Supplementary Information for "Halogen Activation via Interactions with Environmental Ice and Snow": Photolysis lifetimes of halogen-containing species in snowpack

Snowpack is an efficient reactor for photolysis reactions [Domine and Shepson, 2002], with UV and visible solar radiation penetrating tens of centimeters [France et al., 2011a] As part of the review, calculations are presented for the photolysis lifetimes of a number of halogenated species in three hypothetical snowpacks. These photolytic lifetimes allow for comparison to the rates of other processes that may consume the halogen species in the snowpack. The three hypothetical snowpacks are a melting snowpack, a coastal snowpack and a cold polar snowpack, each with different optical properties that will affect the rate of photolysis. The photolysis lifetimes, τ, are calculated as the reciprocal of the photolysis rate coefficient, *J*,

$$\tau = \frac{1}{J} \qquad \text{(SI-I)}$$

Lifetimes were calculated for the following photolysis reactions

$Cl_2 + h\nu \rightarrow 2Cl$ (SI-1)
$Br_2 + h\nu \rightarrow 2Br$ (SI-2)
$BrCl + h\nu \rightarrow Br + Cl$ (SI-3)
$ClO + h\nu \rightarrow Cl + O$ (SI-4)
$BrO + h\nu \rightarrow Br + O$ (SI-5)
$HOCl + h\nu \rightarrow$ products (SI-6)
$HOBr + h\nu \rightarrow$ products (SI-7)
$ClONO_2 + h\nu \rightarrow$ products (SI-8)
$BrONO_2 + h\nu \rightarrow$ products (SI-9)

$CH_2ClI + h\nu \rightarrow$ products (SI-10)
$CH_2Br_2 + h\nu \rightarrow$ products (SI-11)
$CHCl_2Br + h\nu \rightarrow$ products (SI-12)
$CHClBr_2 + h\nu \rightarrow$ products (SI-13)
$CH_3I + h\nu \rightarrow$ products (SI-14)
$CH_2I_2 + h\nu \rightarrow$ products (SI-15)

Note, J is defined (for reaction 1) as

$$\frac{d[Cl_2]}{dt} = -J[Cl_2] \qquad \text{(SI-II)}$$

and calculated by

$$J = \int \sigma(\lambda, T)\Phi(\lambda, T)F(\theta, z, \lambda)\,d\lambda \qquad \text{(SI-III)}$$

where σ, is the gaseous molecular absorption cross-section taken from Sander et al, [2010], as a function of wavelength,λ, and temperature, T; Φ is the quantum yield also taken from Sander et al, [2010] and is unity for reactions; F is the spherical irradiance (or 'actinic flux') as a function of solar zenith angle, θ, depth in the snowpack, z, and wavelength. For the calculations of photolysis lifetime presented here the halogen species in reactions (1-15) are considered as gas-phase species that have been released or advected into the pore space in the snowpack. The photolysis coefficient, *J*, is calculated as a function of solar zenith angle and snowpack depth (snowpack thickness is 1m), and plotted as lifetime, τ, versus solar zenith angle and depth. Values of the photolysis rate constants are calculated using a coupled atmosphere-snow radiative-transfer model, TUV-Snow [Lee-Taylor and Madronich, 2002]. Detailed explanation is by Lee-Taylor and Madronich (2002), and the values of the photolysis rate coefficients are calculated in an analogous manner as described by France et al (2011b). The radiative-transfer calculations used the optical properties of the melting snowpack were σ_{scatt}= 1 $m^2\ kg^{-1}$, σ^{+}_{abs}=10 $cm^2 kg^{-1}$ with a density=0.5 g cm^{-3}; for the coastal snowpack σ_{scatt}= 7 $m^2\ kg^{-1}$, σ^{+}_{abs}=5 $cm^2 kg^{-1}$ with a density=0.4 g cm^{-3} and for the cold polar snowpack σ_{scatt}= 25$m^2\ kg^{-1}$, σ^{+}_{abs}=0.2 $cm^2 kg^{-1}$ with a density=0.3 g cm^{-3}. The optical properties of the melting, coastal and cold polar snowpacks are loosely based on work in Cairngorms/Ny-Alesund, Browning Pass/Barrow, and Dome C/Alert respectively [Fisher et al, 2005;France et al, 2011a;Beine et al, 2006; France et al 2011b; Grenfell and Maykut, 1977; France et al 2011c;King et al, 2001].

The modeled snowpack was 1m thick with an under snow albedo of 0.1. The Earth-Sun distance was 1 au and the atmosphere contained no cloud or aerosol. An ozone column of 300 Dobsons was used for all calculations. An 8 stream pseudo-spherical DISORT scheme was used to calculate radiances. Radiances were calculated at 108 uneven snowpack depths at twenty solar zenith angles between 0°-90° in equal intervals of cosθ. The absorption cross-section of ice is described in [Lee-Taylor and Madronich, 2002].

Figures 1,2 and 3 contain the results of the photolysis lifetime calculations. The lifetimes in seconds are plotted as isopleths against depth and solar zenith angle. Vertical columns of these lifetime plots correspond to the same hypothetical snowpack whilst rows of these lifetime plots correspond to the same photolysis reaction. The exception is row 1 of Figure 1; the albedo and *e*-folding depths for the three hypothetical snowpacks considered are in the top row of Figure 1 to enable other workers to match the snowpack of interest to the correct column of the figure depending on albedo and *e*-folding depth measurements. Albedo measurements are solar zenith angle dependent whilst values of *e*-folding depth are not solar zenith angle dependent. The second row of Figure 1 contains photolysis lifetime data for the photolysis of NO_2 in the snowpack as a comparison with the halogen compounds. The photolytic formation of NO_2 from NO_3^- photolysis has been one of the most studied photolytic systems and thus the photolysis lifetime of NO_2 is included for completeness and comparison. Figures 2 and 3 are a continuation of Figure 1.

Inspection of Figure 1 and 2 highlights that bromine compounds have about an order of magnitude shorter lifetime in the snowpack relative to the chlorine equivalent compound. The melting snowpack has some of the shortest photolytic lifetimes owing to the long *e*-folding depths and the large grains size favouring propagation of light deeper into the snowpack than for the polar coastal snowpacks [Fisher et al 2005]. The largest photolytic lifetimes are associated with the polar costal snowpacks, the photolysis lifetimes in these snowpacks tend to have a weaker solar zenith angle dependence relative to the melting snowpack. The irradiance, photolysis and thus photolysis lifetime display non-asymptotic effects in the top few centimeters of the snowpack as the scattering of direct sunlight is strongly solar zenith angle dependent. Thus the photolysis lifetime calculated at the snow surface is **not** representative of photolysis lifetime in the snowpack directly below it. The scale of Figures 1 and 2 is such that this effect cannot be observed in Figure 1 and 2. For solar zenith angles larger than 50-60° the photolysis lifetime at the snow surface is shorter than the photolysis lifetime in the snowpack a few mm deep. For solar zenith angles less than 50-60° the photolysis lifetime at the snow surface is longer than the photolysis lifetime in the snowpack a few mm deep.

References

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Figure captions

Figure SI-1 Photolysis lifetime isopleths versus snowpack depth and solar zenith angle for the photolysis of NO_2, Cl_2, Br_2, and BrCl in three hypothetical snowpacks: melting, coastal windpack and cold polar. Columns on the figure are for the same snowpack and rows are for the same photolysis reaction. Row 1 details the solar *e*-folding depth and albedo of the three snowpacks as a function of wavelength. Note the *e*-folding depth is invariant with solar zenith angle but albedo is not.

Figure SI-2 Photolysis lifetime isopleths versus snowpack depth and solar zenith angle for the photolysis of HOCl, HOBr, $ClONO_2$, and $BrONO_2$ in three hypothetical snowpacks: melting, coastal windpack and cold polar. Columns on the figure are for the same snowpack and row are for the same photolysis reaction.

Figure SI-3 Photolysis lifetime isopleths versus snowpack depth and solar zenith angle for the photolysis of CH_2ClI, CH_2Br_2, $CHCl_2Br$, $CHClBr_2$, CH_3I and CH_2I_2 in three hypothetical snowpacks: melting, coastal windpack and cold polar. Columns on the figure are for the same snowpack and row are for the same photolysis reaction.

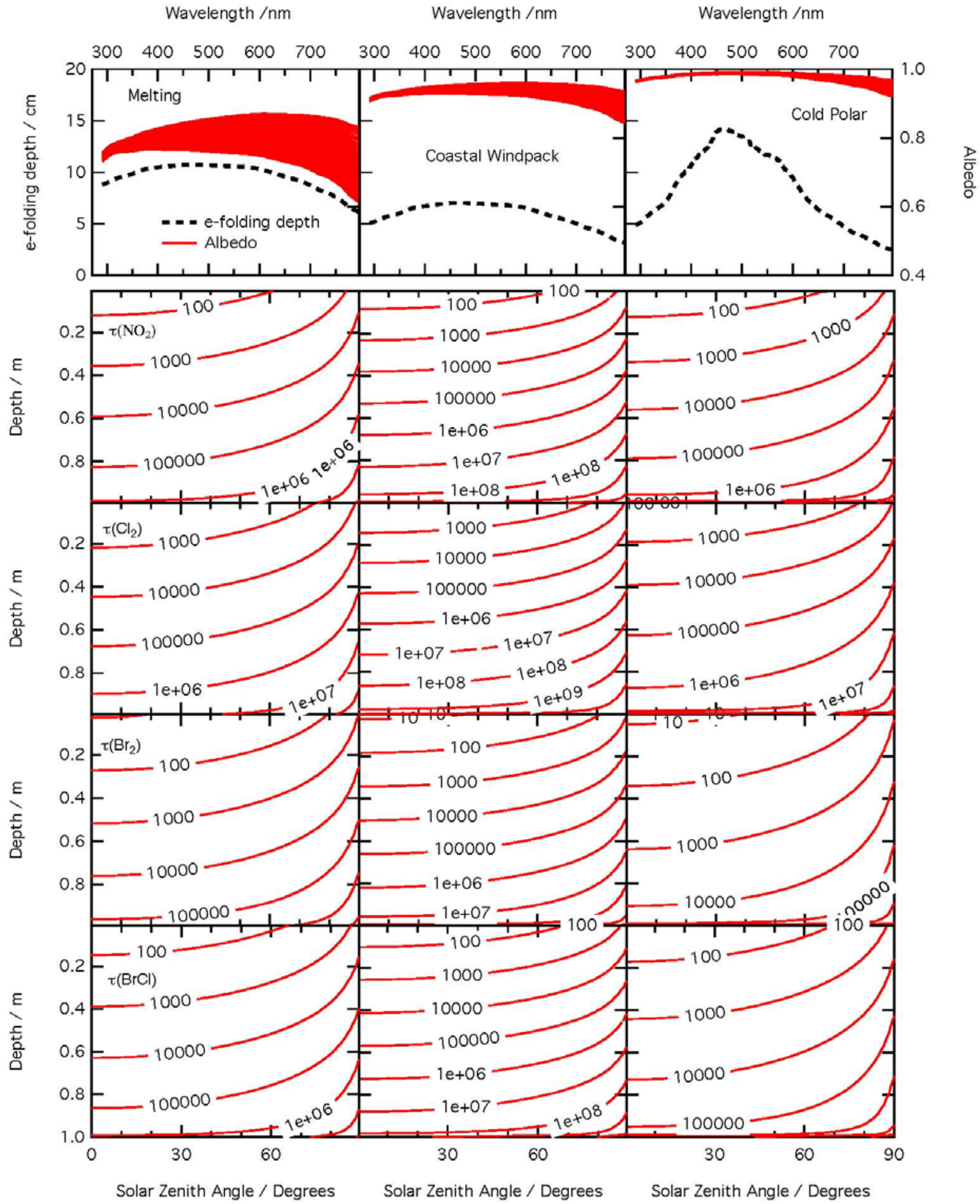

Wavelength /nm
300 400 500 600 700
Melting
Coastal Windpack
Cold Polar
e-folding depth / cm
Albedo
e-folding depth
Albedo
Depth / m
τ(NO2)
τ(Cl2)
τ(Br2)
τ(BrCl)
Solar Zenith Angle / Degrees

Figure SI-1

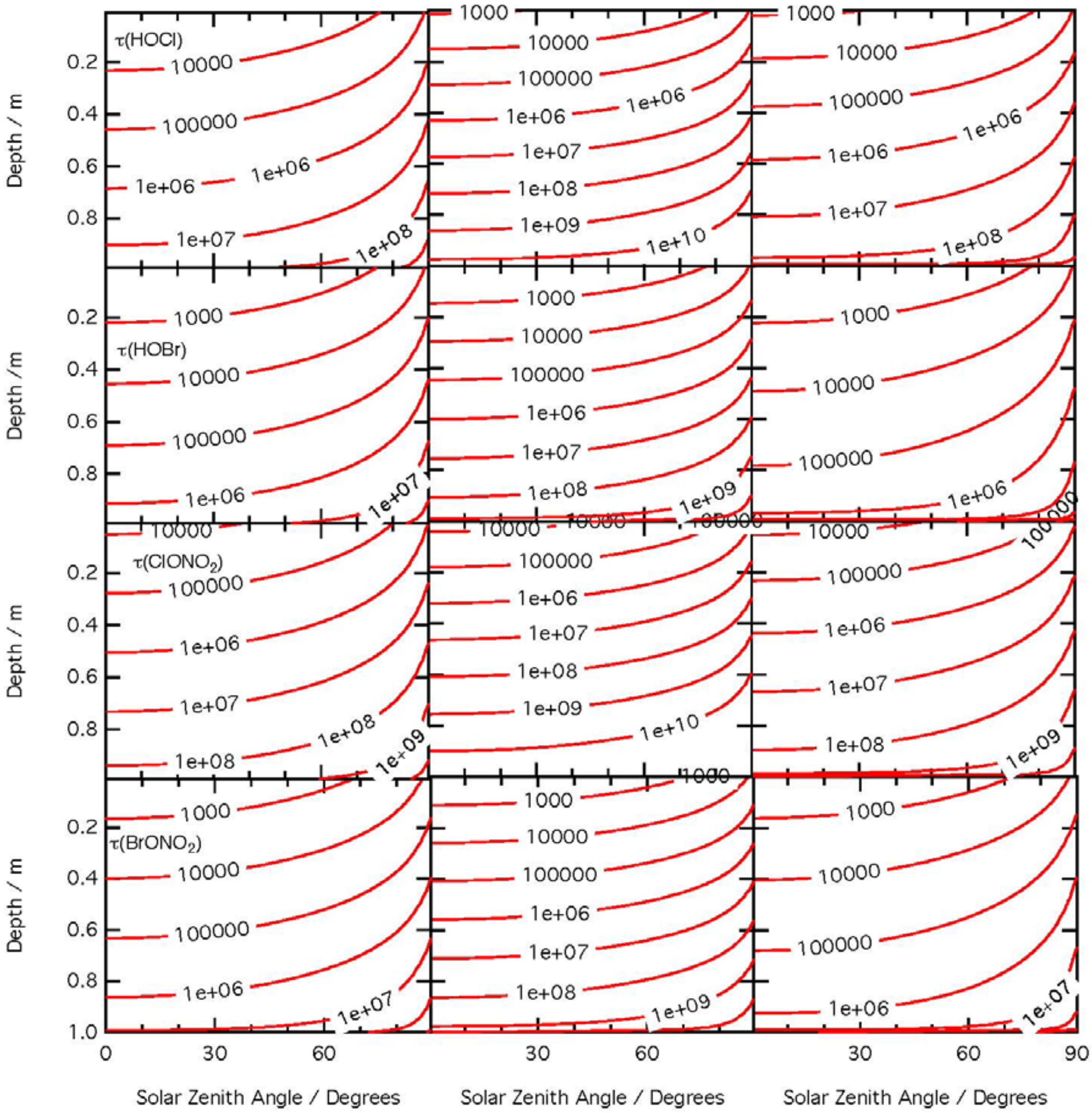
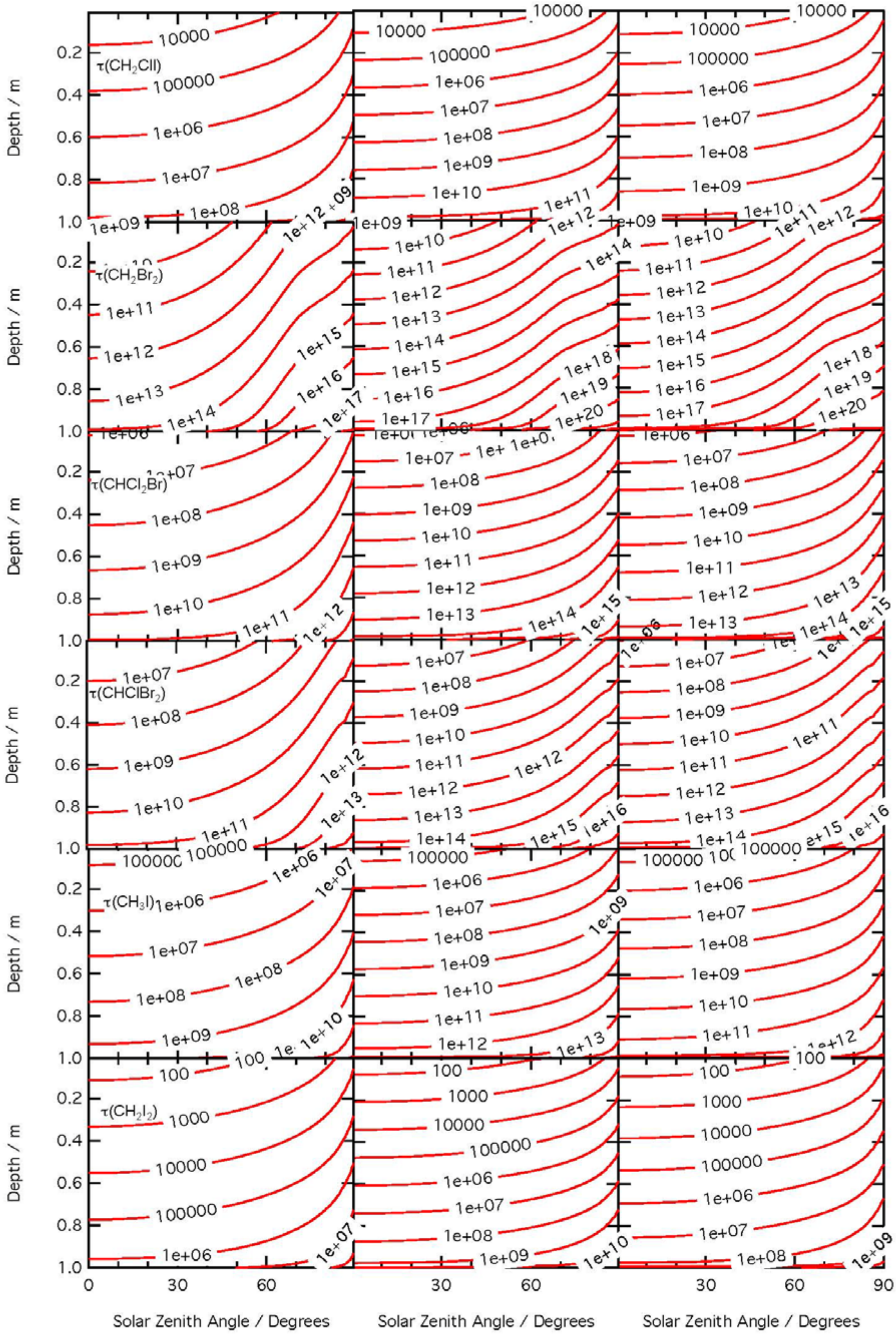

τ(HOCl)
τ(HOBr)
τ(ClONO2)
τ(BrONO2)
Depth / m
Solar Zenith Angle / Degrees

Figure SI-2



τ(CH2ClI)
τ(CH2Br2)
τ(CHCl2Br)
τ(CHClBr2)
τ(CH3I)
τ(CH2I2)
Depth / m
0.2
0.4
0.6
0.8
1.0
0
30
60
90
Solar Zenith Angle / Degrees

Figure SI-3