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Reactive halogen release from the polar snowpack and the depletion of ozone and mercury in the air: Insights from 1-D (mechanistic) and 3-D (chemical transport) models

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YORK U UNIVERSITÉ UNIVERSITY redefine THE POSSIBLE.

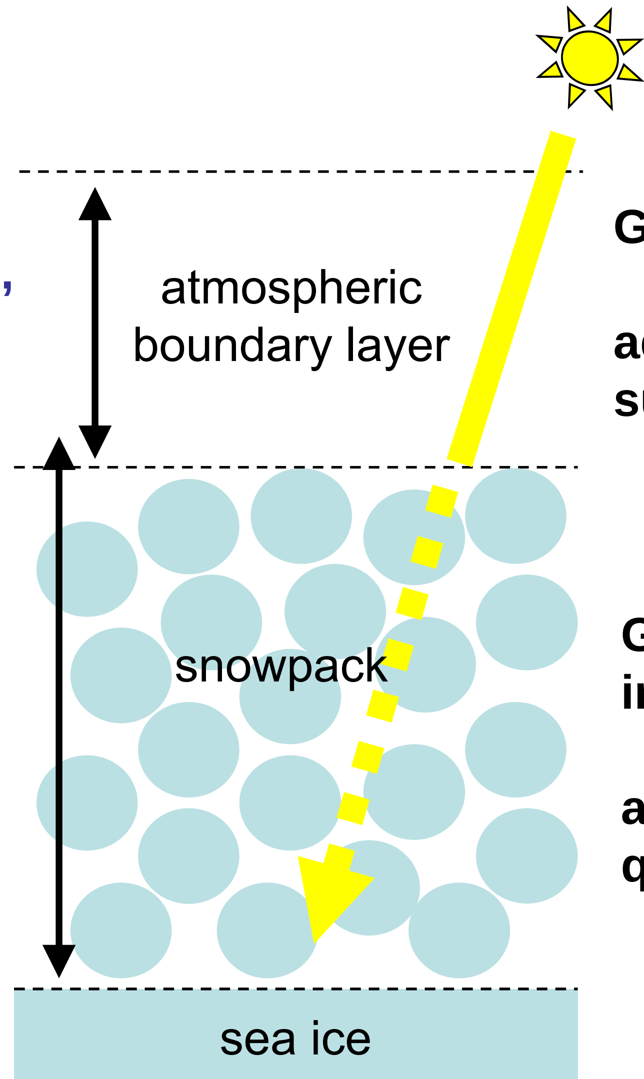
Environment Canada Environnement Canada

Canada

PHANTAS (PHotochemistry ANd Transport between Air and Snowpack)

ABL Top (650 m)

32 grid boxes, turbulent diffusion



Gas-phase reactions
+
aqueous-phase reactions on sulfate aerosols (pH~0.5)

10 grid boxes, molecular diffusion
+
wind-pumping ventilation

Gas-phase reactions in interstitial air
+
aqueous-phase reactions on the quasi-liquid layer of snow grains

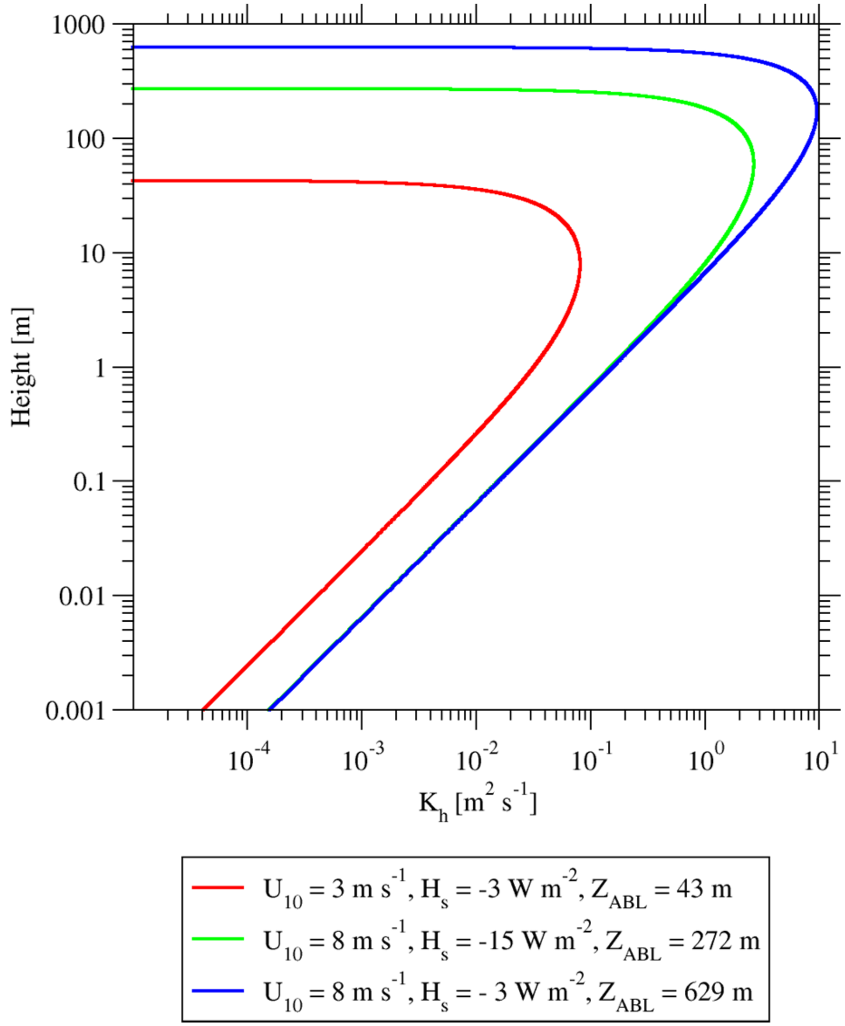
Snow/sea-ice interface (-35 cm)

Multi-phase mass transfer rate expression by Schwartz (1986)

Chemical mechanism

- Ox, HOx, NOx, VOCs ($\leq C_2$), ClOx & BrOx chemistry in the gas- and aqueous-phases with some updates from a model of MBL sea-salt aerosol chemistry (Toyota et al., 2004, ACP) including:
  - $Br_2^- + HO_2(aq) \rightarrow Br_2 + HO_2^-$ (rather than $2\ Br^- + H^+ + O_2$) (Matthew et al., 2003, GRL)
  - T dependence for OH(aq) yields from for NO_3^- & H_2O_2(aq) photolysis on ice surface (Chu and Anastasio, 2003, JPC; 2005, JPC)
  - T dependence for $Br_2Cl^- \Leftrightarrow Br^- + BrCl(aq)$ (Sander et al., 2006, ACP)
  - Hg chemistry is being implemented (underway)

Vertical Diffusivity Profile in ABL



Brost and Wyngaard (1978)

$$K(z) = 1.2\kappa z u_* (1 - z / Z_{ABL})^{1.5} (1 + 4.7 z / L)^{-1}$$

$$Z_{ABL} = d(u_* L / |f|)^{1/2}, \quad d = 0.4$$

Bussinger et al. (1971)

$$U_{10} = \frac{u_*}{\kappa}\left[\ln\left(\frac{10}{z_0}\right) + 4.7\left(\frac{z}{L}\right)\right]$$

$$L^{-1} = -\kappa g H_s / T_s u_*^3$$

Andreas et al. (2005)

$$z_0 = \frac{0.135\nu}{u_*} + 0.035\frac{u_*^2}{g}\left\{F \exp\left[-\left(\frac{u_* - 0.18}{0.1}\right)^2\right] + 1\right\}$$

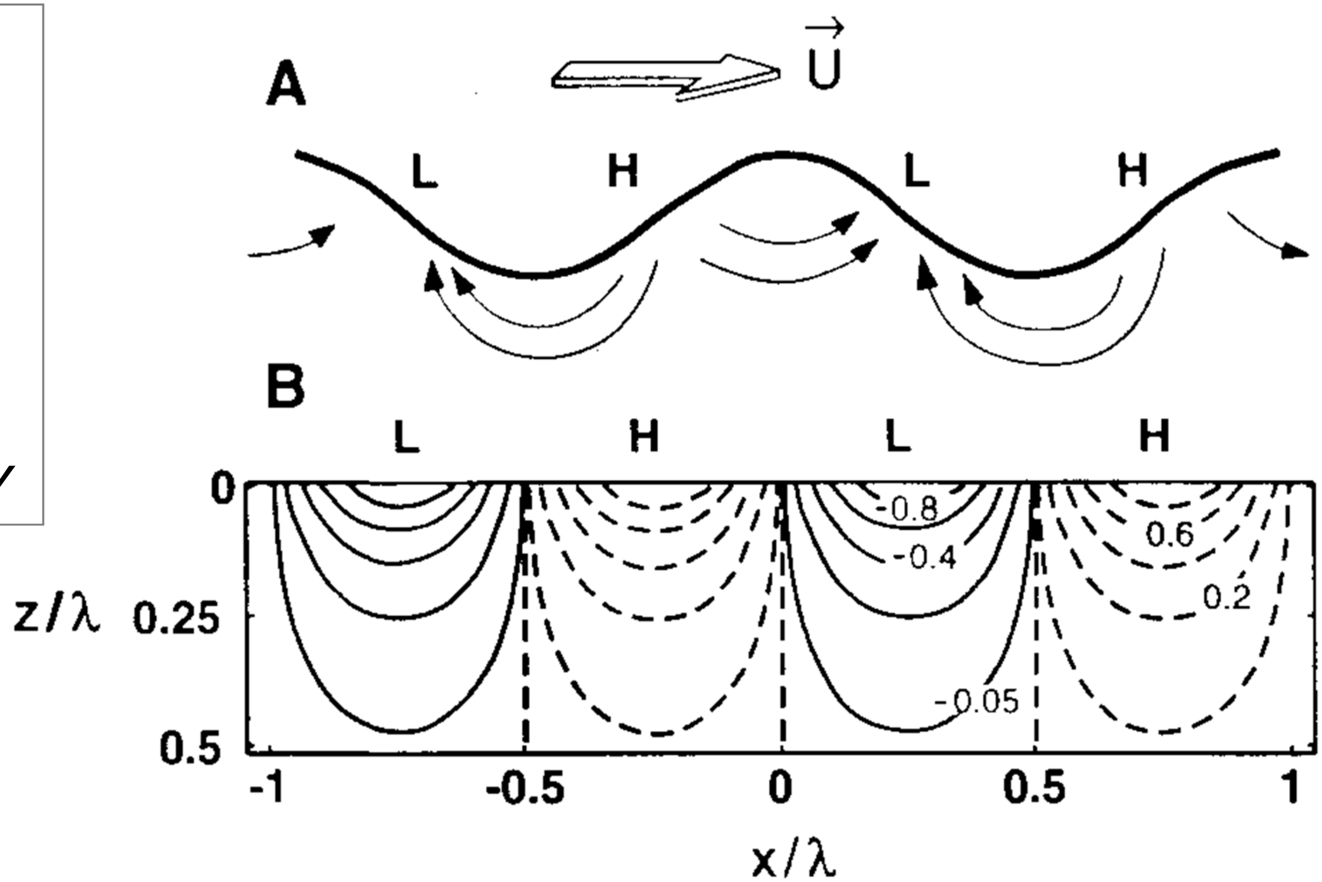
$$(F = 5)$$

Wind-pumping ventilation of snowpack interstitial air

Darcy's Flow

$$V_i = -\frac{k}{\mu}\frac{\partial P}{\partial x_i}$$

k : permeability



Waddington *et al.* (1996)

Wind-pumping ventilation rate

w/ slight mods from Cunningham and Waddington (1993)

- Analytical solution for the average downward Darcy's flow rate (which has the same magnitude as upward counterpart) within snowpack having uniform physical properties and residing on 'non-porous' sea-ice

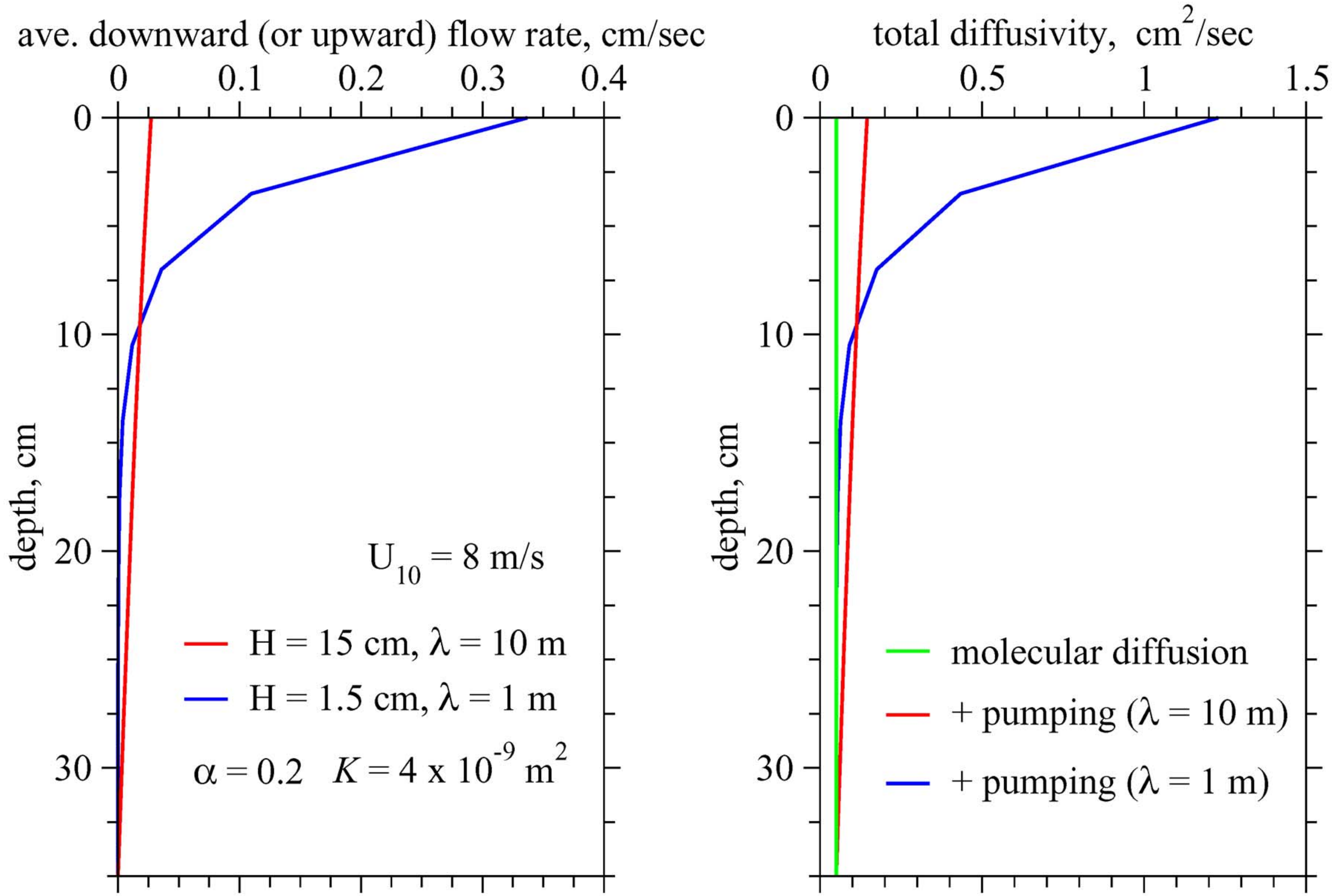
$$\overline{V}_Z = \frac{k}{\mu}\frac{6\rho_{air}U_{10}^2}{\pi}\frac{h}{\lambda}\frac{1}{\lambda}\frac{\sqrt{\alpha^2+1}}{\alpha}\left(C_1\exp\left(-\frac{z}{\delta}\right)-C_2\exp\left(\frac{z}{\delta}\right)\right)$$

where

$$\delta = \frac{\alpha}{\sqrt{\alpha^2+1}}\frac{\lambda}{2\pi} \qquad C_1 = \frac{\exp\left(\frac{H_S}{\delta}\right)}{\exp\left(\frac{H_S}{\delta}\right)+\exp\left(-\frac{H_S}{\delta}\right)} \qquad C_2 = \frac{\exp\left(-\frac{H_S}{\delta}\right)}{\exp\left(\frac{H_S}{\delta}\right)+\exp\left(-\frac{H_S}{\delta}\right)}$$

z : distance from the atmosphere-snowpack interface, H_S : mean snow depth,
k : permeability, μ : dynamic viscosity of air, U_{10} : surface wind speed,
h : relief amplitude, λ : relief wavelength, α : horizonal aspect ratio of reliefs
(if $\alpha < 1$ then elongated in the wind direction like sastrugi)

Total diffusivity = wind-pumping (assume as eddies) + **molecular diffusion**



$$K_{pump} = \overline{V_Z} \times \Delta Z$$

ΔZ : model grid spacing (3.5cm)

Model settings (atmosphere)

- T = 258 K, RH = 80% (ABL) or 100% (in snow)
- Solar zenith angle for April 20, 80^{o}N (24-h sunlit)
- Snow albedo = 0.8; Total ozone = 400 DU
- Initially, O_3 = 40 ppbv, inorganic Br (gas) = 0, C_2H_2 = 400 pptv, etc. etc.
- C_2H_4 = 0 (for now not to handle oxygenated organic bromine formation)
- Sub-μm sulfate aerosols (esp. for halogen recycling):

    pH ~ 0.5

    LWC = 3.0×10^{-12} cm^3(aq)/cm^3(air)

    Particle radius = 0.1 μm

Model settings (snowpack)

- Snow depth: 35 cm
- Snow density: 0.31 g/cm^3 (porosity = 0.663)
- Grain radius: 0.5 mm
- Permeability: 4×10^{-9} m^2
- Actinic flux e-folding depth: 10 cm
- Prescribed photochemical release to snowpack interstitial air, scaled by $J(O_3 \rightarrow O^1D)$ changes in time and depth in the snow
  - HCHO: 4.8E+8 molecule cm^{-2} sec^{-1} (daily mean)
  - CH_3CHO: 4.25E+8 molecule cm^{-2} sec^{-1} (daily mean)

Snowpack brine layer conditions

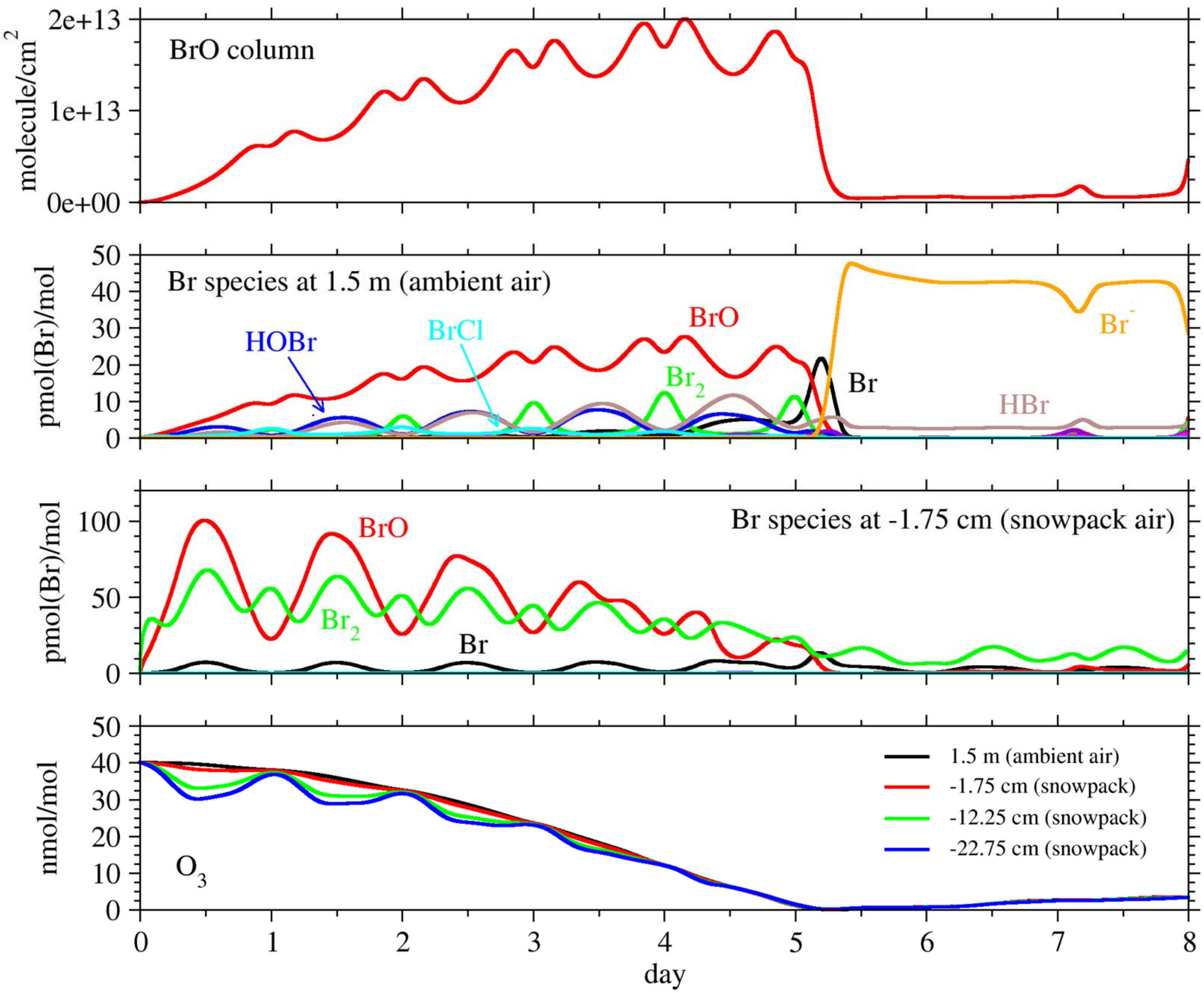
- Initial bulk concentrations of solutes (in mol/L):

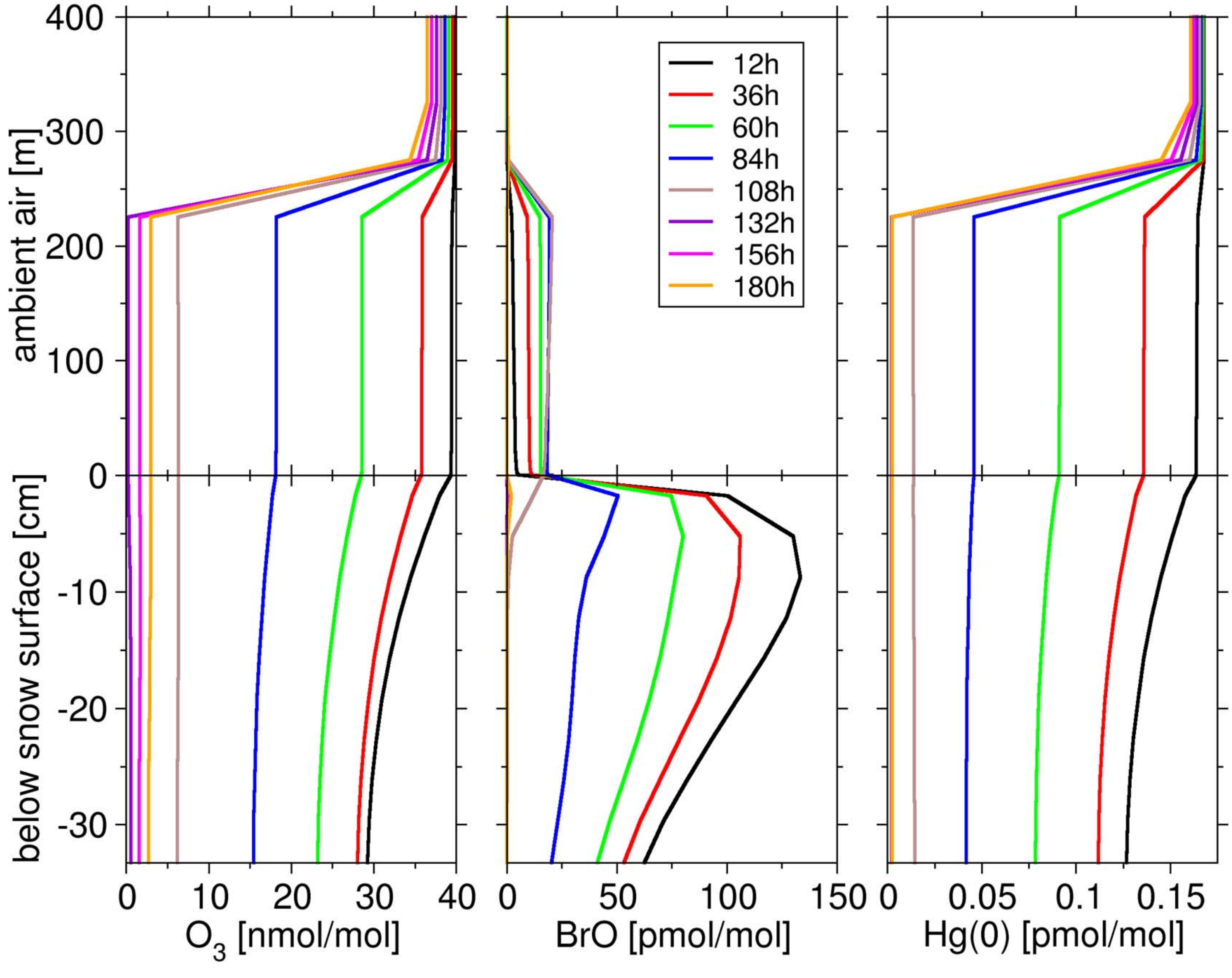
  $[Na^+]$ = 7.5E-05, $[Cl^-]$= 7.0E-05,

  $[NO_3^-]$ = 5.0E-06, $[Br^-]$ = 1.15E-07,

  Alkalinity = 0 (assumed to have been titrated by nitrate)
- Brine volume fraction (at 258 K) ~ 1.6E-05
  - Based on a FPD-type model by Cho et al. (2002)
- pH in brine layer ~ 3 to 4
  - Buffered by gaseous HCl around 100 pmol/mol in the present model runs (perhaps)

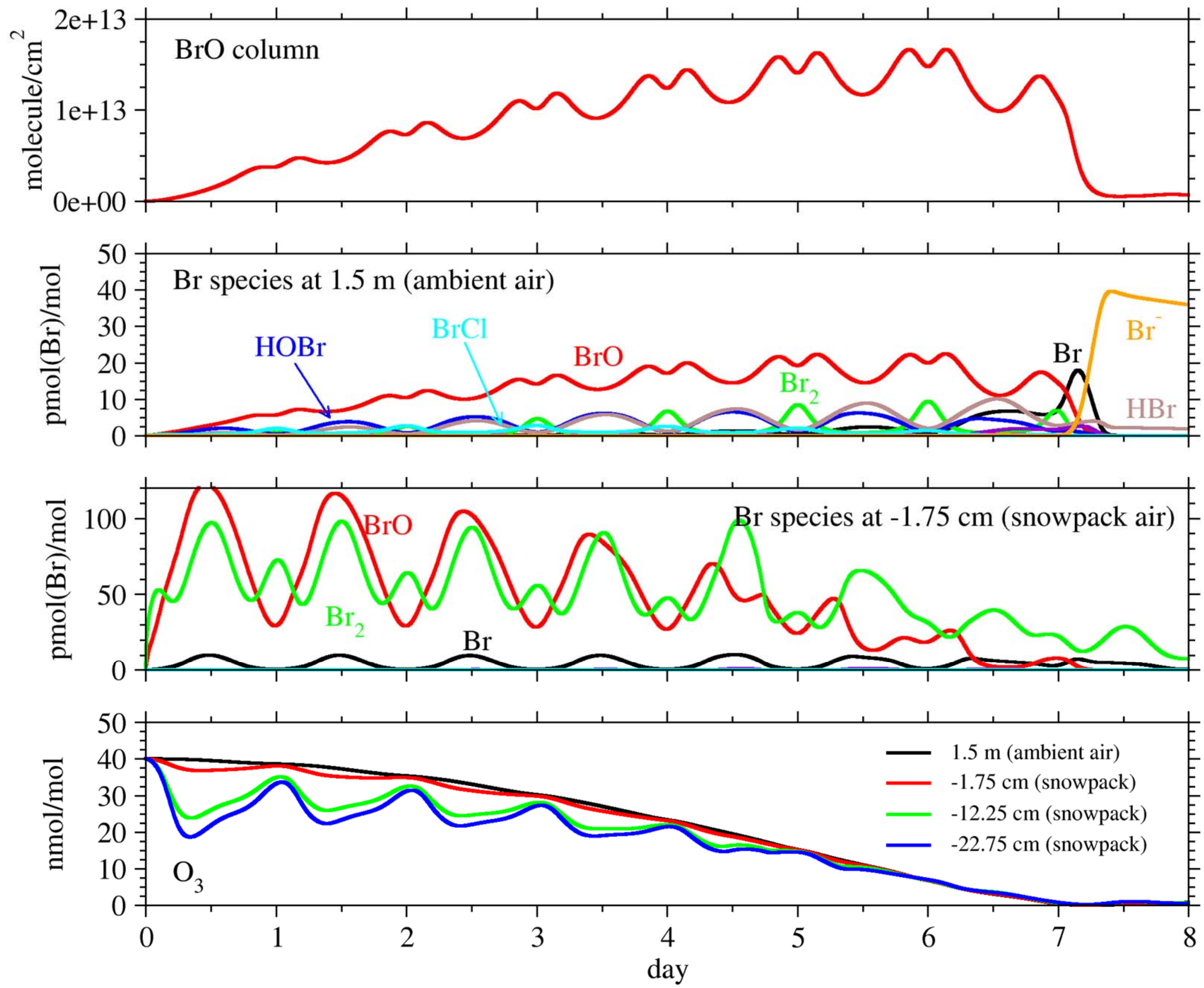
U_{10} = 8 m/s, H_s = -15 W/m^2 (➔ Z_{ABL} = 272 m)
Wind-pumping "diffusion" caused by bumps of 10-m wide & 15-cm high

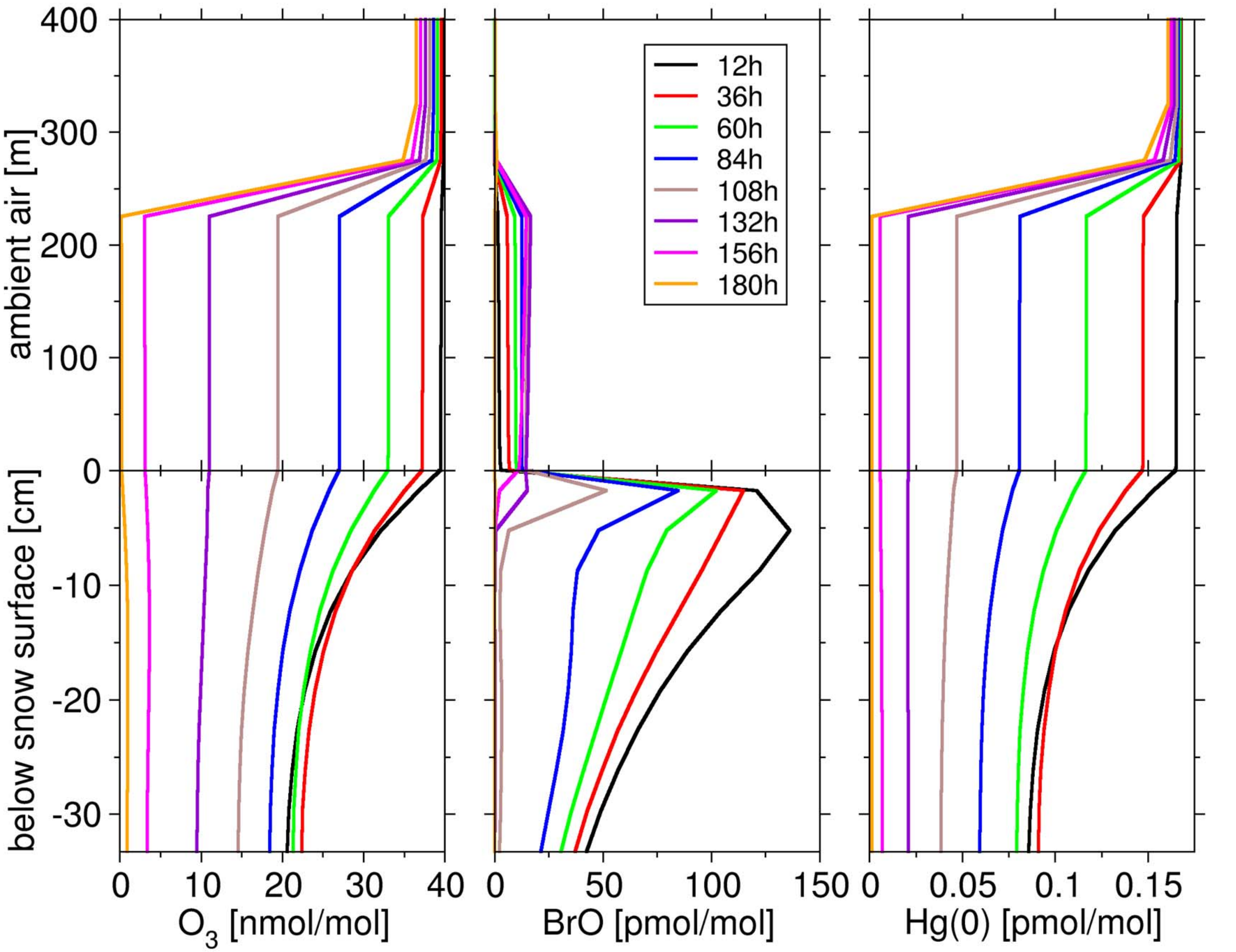




400
300
200
100
0
-10
-20
-30
ambient air [m]
below snow surface [cm]
0 10 20 30 40
O3 [nmol/mol]
0 50 100 150
BrO [pmol/mol]
0 0.05 0.1 0.15
Hg(0) [pmol/mol]
12h
36h
60h
84h
108h
132h
156h
180h

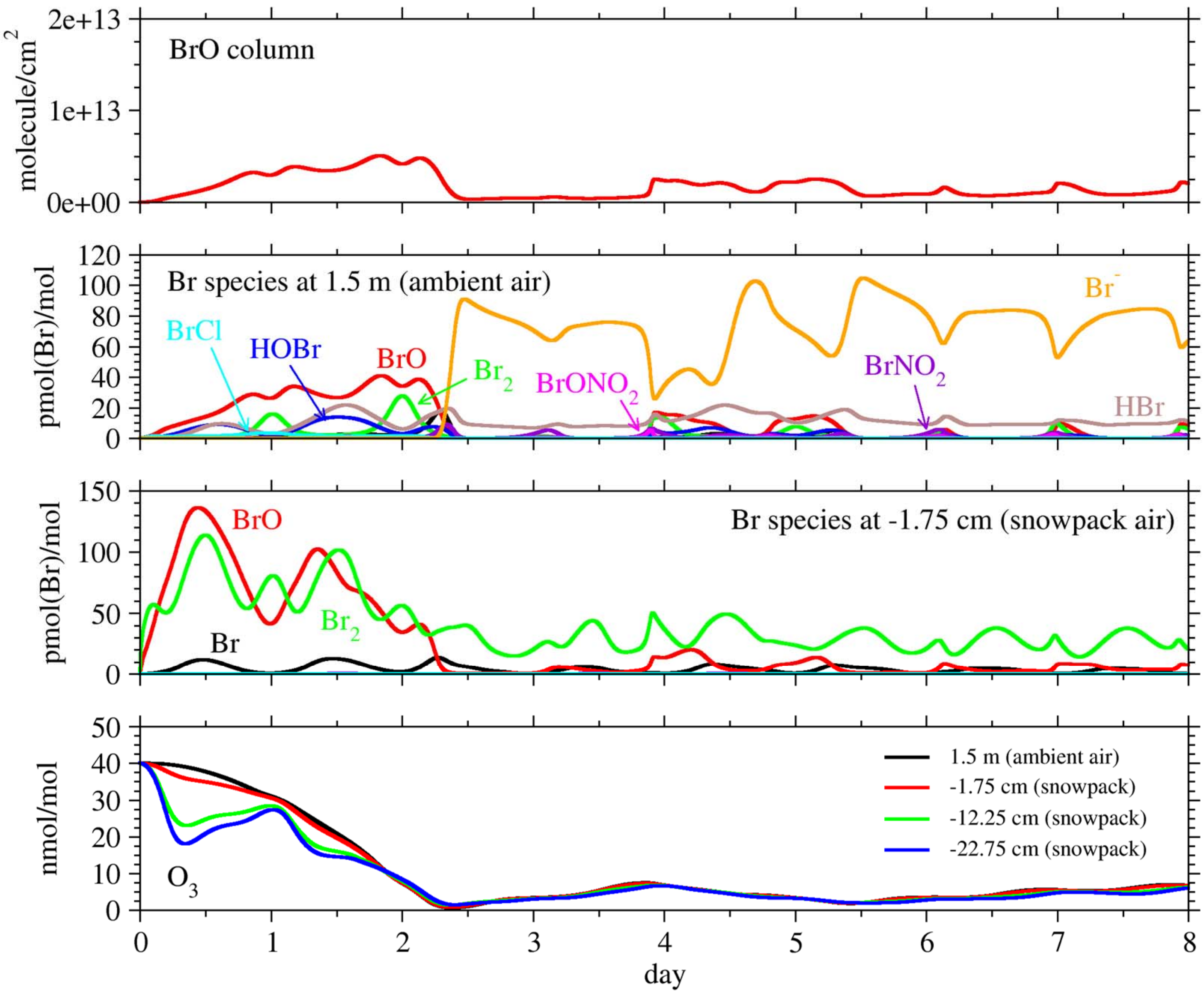
U_{10} = 8 m/s, H_s = -15 W/m^2 (➔ Z_{ABL} = 272 m)
Wind-pumping "diffusivity" is switched off

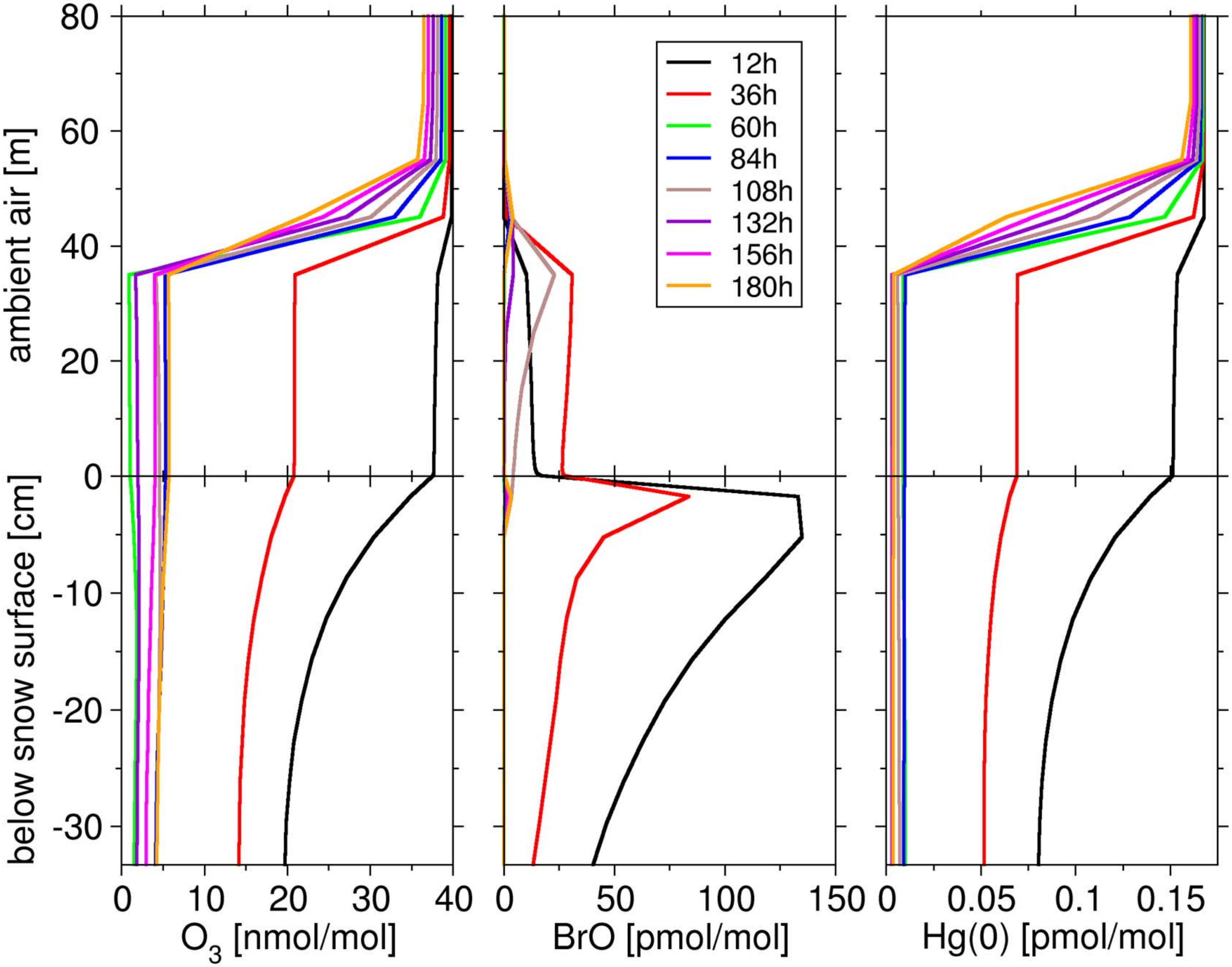




12h
36h
60h
84h
108h
132h
156h
180h
ambient air [m]
below snow surface [cm]
400
300
200
100
0
-10
-20
-30
0
10
20
30
40
50
100
150
0.05
0.1
0.15
O3 [nmol/mol]
BrO [pmol/mol]
Hg(0) [pmol/mol]

U_{10} = 3 m/s, H_s = -3 W/m^2 (➔ Z_{ABL} = 43 m)
Wind-pumping “diffusivity” is switched off





12h
36h
60h
84h
108h
132h
156h
180h
ambient air [m]
below snow surface [cm]
80
60
40
20
0
-10
-20
-30
0
10
20
30
40
O_3 [nmol/mol]
0
50
100
150
BrO [pmol/mol]
0
0.05
0.1
0.15
Hg(0) [pmol/mol]

1-D model summary

- In our model, BrO, Br_2 and Br-atom are among the most major gaseous bromine species in the snowpack interstitial air.
- Higher ozone levels in ambient air enhances the production of reactive bromine gases in the snowpack (for which HOBr and $BrONO_2$ are perhaps involved).
- Under calm conditions, shallow (<100 m) boundary layer ODEs may well be attained in 1-2 days by reactive bromine production and subsequent release to the atmosphere via molecular diffusion of gases in the snowpack interstitial air. Small BrO columns associated with such events will be hard to detect from space.
- Under strong wind conditions, wind-pumping promotes the bromine release from the snowpack. However, one should also examine the role of drifting/blowing snow at U > 6-7 m/s.

3-D Air Quality Model (GEM-AQ) with Simplified Air-Snowpack Chemical Interaction Scheme

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Atmospheric Chemistry and Physics

Analysis of reactive bromine production and ozone depletion in the Arctic boundary layer using 3-D simulations with GEM-AQ: inference from synoptic-scale patterns

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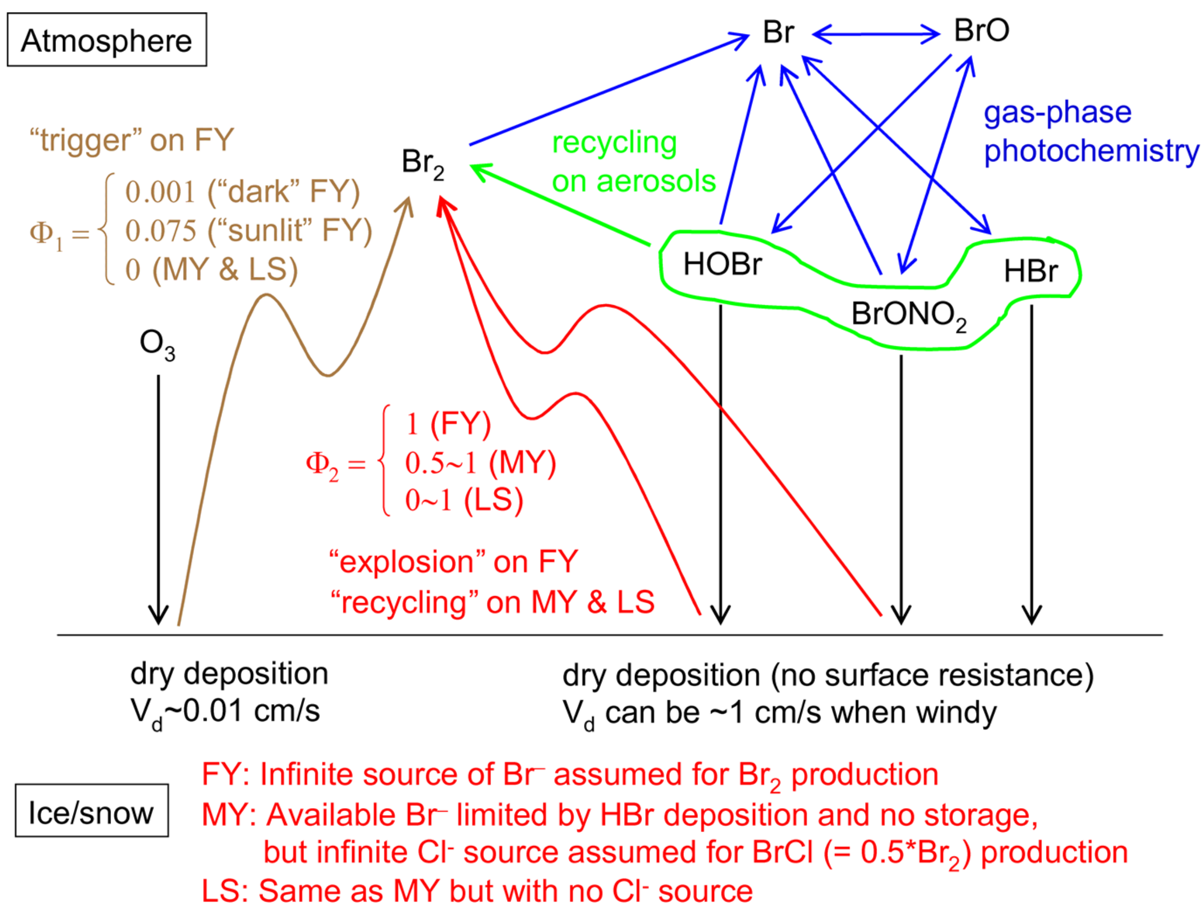
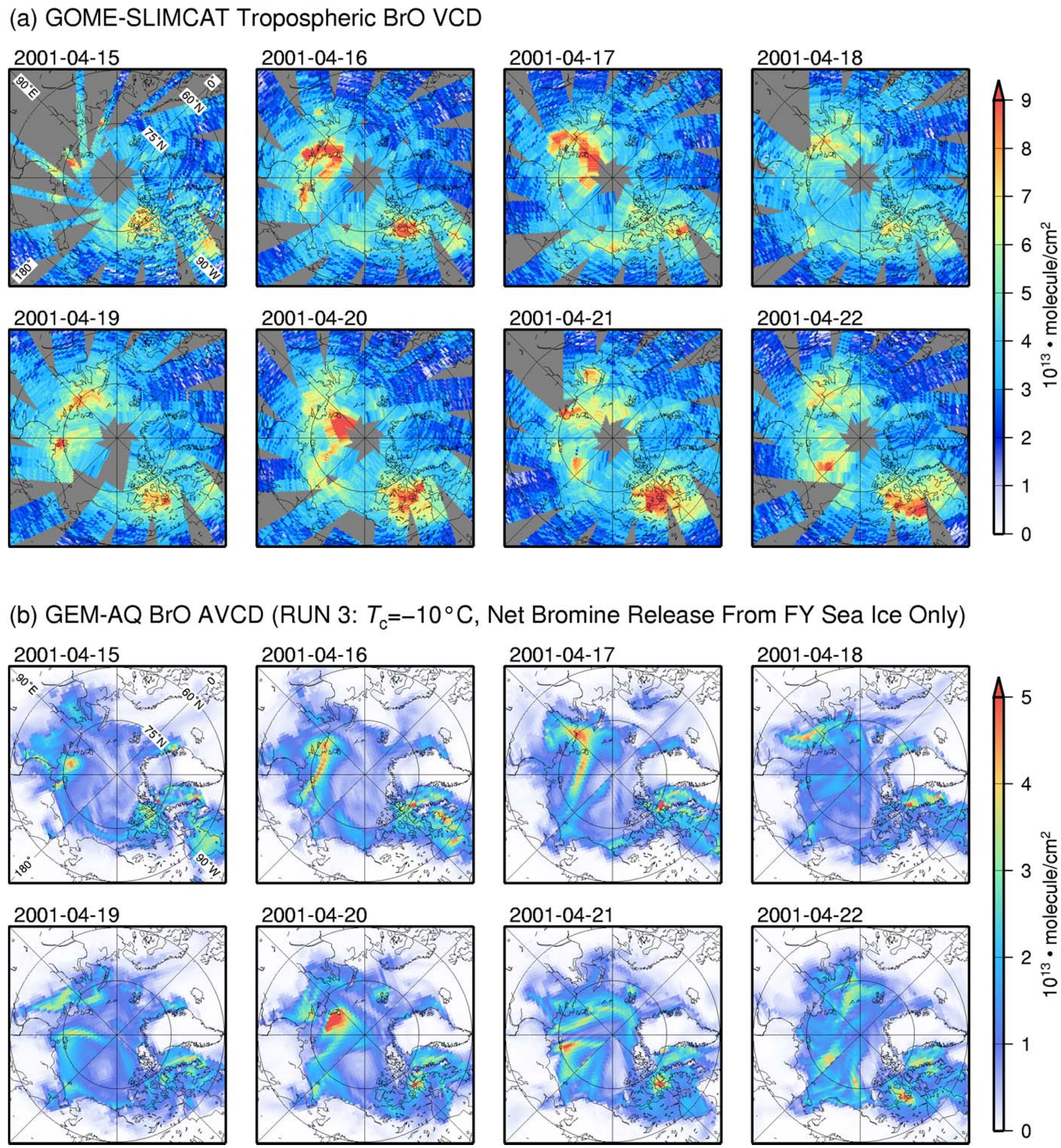
Case Study for Surface ODEs and "BrO clouds" for April 2001

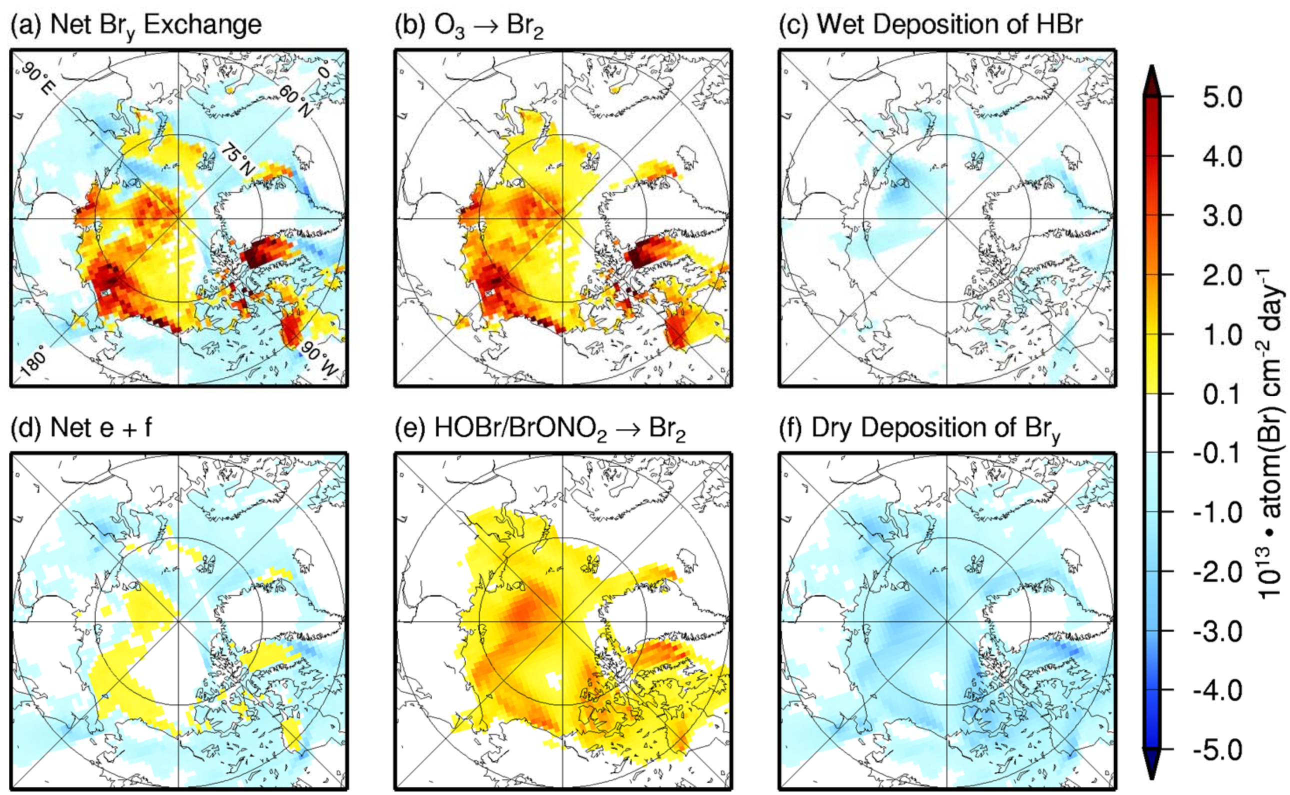
- Model meteorology constrained by CMC objective analysis
- Horizontal resolution ~97.8 x 97.8 km^2

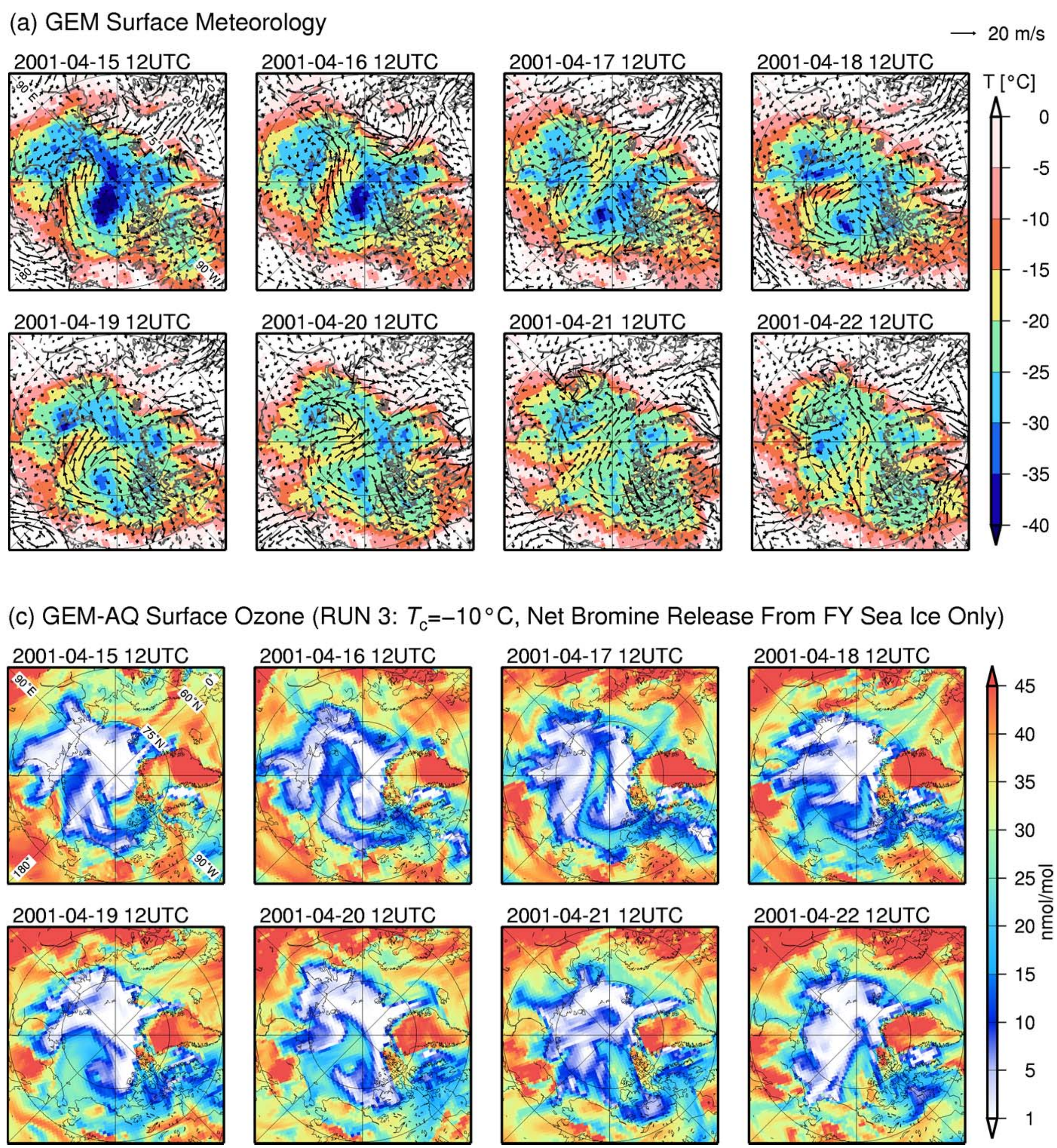




(a) GOME-SLIMCAT Tropospheric BrO VCD
2001-04-15
2001-04-16
2001-04-17
2001-04-18
2001-04-19
2001-04-20
2001-04-21
2001-04-22
90°E
0°
60°N
75°N
180°
90°W
0
1
2
3
4
5
6
7
8
9
10^{13} • molecule/cm^2
(b) GEM-AQ BrO AVCD (RUN 3: T_c=−10 °C, Net Bromine Release From FY Sea Ice Only)
2001-04-15
2001-04-16
2001-04-17
2001-04-18
2001-04-19
2001-04-20
2001-04-21
2001-04-22
90°E
0°
60°N
75°N
180°
90°W
0
1
2
3
4
5
10^{13} • molecule/cm^2

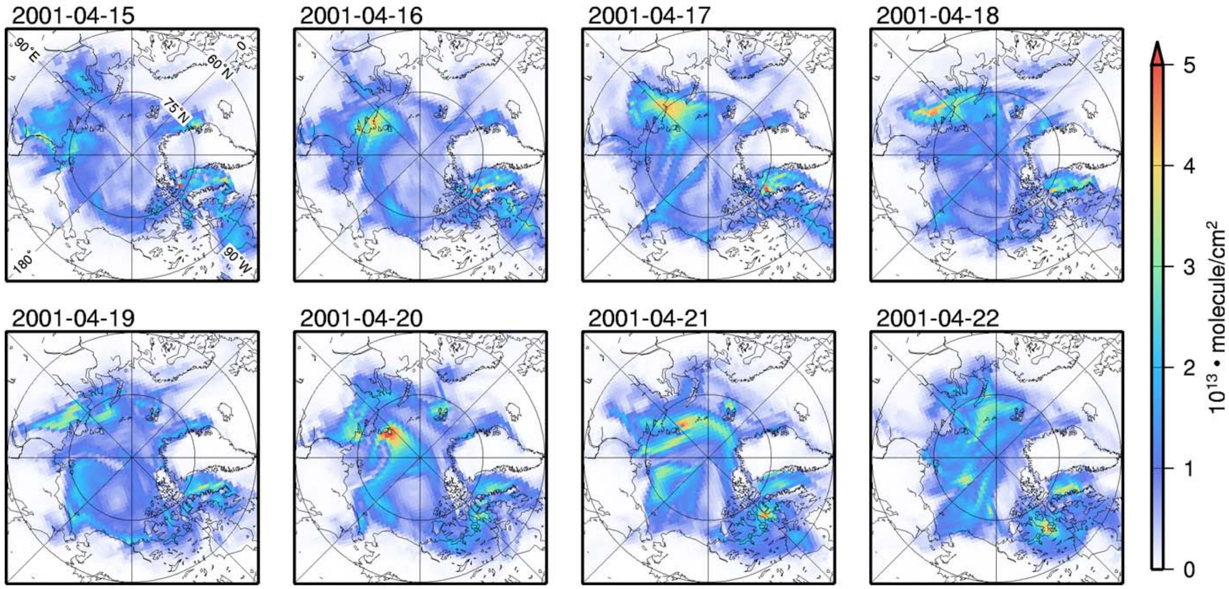
Air-Surface Bromine Exchange Rate over 24 h on 20 April 2001



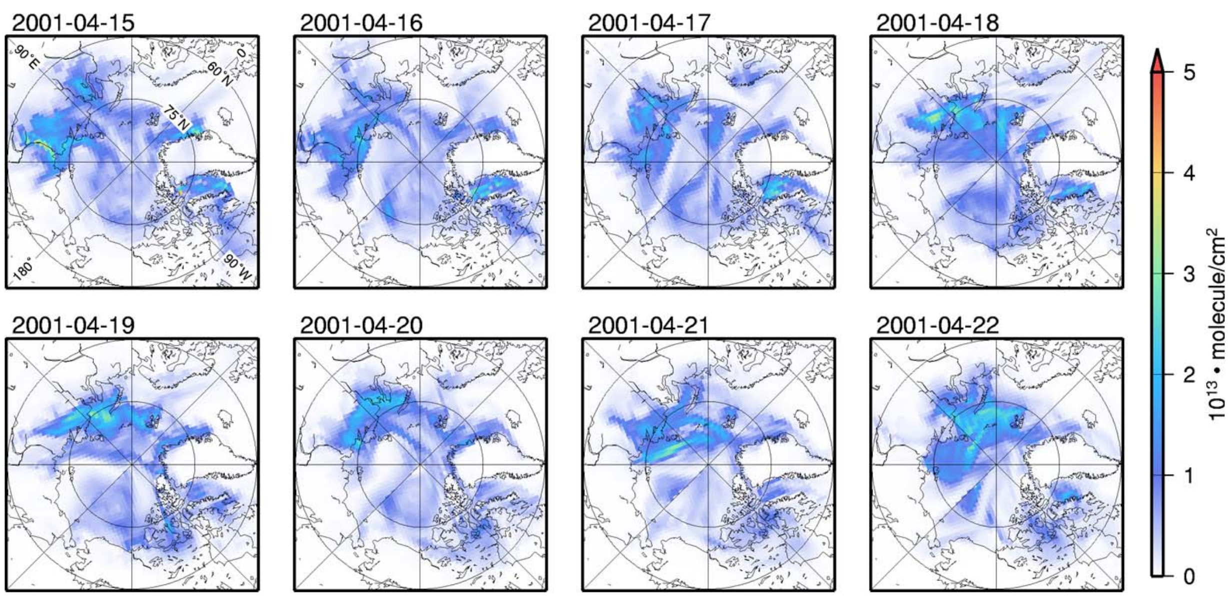


(a) GEM Surface Meteorology
20 m/s
2001-04-15 12UTC
2001-04-16 12UTC
2001-04-17 12UTC
2001-04-18 12UTC
2001-04-19 12UTC
2001-04-20 12UTC
2001-04-21 12UTC
2001-04-22 12UTC
90°E
0°
60°N
75°N
180°
90°W
T [°C]
0
-5
-10
-15
-20
-25
-30
-35
-40
(c) GEM-AQ Surface Ozone (RUN 3: T_c=−10 °C, Net Bromine Release From FY Sea Ice Only)
2001-04-15 12UTC
2001-04-16 12UTC
2001-04-17 12UTC
2001-04-18 12UTC
2001-04-19 12UTC
2001-04-20 12UTC
2001-04-21 12UTC
2001-04-22 12UTC
90°E
0°
60°N
75°N
180°
90°W
nmol/mol
45
40
35
30
25
20
15
10
5
1

(c) GEM-AQ BrO AVCD (RUN 4: T_c=−15 °C, Net Bromine Release From FY Sea Ice Only)



(d) GEM-AQ BrO AVCD (RUN 5: T_c=−20 °C, Net Bromine Release From FY Sea Ice Only)



3-D model summary

- 3-D model with a highly simplified scheme of air-snow/ice surface interactions for reactive bromine release, largely controlled by surface ozone levels, reasonably simulates satellite observations of BrO columns in the high Arctic
- Reactive bromine release from snowpack and/or sea ice in the springtime Arctic appears to be quite active at temperatures as high as -10 ^{o}C or possibly higher.

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