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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**PHANTAS (PHotochemistry ANd Transport between Air and Snowpack)**

- ABL Top (650 m)
  - 32 grid boxes, turbulent diffusion
- Snowpack
  - 10 grid boxes, molecular diffusion
  - wind-pumping ventilation
  - Snow/sea-ice interface (-35 cm)
  - Gas-phase reactions in interstitial air
  - aqueous-phase reactions on the quasi-liquid layer of snow grains

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

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

- Ox, HOx, NOx, VOCs (≤C₂), 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:
  - \( \text{Br}_2^- + \text{HO}_2(aq) \rightarrow \text{Br}_2 + \text{HO}_2^- \) (rather than \( 2 \text{Br}^- + \text{H}^+ + \text{O}_2 \)) (Matthew et al., 2003, GRL)
  - T dependence for OH(aq) yields from for NO₃⁻ & H₂O₂(aq) photolysis on ice surface (Chu and Anastasio, 2003, JPC; 2005, JPC)
  - T dependence for \( \text{Br}_2\text{Cl}^- \leftrightarrow \text{Br}^- + \text{BrCl}(aq) \) (Sander et al., 2006, ACP)
  - Hg chemistry is being implemented (underway)
Vertical Diffusivity Profile in ABL

Brost and Wyngaard (1978)

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

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

Bussinger et al. (1971)

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

\[ L^1 = -\kappa g H_s / T u_*^3 \]

Andreas et al. (2005)

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

\[ (F = 5) \]
Wind-pumping ventilation of snowpack interstitial air

Darcy's Flow

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

\( k: \) 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

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

where

\[
\delta = \frac{\alpha}{\sqrt{\alpha^2 + 1}} \frac{\lambda}{2\pi}
\]

\[
C_1 = \frac{\exp \left( \frac{H_S}{\delta} \right)}{\exp \left( \frac{H_S}{\delta} \right) + \exp \left( -\frac{H_S}{\delta} \right)}
\]

\[
C_2 = \frac{\exp \left( -\frac{H_S}{\delta} \right)}{\exp \left( \frac{H_S}{\delta} \right) + \exp \left( -\frac{H_S}{\delta} \right)}
\]

\(z\): distance from the atmosphere-snowpack interface, \(H_S\): mean snow depth,
\(k\): permeability, \(\mu\): dynamic viscosity of air, \(U_{10}\): surface wind speed,
\(h\): relief amplitude, \(\lambda\): relief wavelength, \(\alpha\): horizontal aspect ratio of reliefs

(if \(\alpha < 1\) then elongated in the wind direction like sastrugi)
Total diffusivity = wind-pumping (assume as eddies) + molecular diffusion

\[ K_{pump} = \overline{V}_Z \times \Delta Z \]

\[ \Delta Z : \text{model grid spacing (3.5cm)} \]

U_{10} = 8 \text{ m/s}

- red: H = 15 cm, \( \lambda = 10 \text{ m} \)
- blue: H = 1.5 cm, \( \lambda = 1 \text{ m} \)

\[ \alpha = 0.2 \quad K = 4 \times 10^{-9} \text{ m}^2 \]
Model settings (atmosphere)

- T = 258 K, RH = 80% (ABL) or 100% (in snow)
- Solar zenith angle for April 20, 80°N (24-h sunlit)
- Snow albedo = 0.8; Total ozone = 400 DU
- Initially, O₃ = 40 ppbv, inorganic Br (gas) = 0, C₂H₂ = 400 pptv, etc. etc.
- C₂H₄ = 0 (for now not to handle oxygenated organic bromine formation)
- Sub-μm sulfate aerosols (esp. for halogen recycling):
  - pH ~ 0.5
  - LWC = 3.0x10⁻¹² cm³(aq)/cm³(air)
  - Particle radius = 0.1 μm
Model settings (snowpack)

- Snow depth: 35 cm
- Snow density: 0.31 g/cm³ (porosity = 0.663)
- Grain radius: 0.5 mm
- Permeability: 4x10⁻⁹ m²
- 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)
  - CH₃CHO: 4.25E+8 molecule cm⁻² sec⁻¹ (daily mean)
Snowpack brine layer conditions

- Initial bulk concentrations of solutes (in mol/L):
  \[ \text{[Na}^+\text{]} = 7.5\times10^{-5}, \text{[Cl}^-\text{]} = 7.0\times10^{-5}, \]
  \[ \text{[NO}_3^-\text{]} = 5.0\times10^{-6}, \text{[Br}^-\text{]} = 1.15\times10^{-7}, \]
  Alkalinity = 0 (assumed to have been titrated by nitrate)
- Brine volume fraction (at 258 K) \(\sim 1.6\times10^{-5}\)
  - Based on a FPD-type model by Cho et al. (2002)
- pH in brine layer \(\sim 3\) to 4
  - Buffered by gaseous HCl around 100 pmol/mol in the present model runs (perhaps)
$U_{10} = 8 \text{ m/s}$, $H_s = -15 \text{ W/m}^2$ (⇒ $Z_{ABL} = 272 \text{ m}$)

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

Wind-pumping “diffusivity” is switched off
$U_{10} = 3 \text{ m/s}, H_s = -3 \text{ W/m}^2 \Rightarrow Z_{ABL} = 43 \text{ m}$

Wind-pumping “diffusivity” is switched off
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
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 km²

FY: Infinite source of Br⁻ assumed for Br₂ production
MY: Available Br⁻ limited by HBr deposition and no storage,
    but infinite Cl⁻ source assumed for BrCl (= 0.5*Br₂) production
LS: Same as MY but with no Cl⁻ source
Air-Surface Bromine Exchange
Rate over 24 h on 20 April 2001
(a) GEM Surface Meteorology

(b) GEM-AQ Surface Ozone (RUN 3: $T_c = -10^\circ C$, Net Bromine Release From FY Sea Ice Only)
(c) GEM-AQ BrO AVCD (RUN 4: $T_e = -15^\circ C$, Net Bromine Release From FY Sea Ice Only)

(d) GEM-AQ BrO AVCD (RUN 5: $T_e = -20^\circ C$, 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 °C or possibly higher.
Acknowledgment

• CFCAS, OME, CFI, OME, CFI, OIT & NSERC (for GEM-AQ & PHANTAS)
• EC CARA II (for PHANTAS plus Hg chemistry)
• Univ. of Bremen & EU THALOZ project (for GOME)
• UK NCEO (for SLIMCAT)