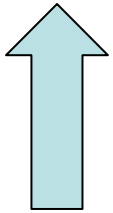



Daily peak solar
RGM
Ozone
Ozone ppb
RGM pg m-3
67
66
65
64
63
62
61
60
59
300
250
200
150
100
50
0
5/16/07 0:00
5/16/07 12:00
5/17/07 0:00
5/17/07 12:00
5/18/07 0:00
5/18/07 12:00
5/19/07 0:00

Fluxes

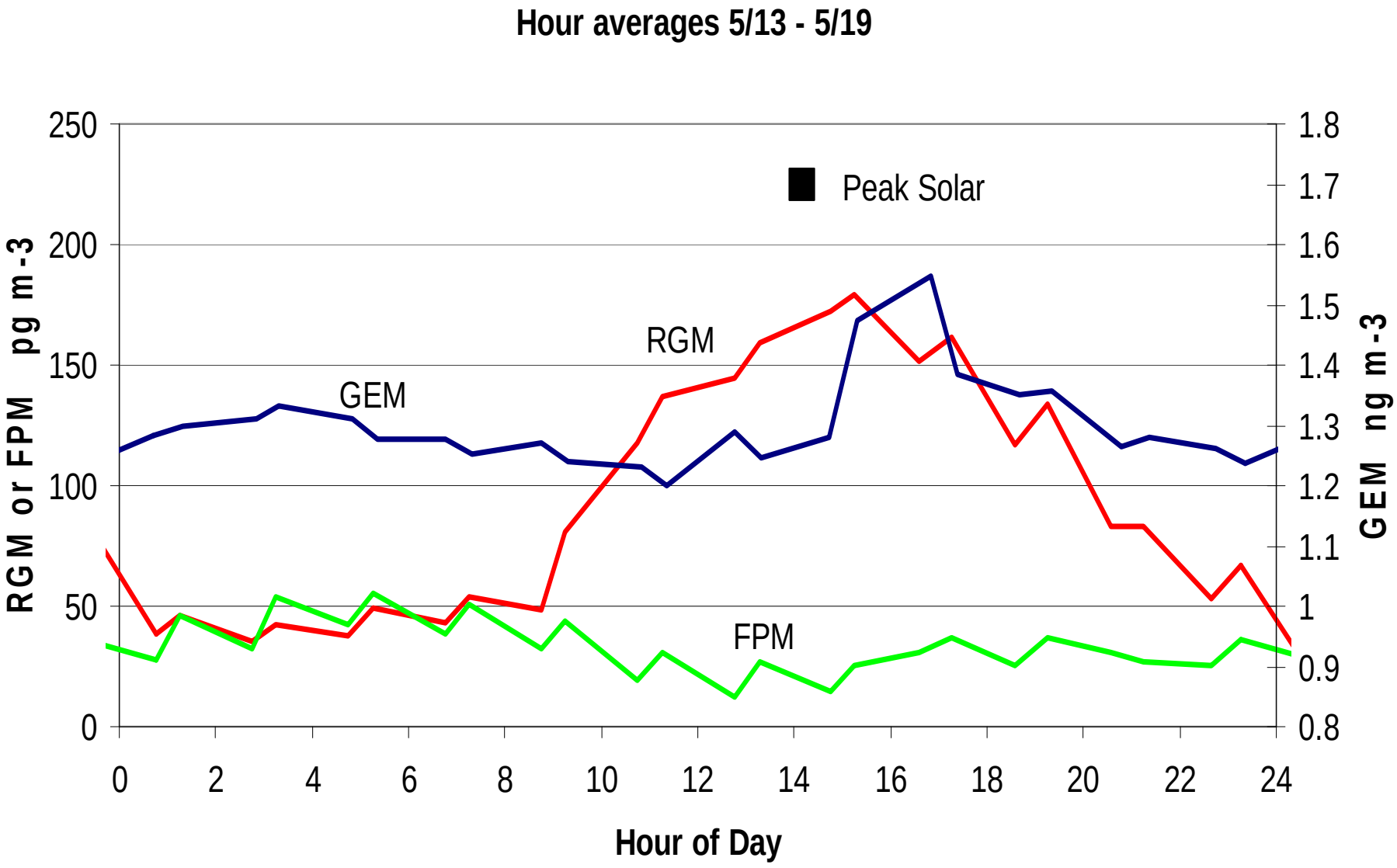
Hg^o + Br => HgBr =>
Reactive Gaseous Mercury,
HgBrX

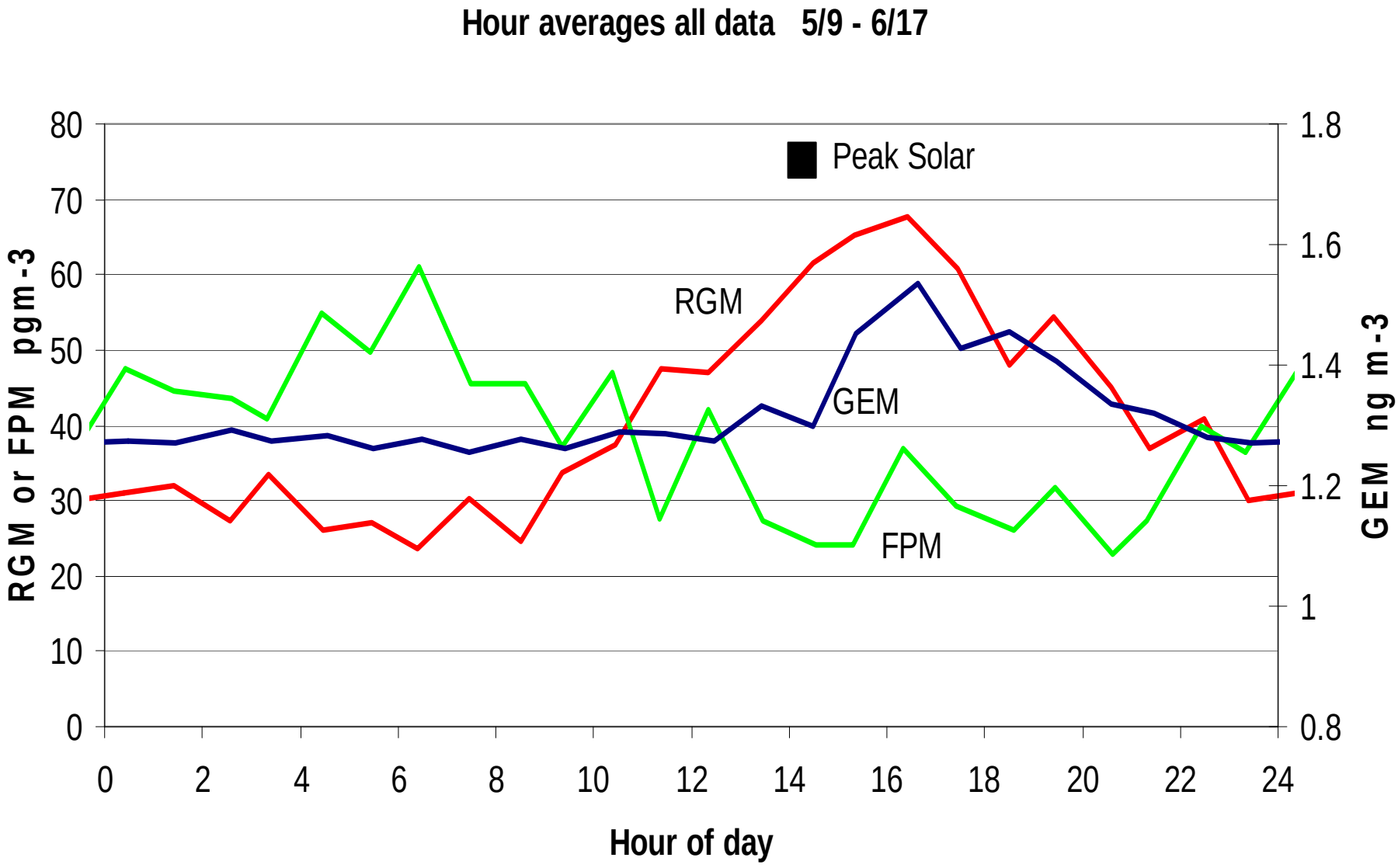


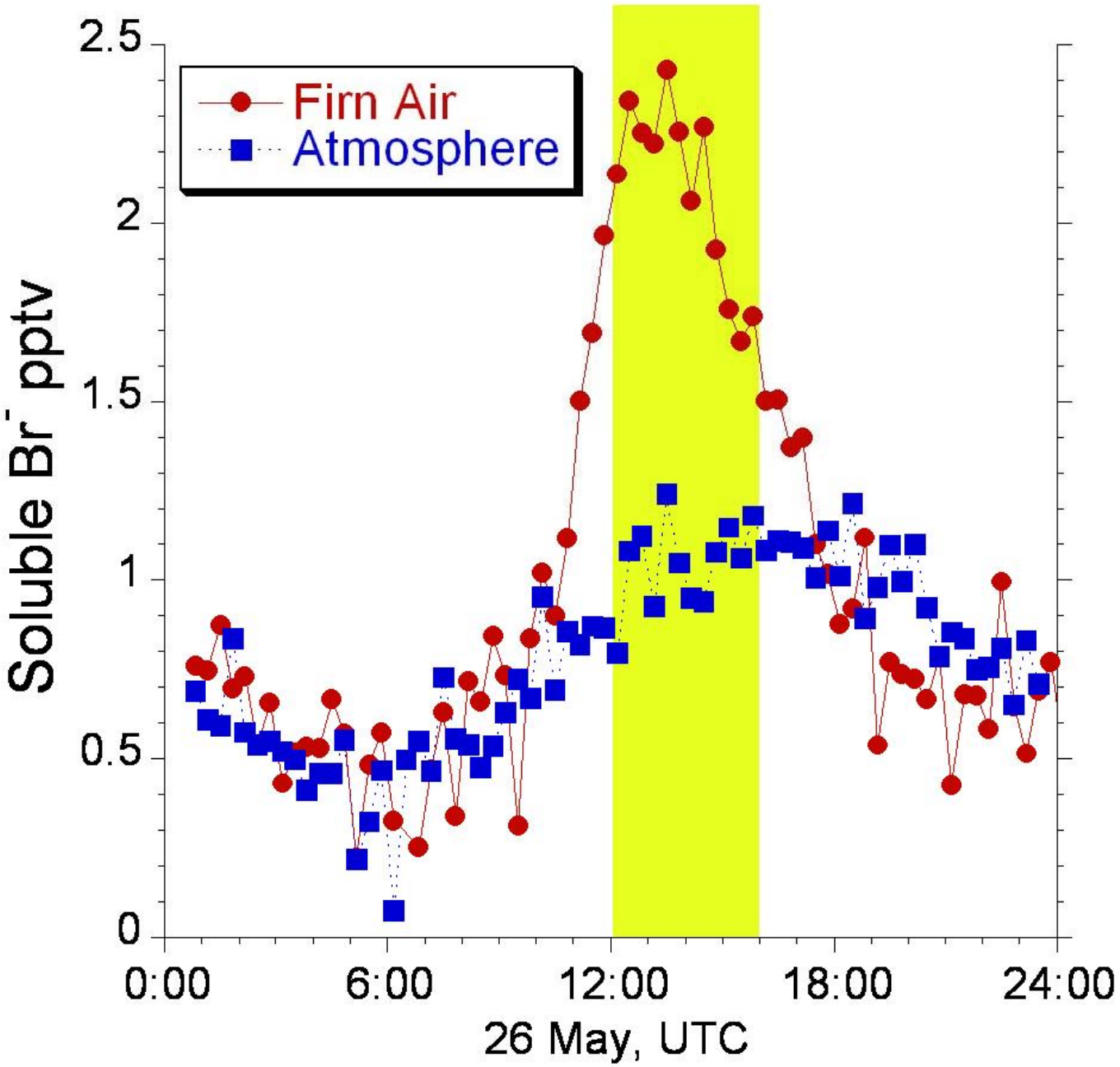


Photoreduction
Gaseous Elemental
Mercury, Hg^o

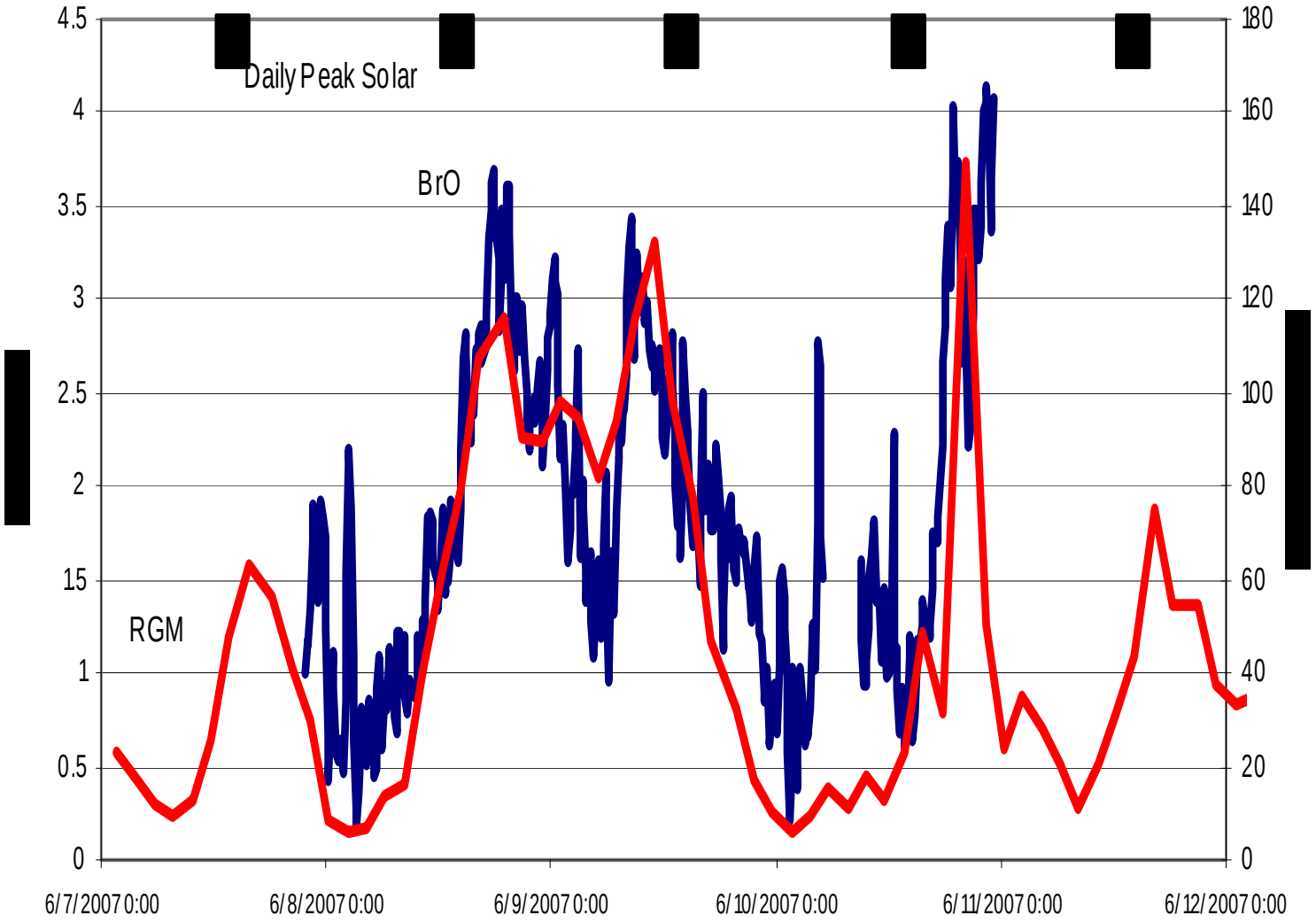
Snow Surface


Hour averages 5/13 - 5/19
Peak Solar
GEM
RGM
FPM
RGM or FPM pg m-3
GEM ng m-3
Hour of Day
250
200
150
100
50
0
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0
2
4
6
8
10
12
14
16
18
20
22
24


Hour averages all data 5/9 - 6/17
Peak Solar
RGM
GEM
FPM
RGM or FPM pgm-3
GEM ng m-3
Hour of day
0
10
20
30
40
50
60
70
80
0.8
1
1.2
1.4
1.6
1.8
0
2
4
6
8
10
12
14
16
18
20
22
24



Summit, Greenland
Jack Dibb
UNH


Daily Peak Solar
BrO
RGM
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
180
160
140
120
100
80
60
40
20
0
6/7/2007 0:00
6/8/2007 0:00
6/9/2007 0:00
6/10/2007 0:00
6/11/2007 0:00
6/12/2007 0:00

Summit Vs. Barrow

- Barrow
- BrO 0-40 ppt
- Hg^o Depletions
- Surface O_3 Depletions
- Hg in snow released to melt water
- Bromine primarily from local sea ice formation

- Summit
- BrO 0-5 ppt
- Hg^o Drops 10%
- O_3 Drops by 5ppb
- Hg in snow sequestered at depth
- Bromine primarily from snow pack recycling

Global Implications

- Barrow and the coastal Polar Regions – Mercury is preferentially deposited (net 100-200 tons/year) and is added to the mercury burden in biota
- Antarctic Polar Plateau – deposited mercury buried by snow sequesters 60 metric tons per year at depth (Brooks et al. Atmos Envir. 2008)
- Greenland Ice Sheet – due to more rapid burial sequesters ~38 metric tons per year

Anthropogenic Emissions are 1500 metric tons/year
Sequestration is total Hg buried below 1m
All US coal combustion emissions are 48 tons/year