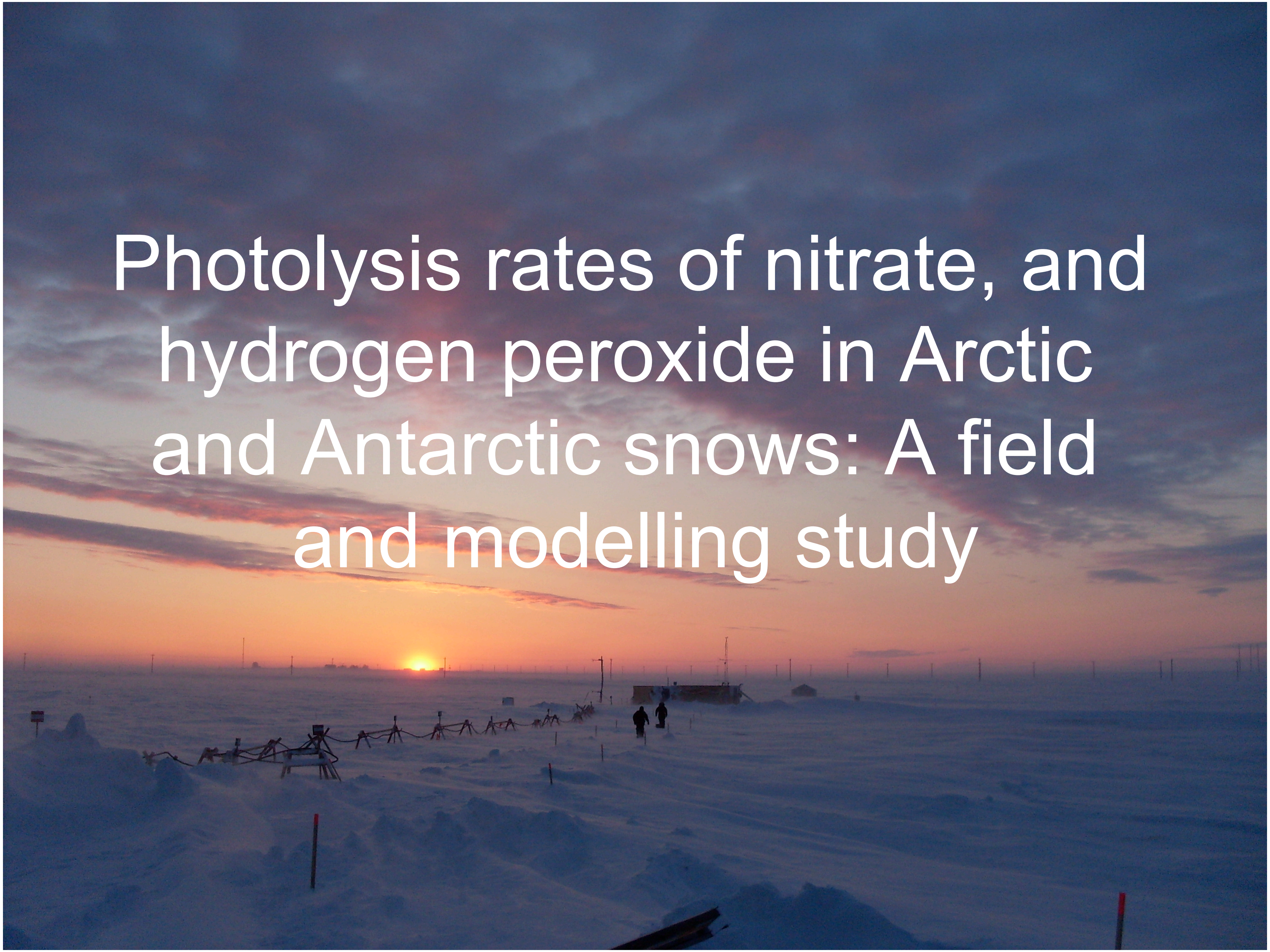
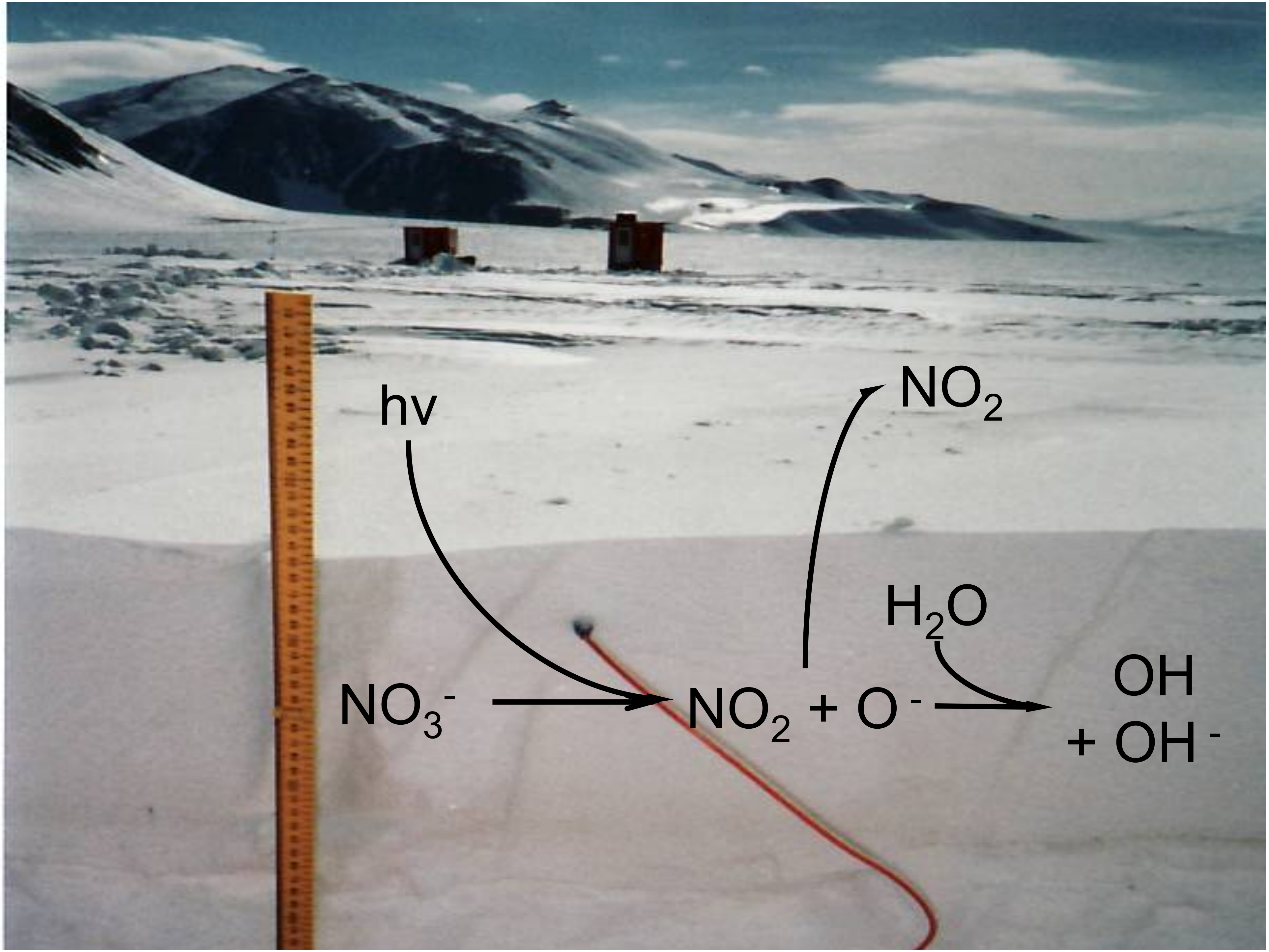
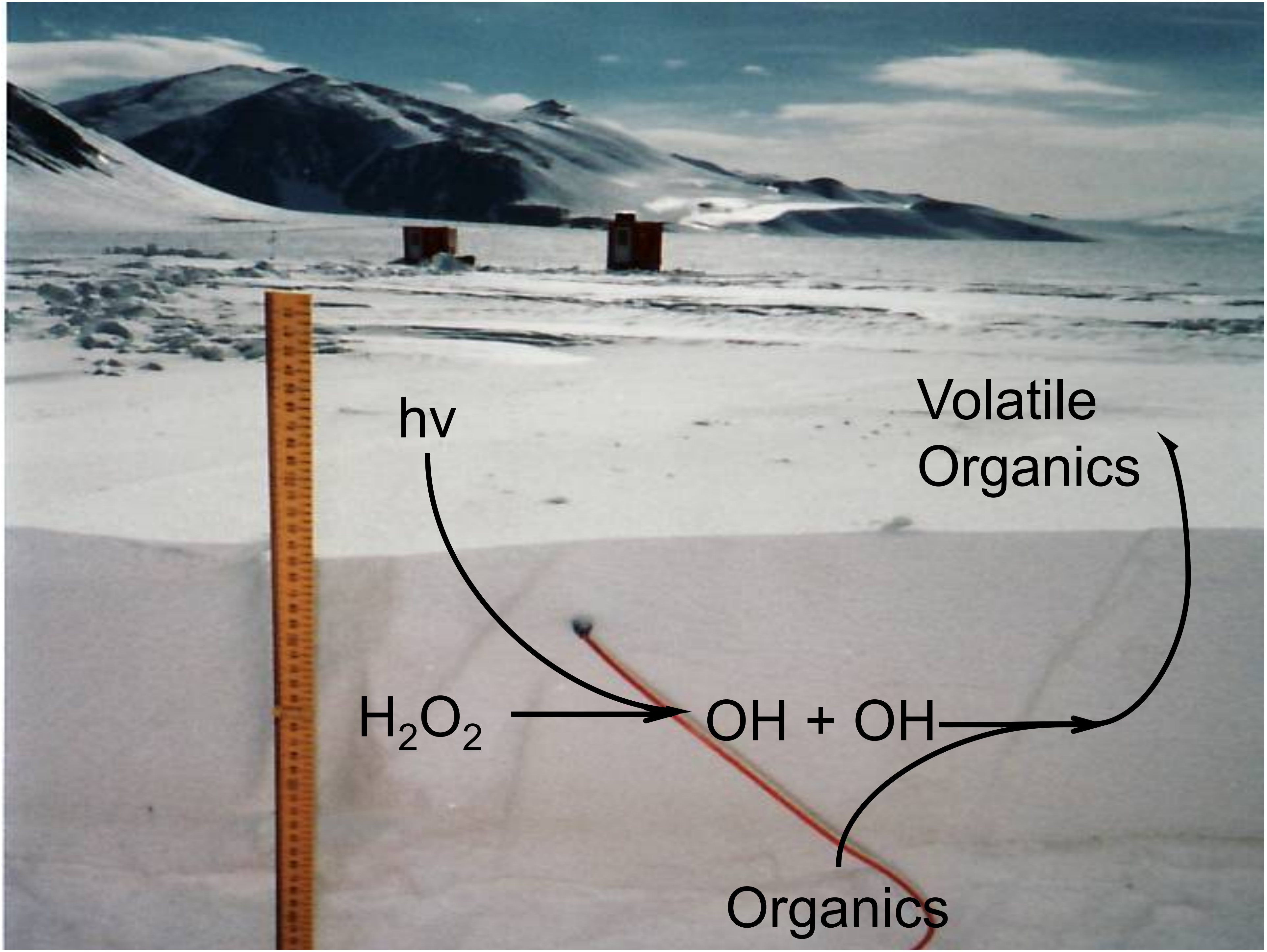


Photolysis rates of nitrate, and hydrogen peroxide in Arctic and Antarctic snows: A field and modelling study

Collaborators and funders.

- RHUL
  - Holly Reay and James France
- BAS
  - Markus Frey
- LGGE
  - Didier Vioson, Florent Domine, Joel Savarino & OPALE
- University of California Davis
  - Cort Anastasio and Harry Beine
- NCAR
  - Julia Lee-Taylor
- Funders
  - NERC, NSF, NERC-FSF, TH RC,


hv
NO_2
H_2O
NO_3^-
$NO_2 + O^-$
OH
$+ OH^-$



hv
Volatile Organics
H2O2
OH + OH
Organics

Calculate a photolysis rate of NO_3^-

$$J = \int \sigma(\lambda)\Phi(\lambda)F_{tot}(\lambda)d\lambda$$

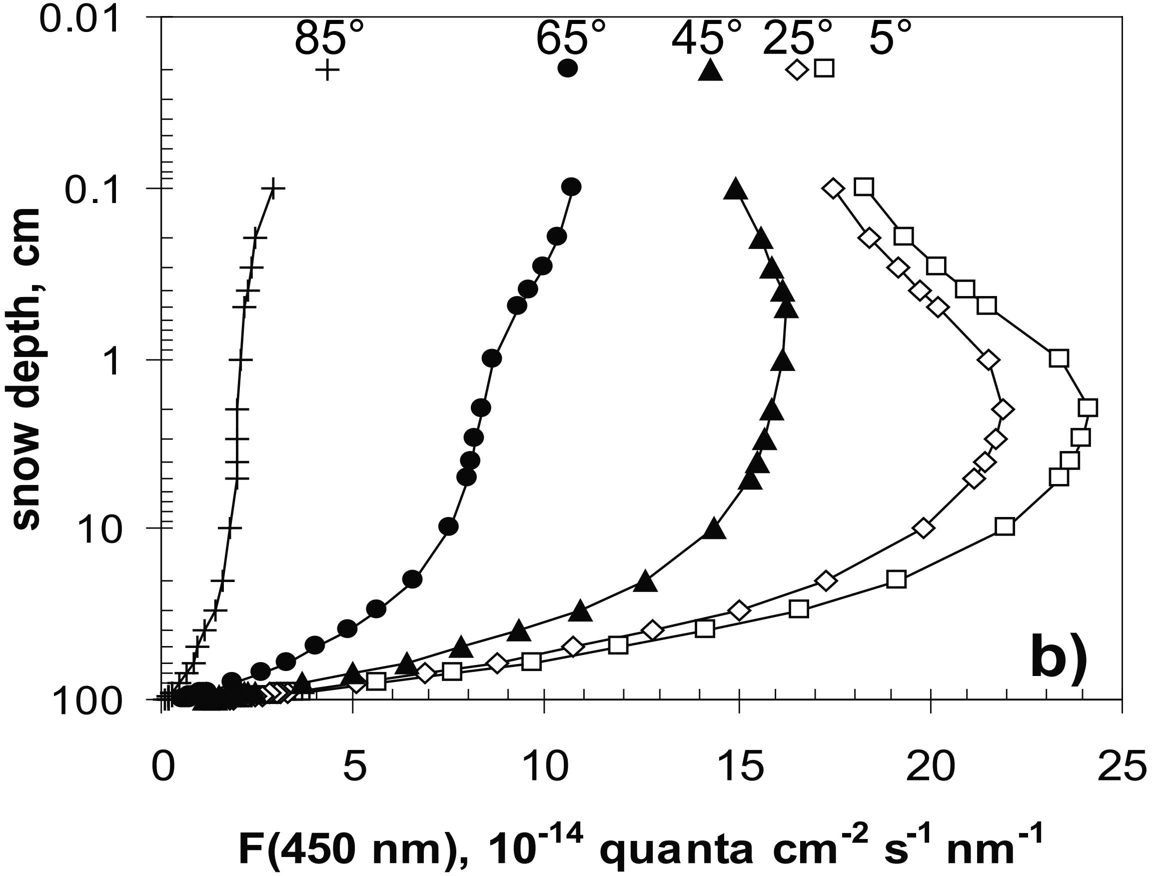
J is the photolytic rate constant (s^{-1}).

σ is the absorption cross section.

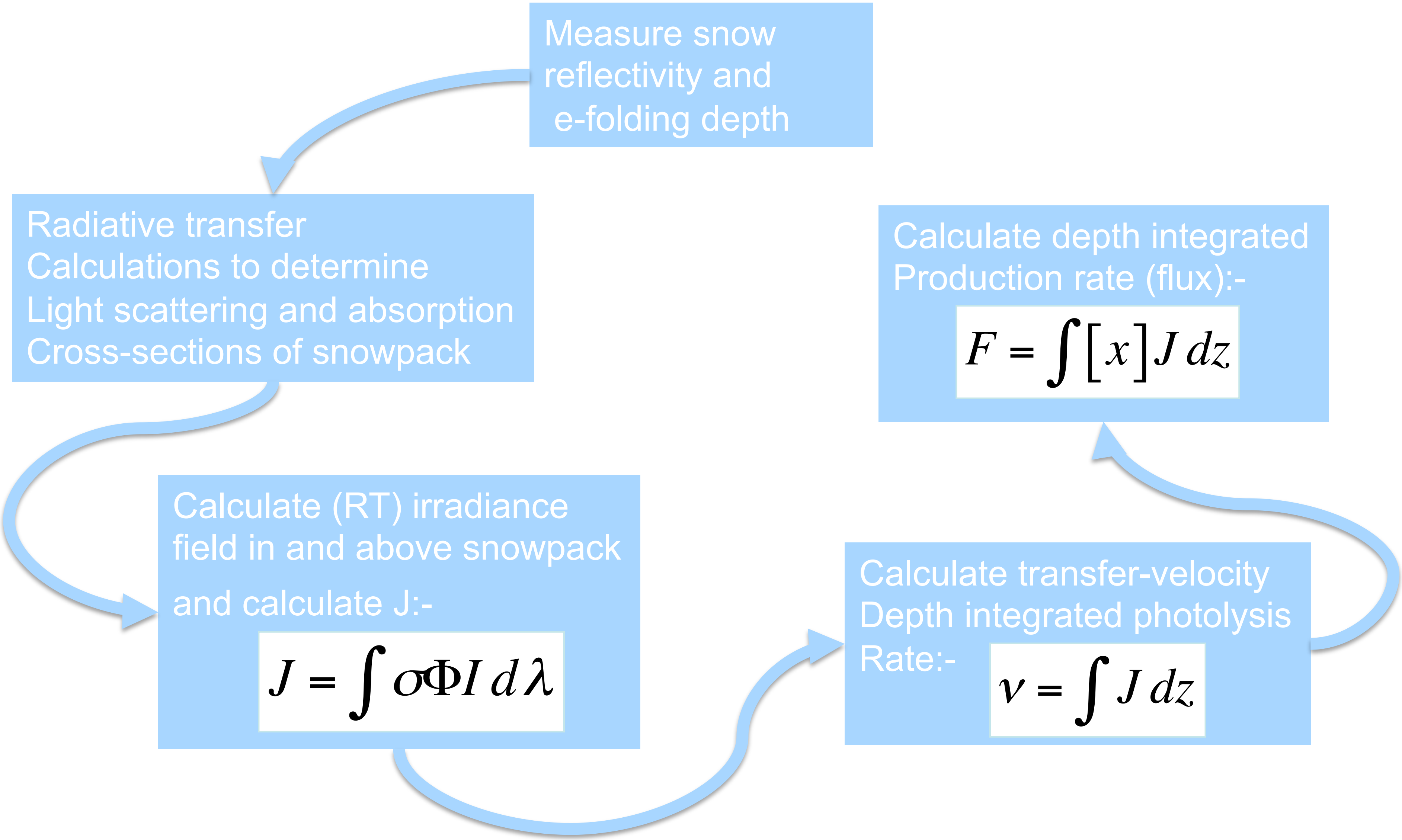
Φ is the quantum yield.

F_{tot} is the total actinic flux

“Actinic flux” in snowpack

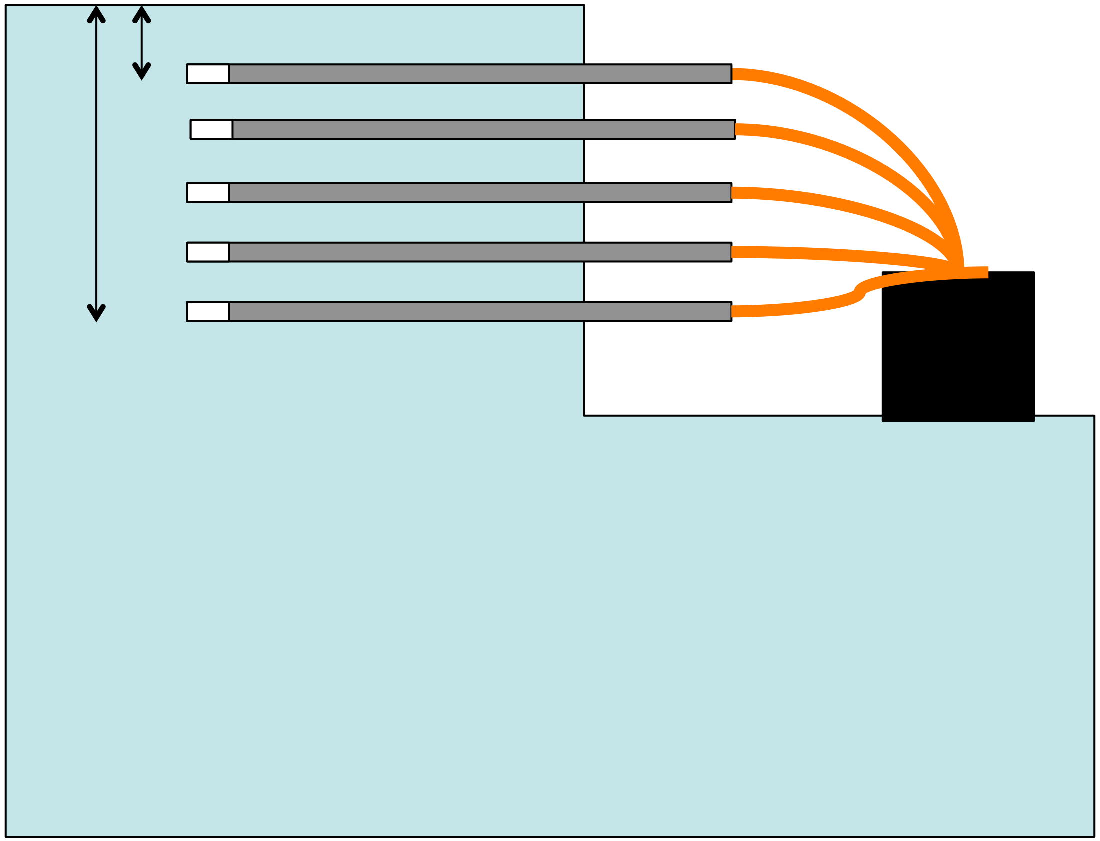


Lee-Taylor and Madronich 2002


Measure snow reflectivity and e-folding depth
Radiative transfer Calculations to determine Light scattering and absorption Cross-sections of snowpack
Calculate (RT) irradiance field in and above snowpack and calculate J:-
$J = \int \sigma \Phi I \, d\lambda$
Calculate transfer-velocity Depth integrated photolysis Rate:-
$\nu = \int J \, dz$
Calculate depth integrated Production rate (flux):-
$F = \int [x] J \, dz$

e-folding depth

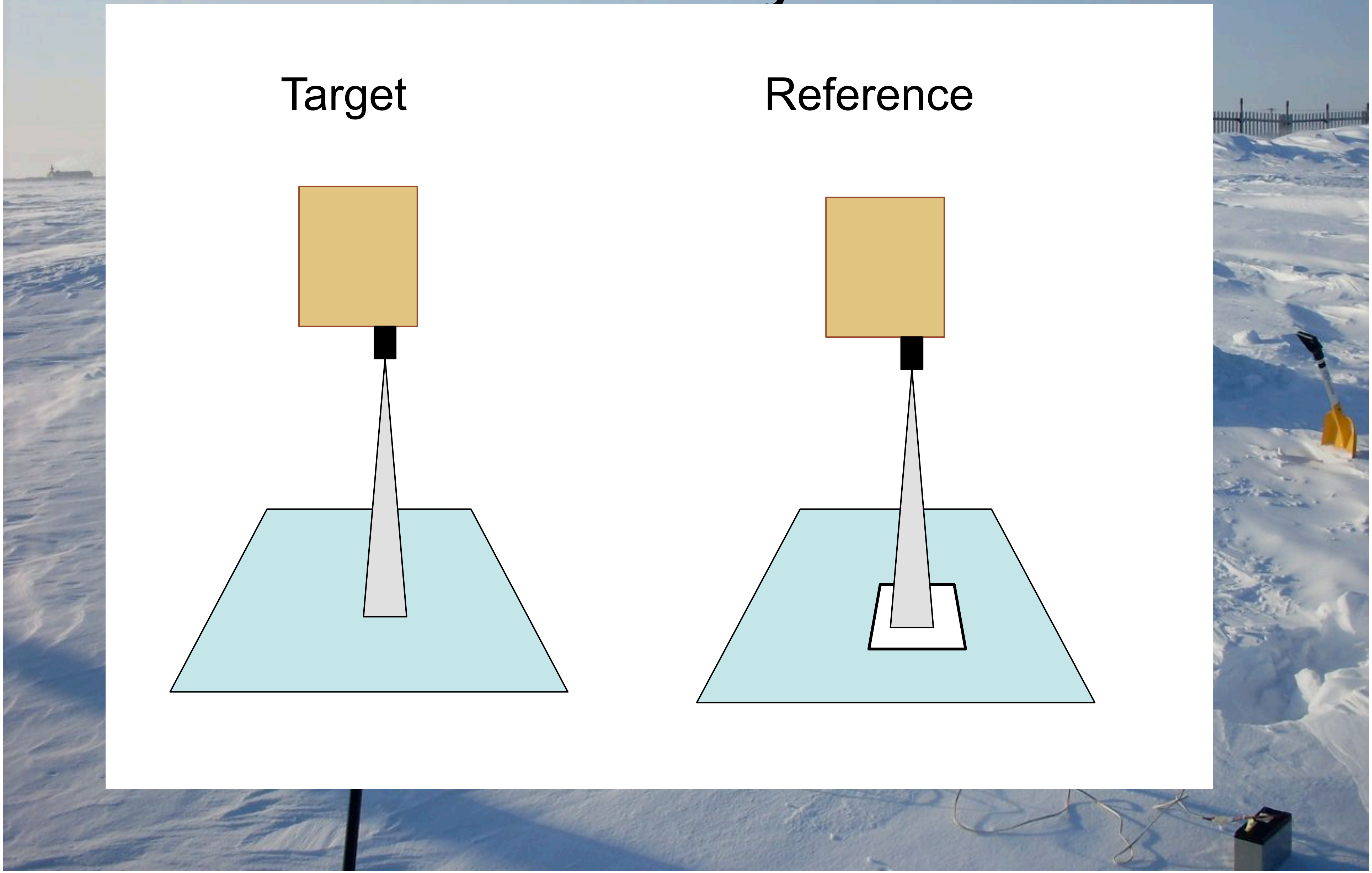
E-folding depth



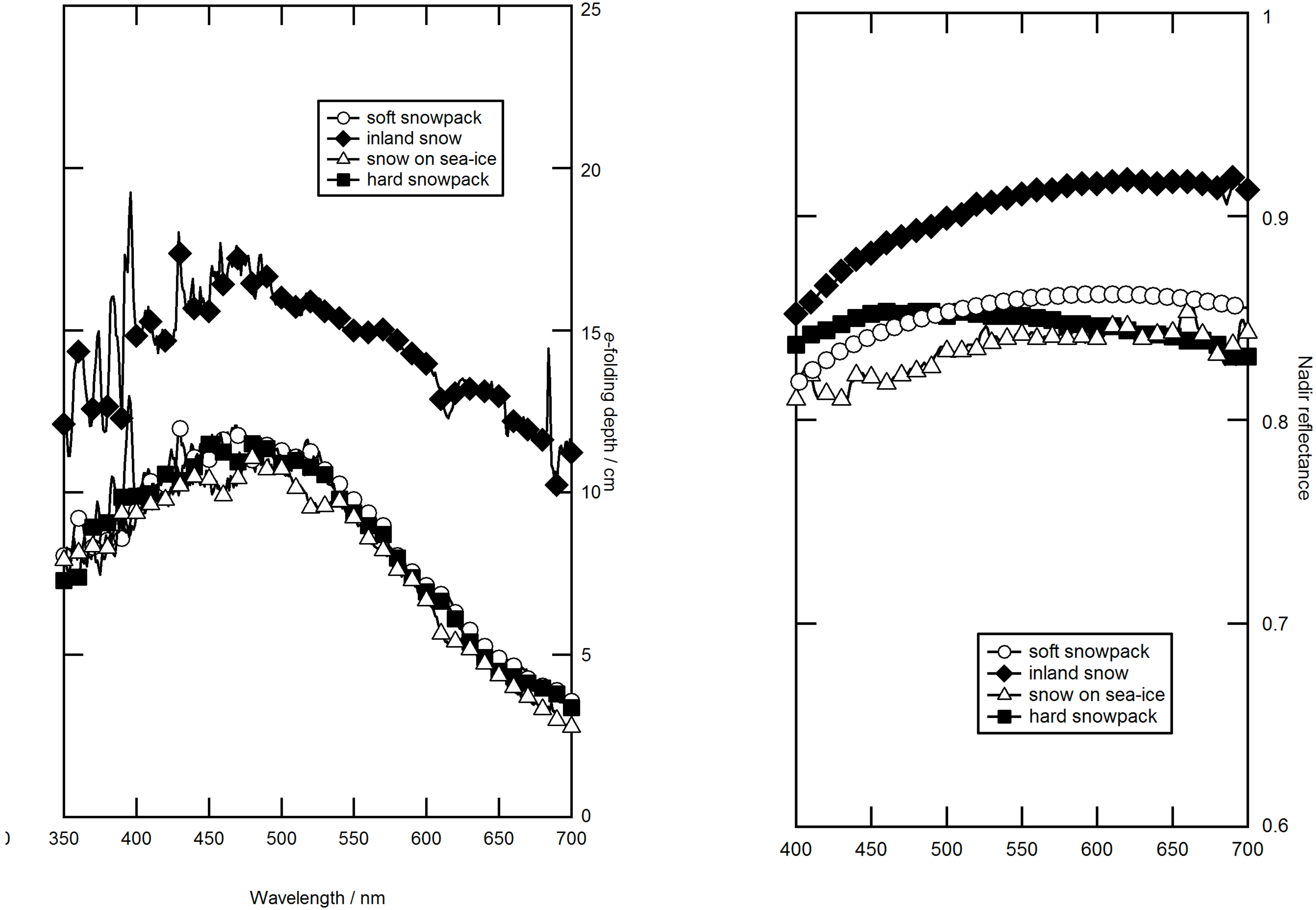
$$\frac{I}{I_0} = e^{\frac{-(d-d')}{\varepsilon}}$$

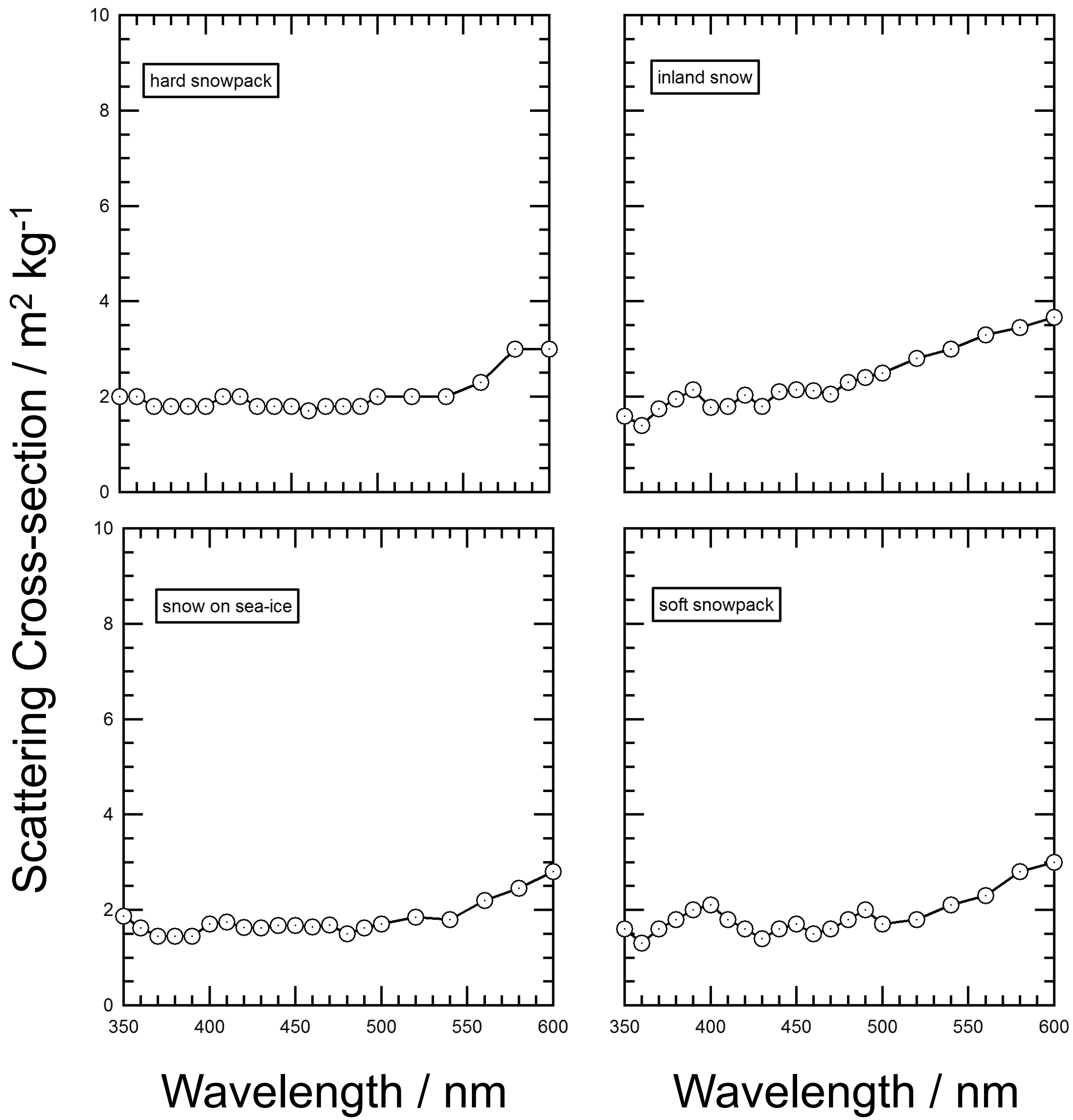
Nadir reflectivity - “albedo”

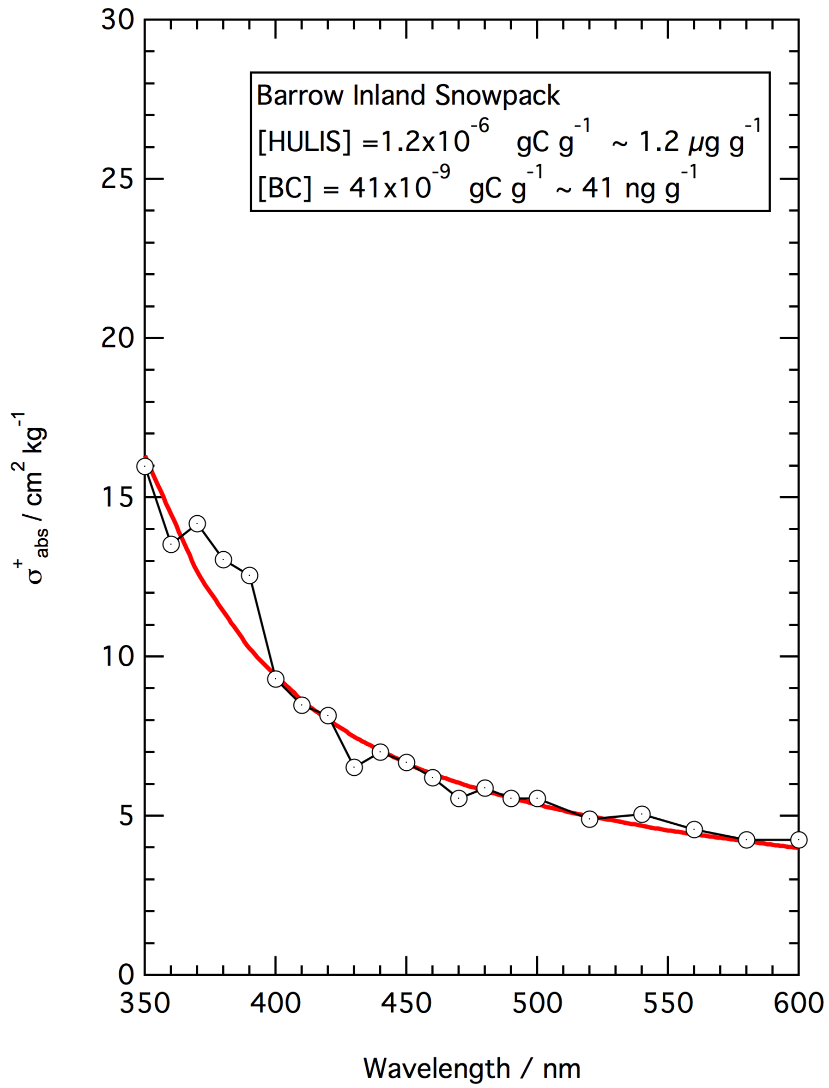
Nadir reflectivity - “albedo”

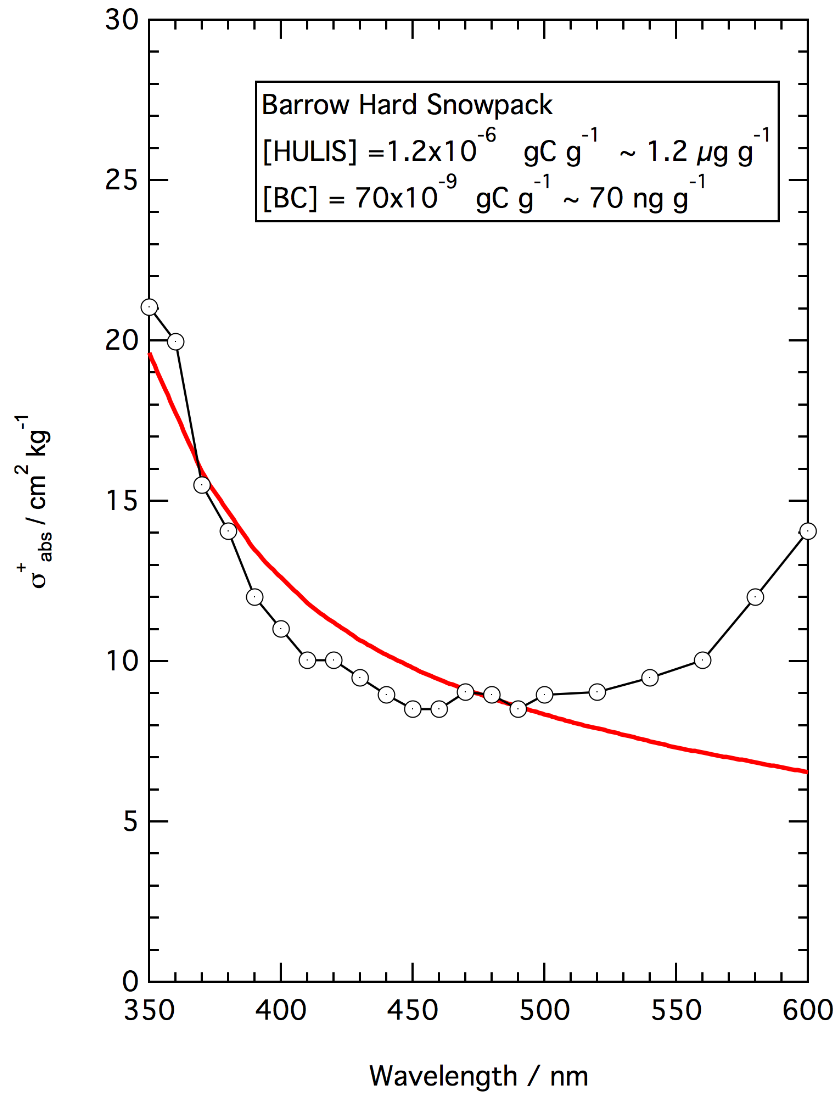


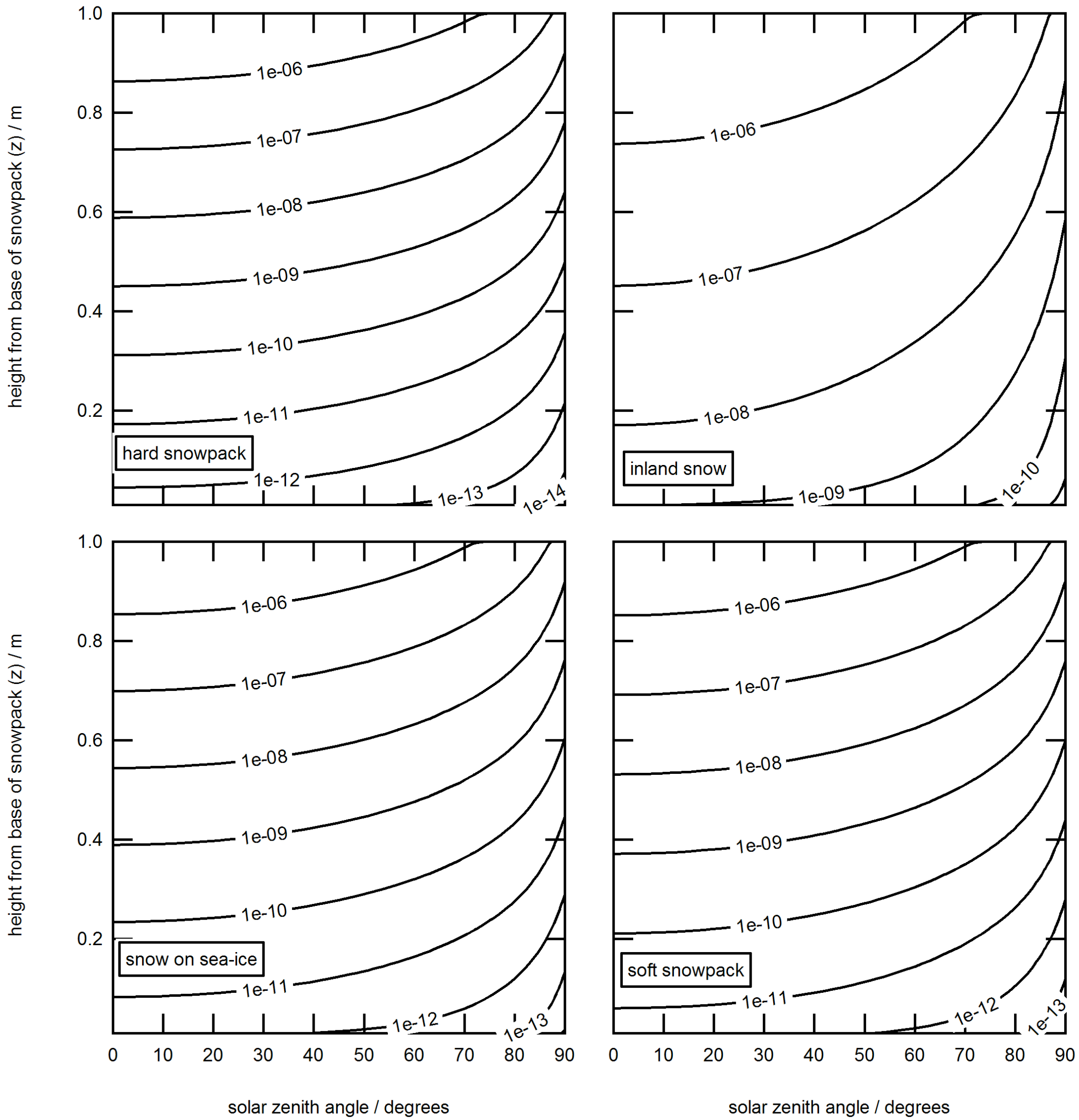

Barrow, Alaska, OASIS 2009


soft snowpack
inland snow
snow on sea-ice
hard snowpack
0
5
10
15
20
25
e-folding depth / cm
350
400
450
500
550
600
650
700
Wavelength / nm
soft snowpack
inland snow
snow on sea-ice
hard snowpack
0.6
0.7
0.8
0.9
1
Nadir reflectance
400
450
500
550
600
650
700


hard snowpack
inland snow
snow on sea-ice
soft snowpack
Scattering Cross-section / m2 kg-1
Wavelength / nm
Wavelength / nm
0
2
4
6
8
10
350
400
450
500
550
600

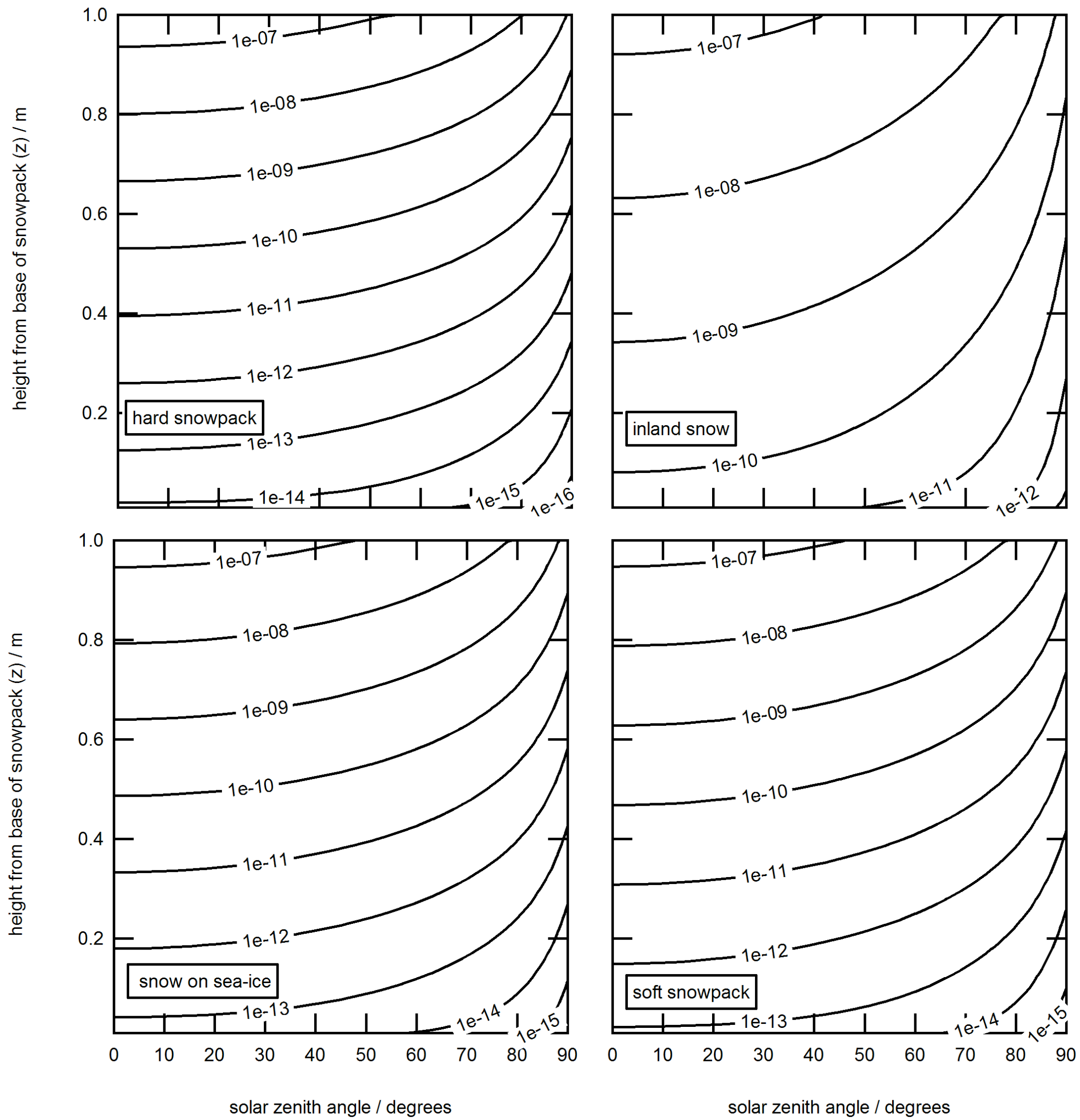

Barrow Inland Snowpack
[HULIS] =1.2x10^-6 gC g^-1 ~ 1.2 μg g^-1
[BC] = 41x10^-9 gC g^-1 ~ 41 ng g^-1
σ+abs / cm2 kg-1
Wavelength / nm


Barrow Hard Snowpack
[HULIS] =1.2x10^-6 gC g^-1 ~ 1.2 μg g^-1
[BC] = 70x10^-9 gC g^-1 ~ 70 ng g^-1
σ+abs / cm2 kg-1
Wavelength / nm



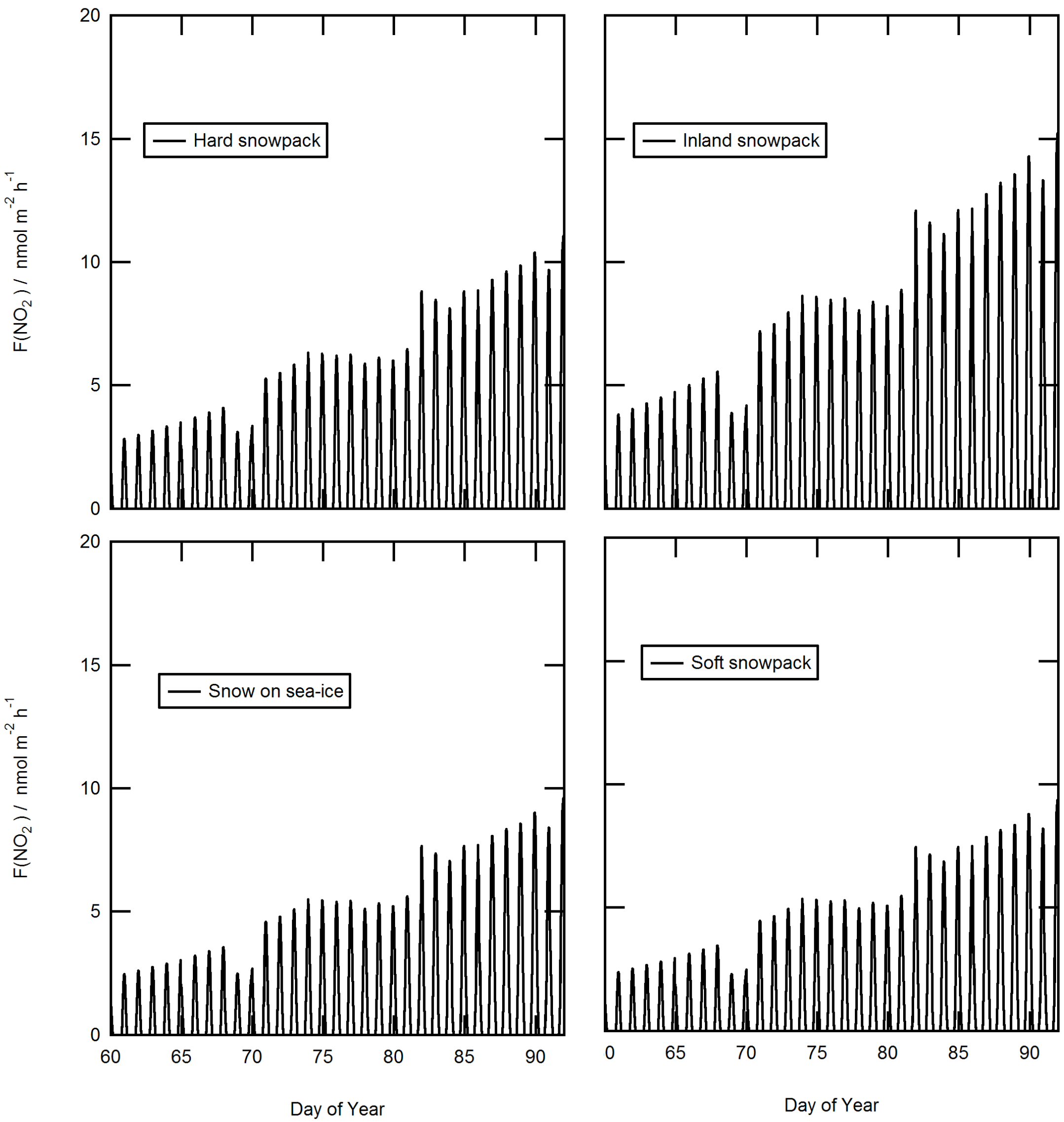
hard snowpack
inland snow
snow on sea-ice
soft snowpack
1e-06
1e-07
1e-08
1e-09
1e-10
1e-11
1e-12
1e-13
1e-14
height from base of snowpack (z) / m
solar zenith angle / degrees
0
10
20
30
40
50
60
70
80
90
0.2
0.4
0.6
0.8
1.0

J(NO_3^-)

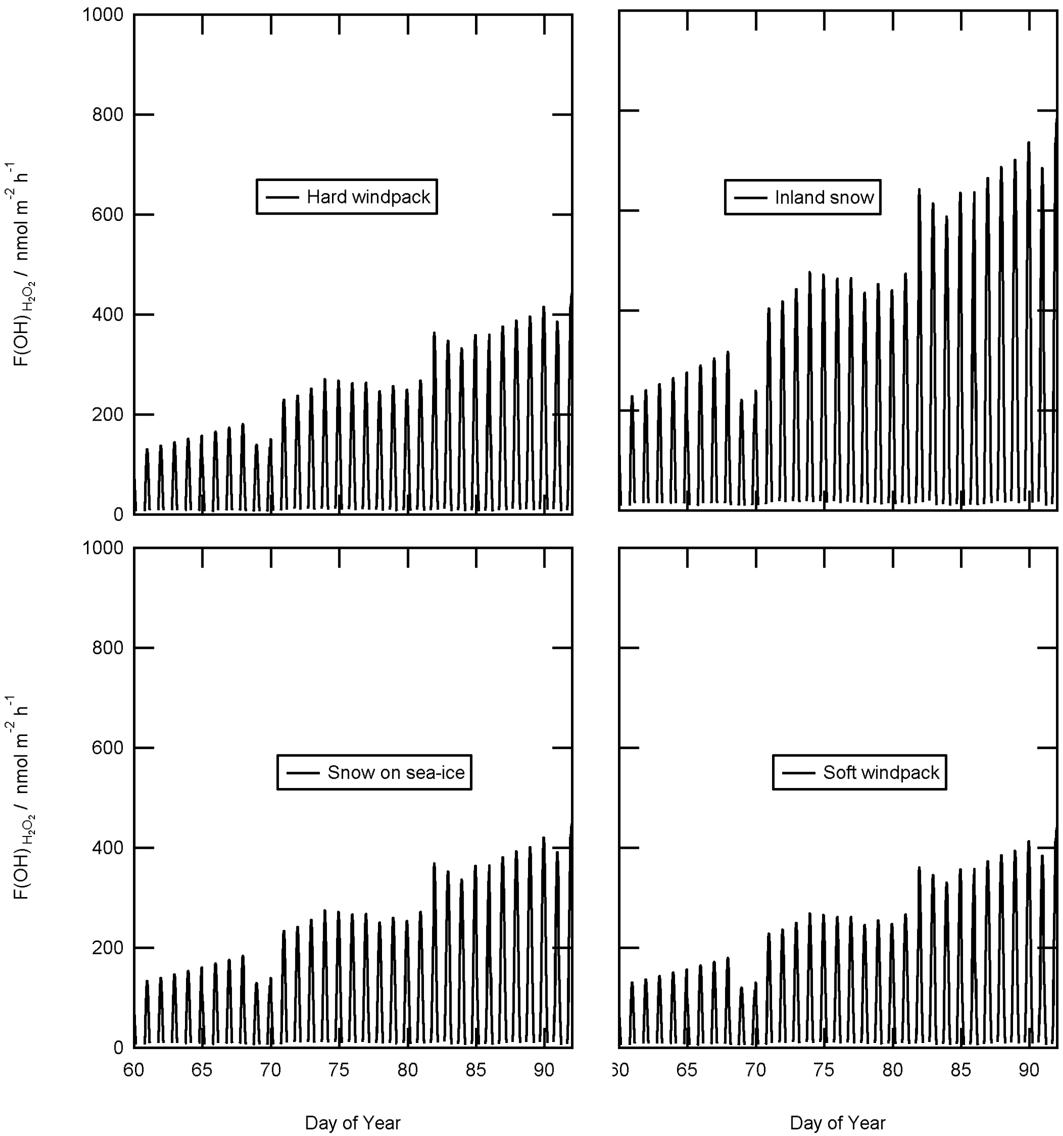


hard snowpack
inland snow
snow on sea-ice
soft snowpack
height from base of snowpack (z) / m
solar zenith angle / degrees
1e-07
1e-08
1e-09
1e-10
1e-11
1e-12
1e-13
1e-14
1e-15
1e-16

$J(H_2O_2)$



Depth-integrated production rate "Potential flux"

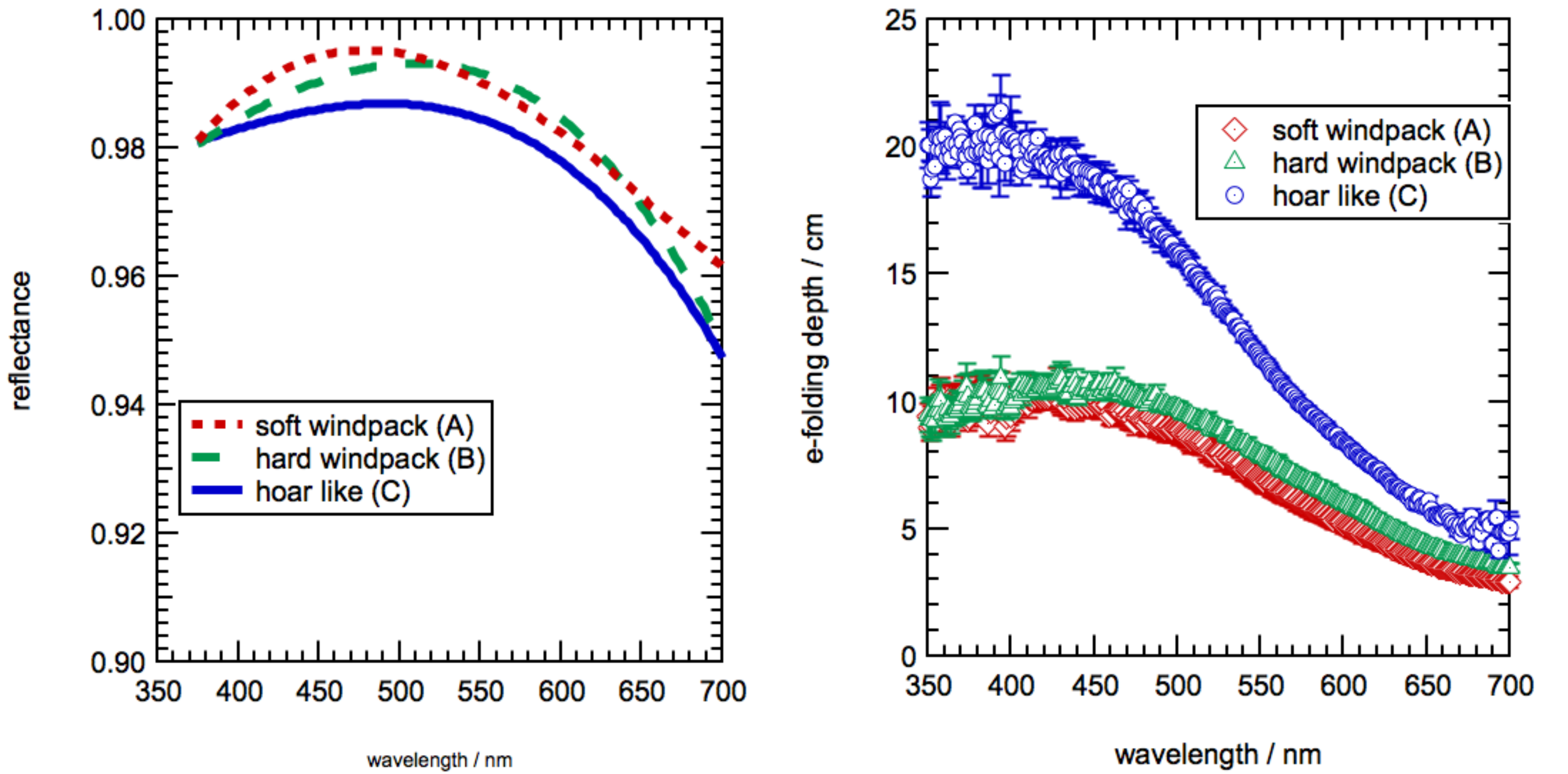


Hard windpack
Inland snow
Snow on sea-ice
Soft windpack
$F(OH)_{H_2O_2}$ / nmol m^{-2} h^{-1}
Day of Year

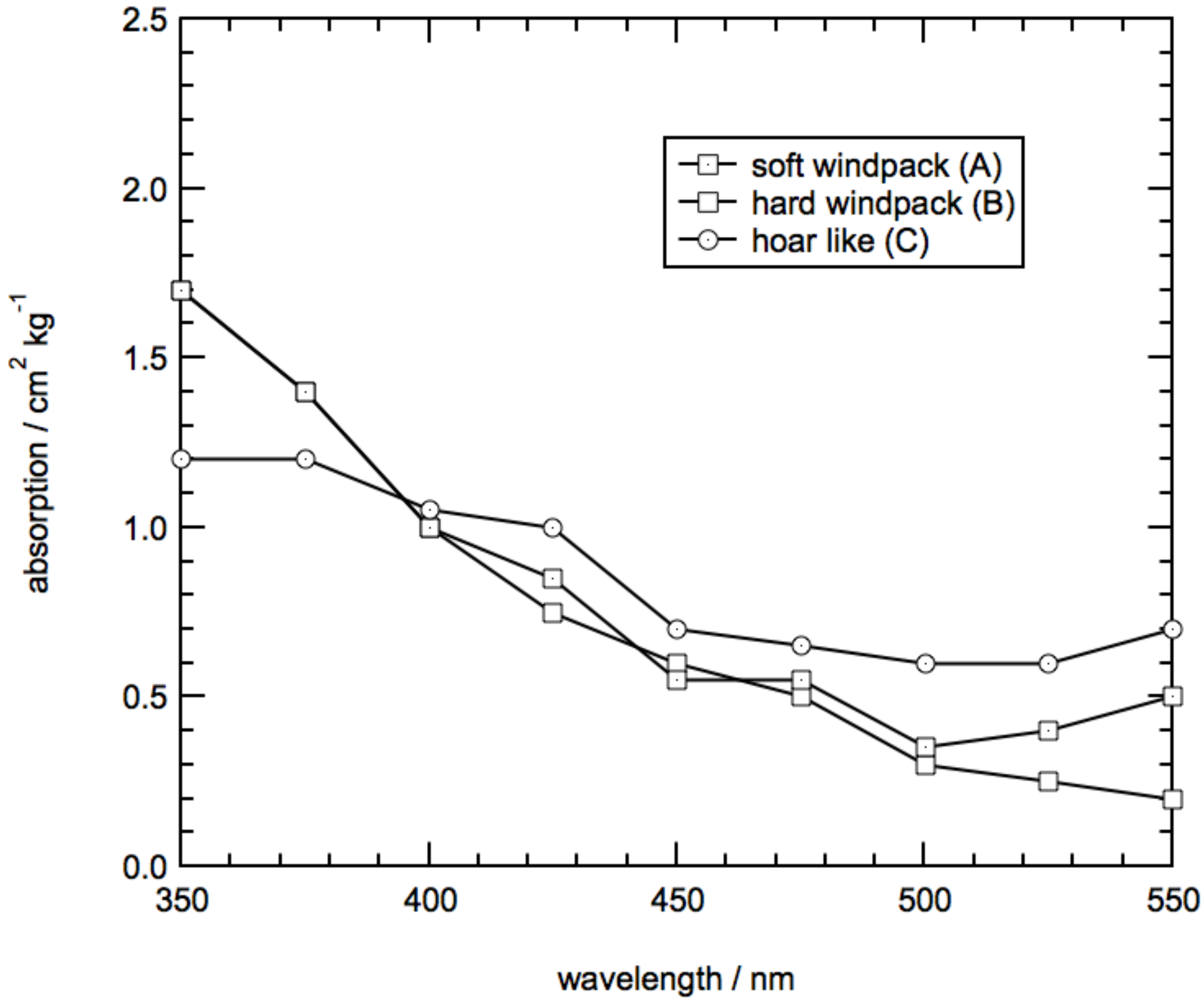

DOME C

DOME C

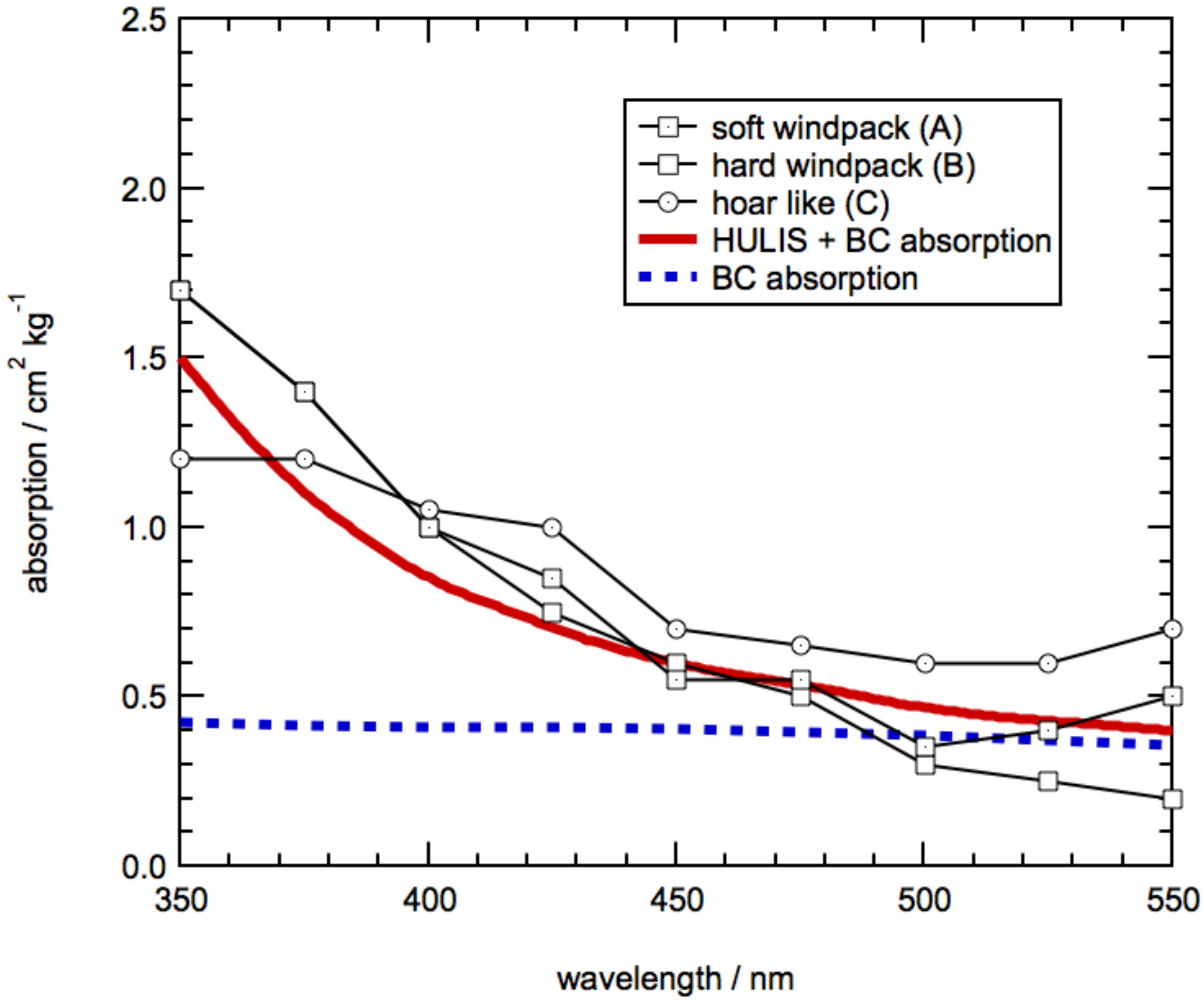
- Three snow layers
- Soft windpack, ε~10cm, A<0.98 (λ~400nm)
- Hard windpack, ε~10cm, A<0.98 (λ~400nm)
- Hoar-like layer, ε~20cm, A<0.98 (λ~400nm)



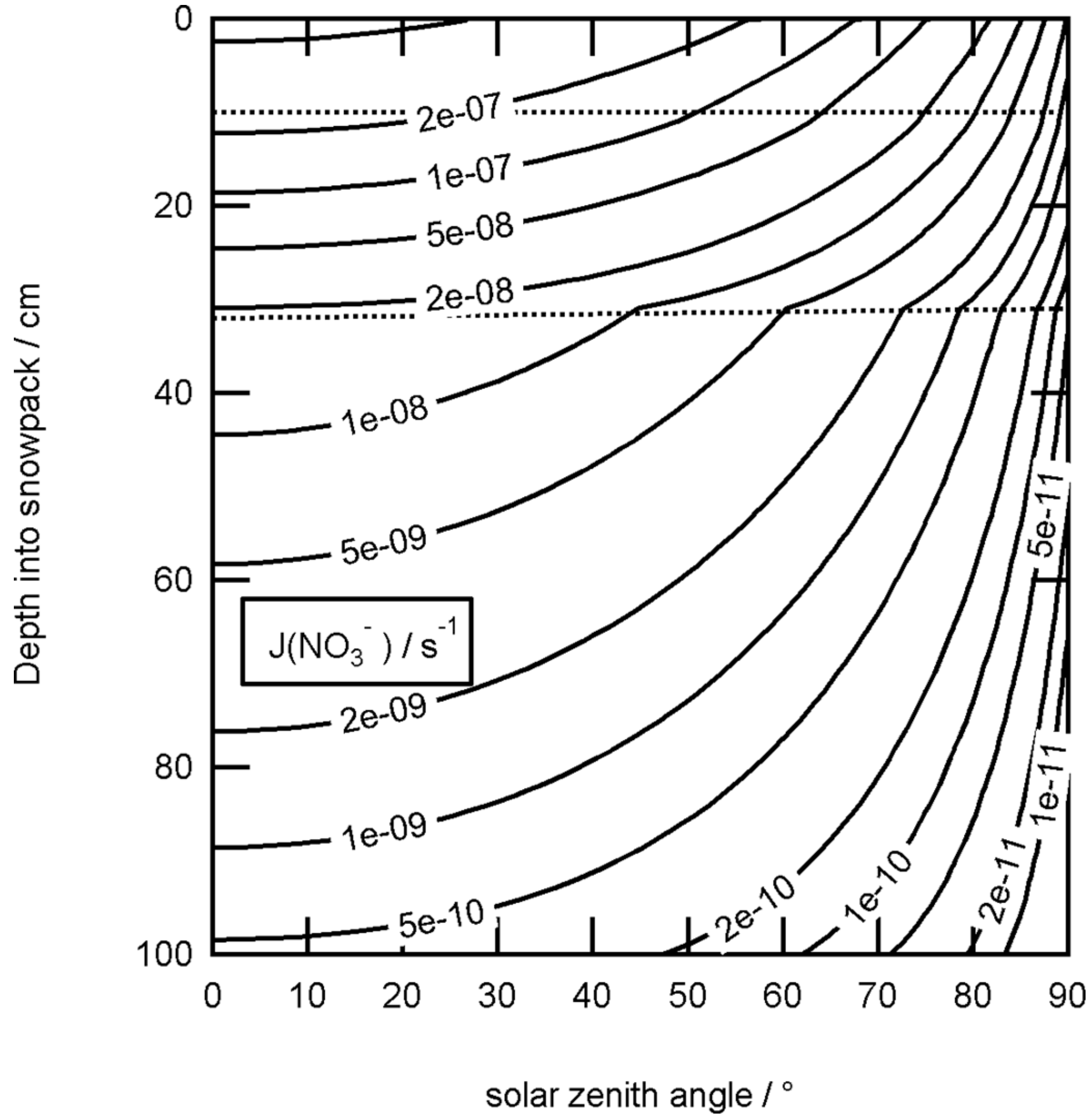
reflectance
1.00
0.98
0.96
0.94
0.92
0.90
350
400
450
500
550
600
650
700
wavelength / nm
soft windpack (A)
hard windpack (B)
hoar like (C)
e-folding depth / cm
25
20
15
10
5
0
350
400
450
500
550
600
650
700
wavelength / nm
soft windpack (A)
hard windpack (B)
hoar like (C)



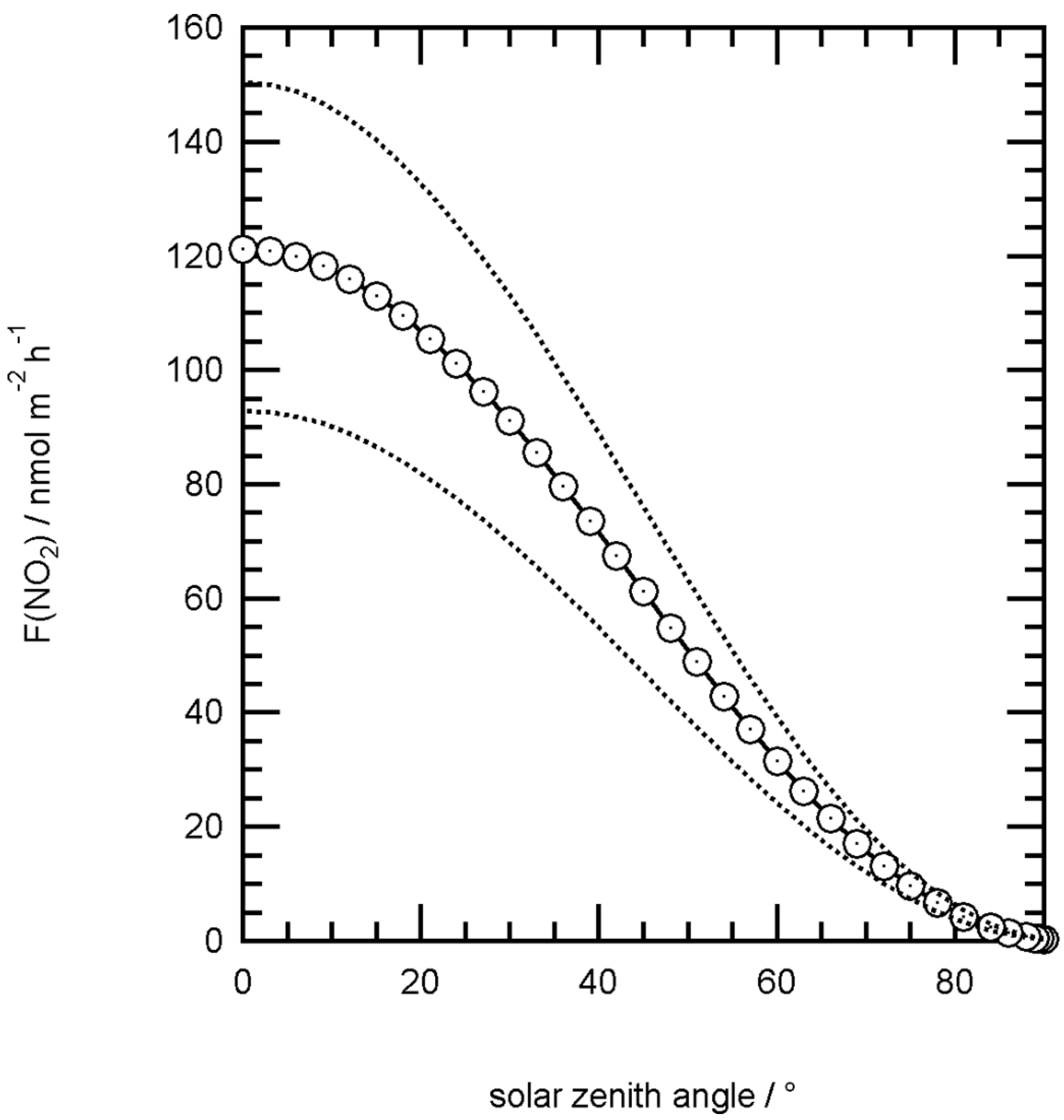
2.5
2.0
1.5
1.0
0.5
0.0
absorption / cm^2 kg^{-1}
350
400
450
500
550
wavelength / nm
soft windpack (A)
hard windpack (B)
hoar like (C)



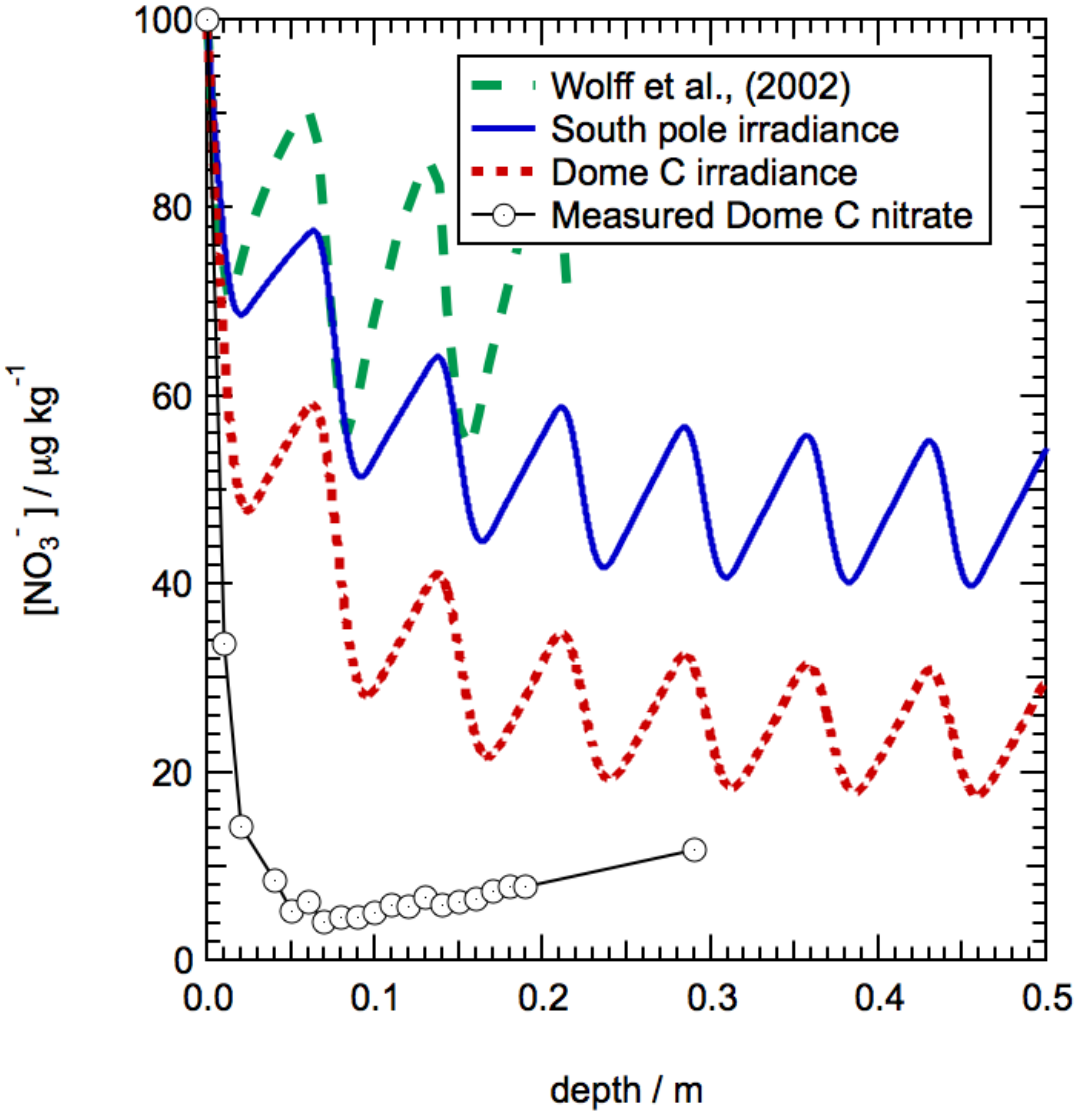
absorption / cm^2 kg^{-1}
wavelength / nm
2.5
2.0
1.5
1.0
0.5
0.0
350
400
450
500
550
soft windpack (A)
hard windpack (B)
hoar like (C)
HULIS + BC absorption
BC absorption



Depth into snowpack / cm
solar zenith angle / °
J(NO3-) / s-1
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
2e-07
1e-07
5e-08
2e-08
1e-08
5e-09
2e-09
1e-09
5e-10
2e-10
1e-10
5e-11
2e-11
1e-11



160
140
120
100
80
60
40
20
0
0
20
40
60
80
F(NO2) / nmol m-2 h-1
solar zenith angle / °



Wolff et al., (2002)
South pole irradiance
Dome C irradiance
Measured Dome C nitrate
[NO3-] / µg kg-1
depth / m
100
80
60
40
20
0
0.0
0.1
0.2
0.3
0.4
0.5

Conclusions

- Optical properties of snow on seaice *may* be the same as snow on coast.
- HULIS, and black carbon are needed to explain snow pack absorption.
- Photolysis may account for ~70% of post deposition loss at Dome C.

Questions?

Questions?

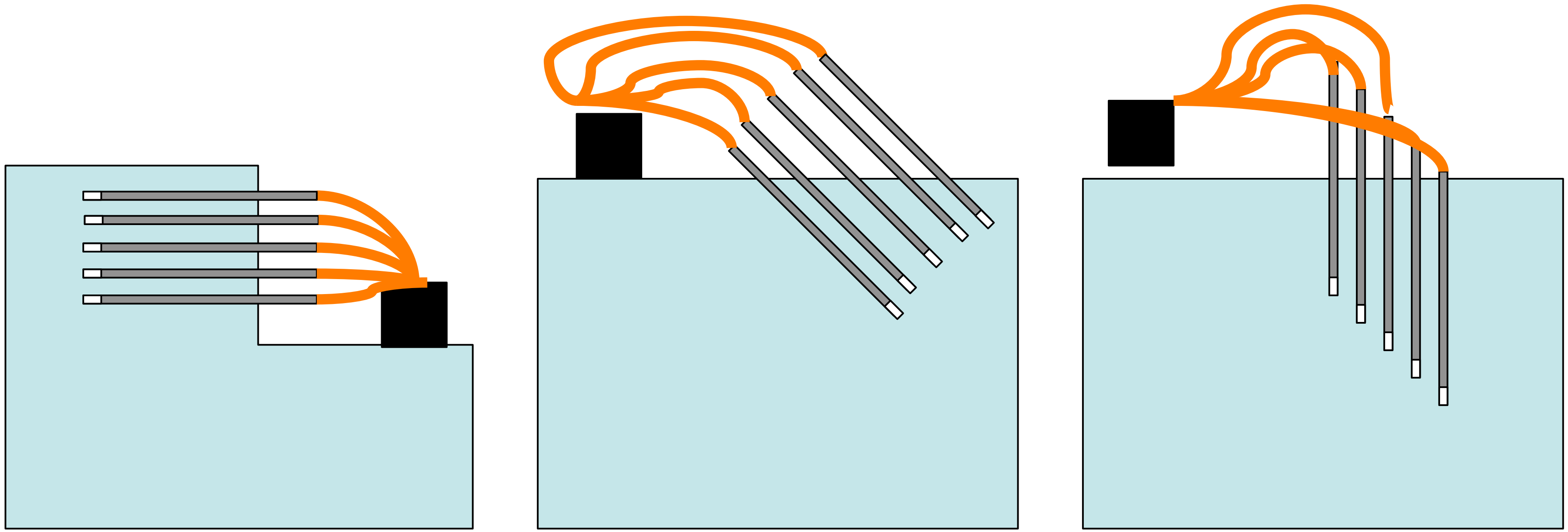
- “Does digging snowpit effect measurement of e-folding depth?”
- “Is photochemistry at the snow surface a reliable measure of the total snowpack photochemistry?”
- “Is the concentration-depth dependence of photolysing chemical important?”
- “Is the snowpack thickness important for photochemistry?”

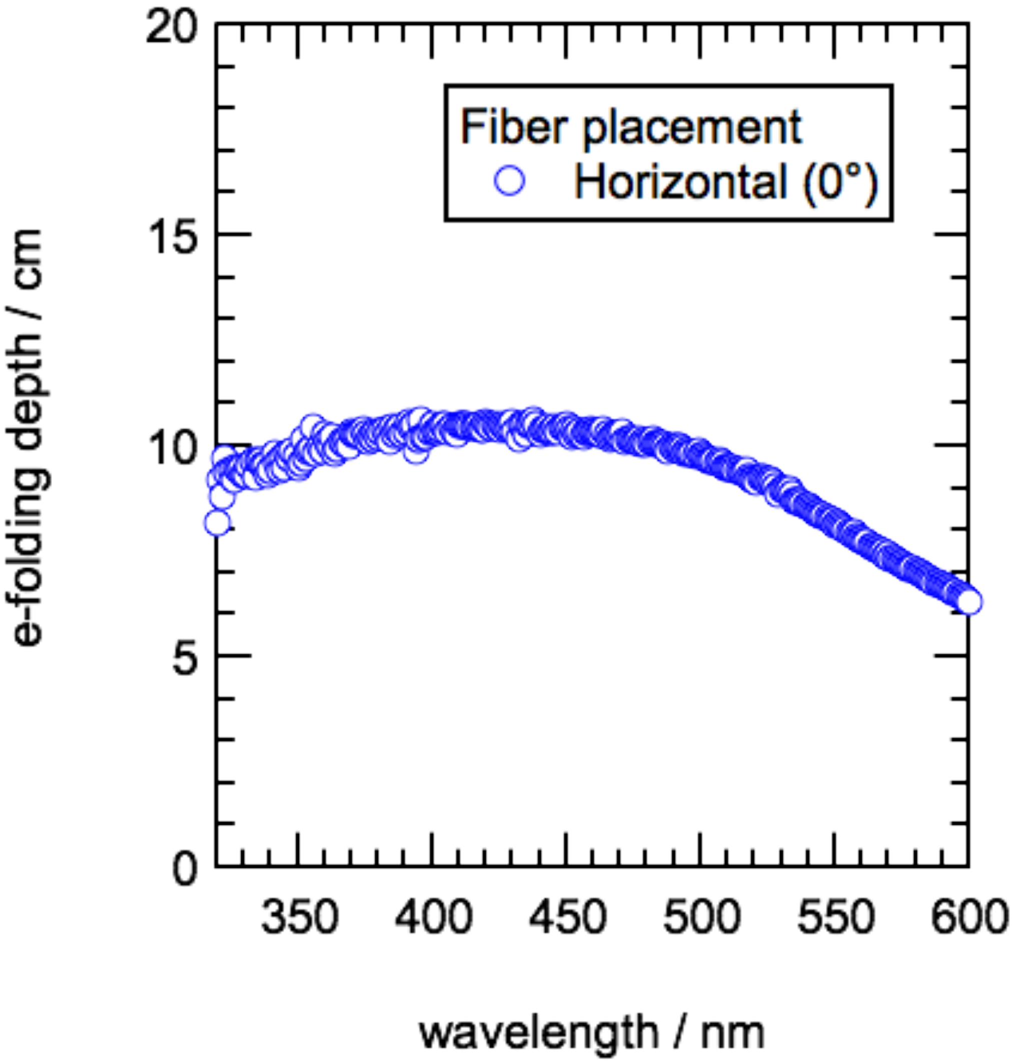
Does digging snowpit effect measurement of e-folding depth?

Does digging snowpit effect measurement of e-folding depth?

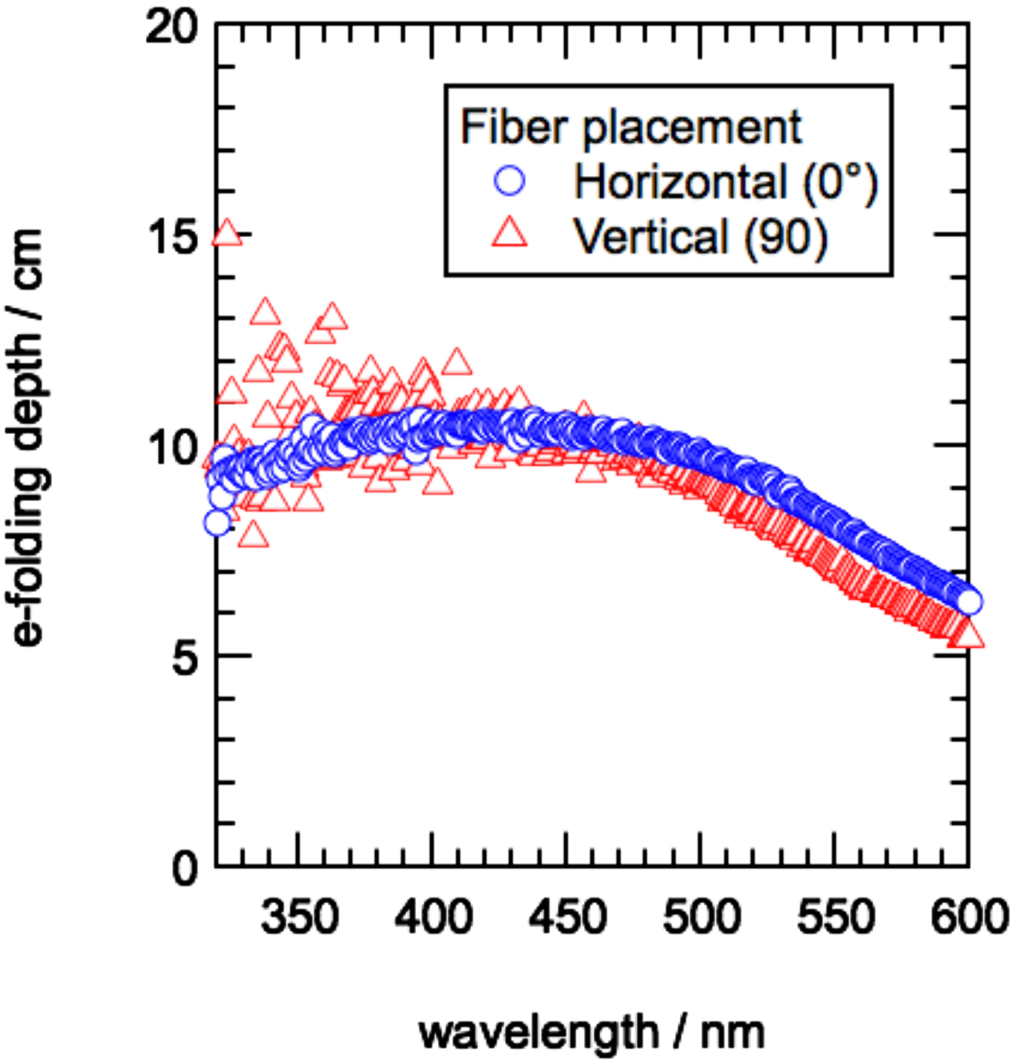
NO

Does digging snowpit effect measurement of e-folding depth?

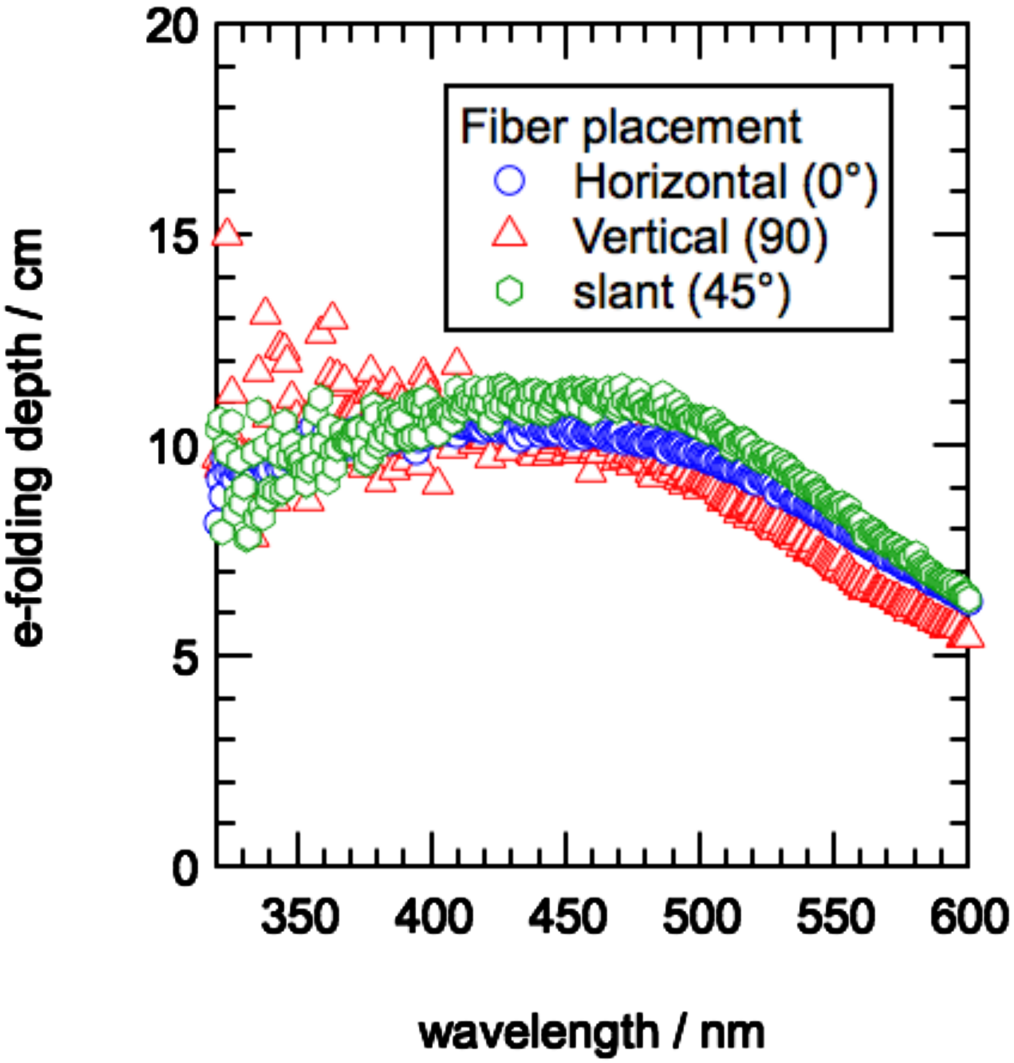




Fiber placement
Horizontal (0°)
e-folding depth / cm
wavelength / nm
0
5
10
15
20
350
400
450
500
550
600



20
15
10
5
0
350
400
450
500
550
600
e-folding depth / cm
wavelength / nm
Fiber placement
Horizontal (0°)
Vertical (90)

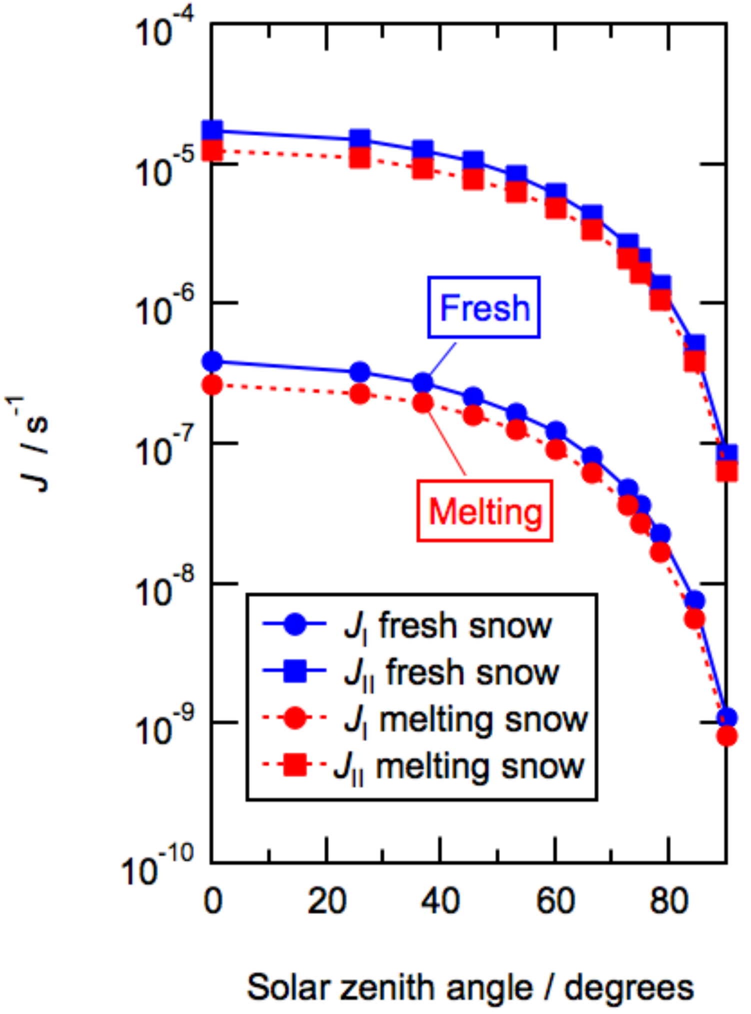


e-folding depth / cm
wavelength / nm
Fiber placement
Horizontal (0°)
Vertical (90)
slant (45°)
0
5
10
15
20
350
400
450
500
550
600

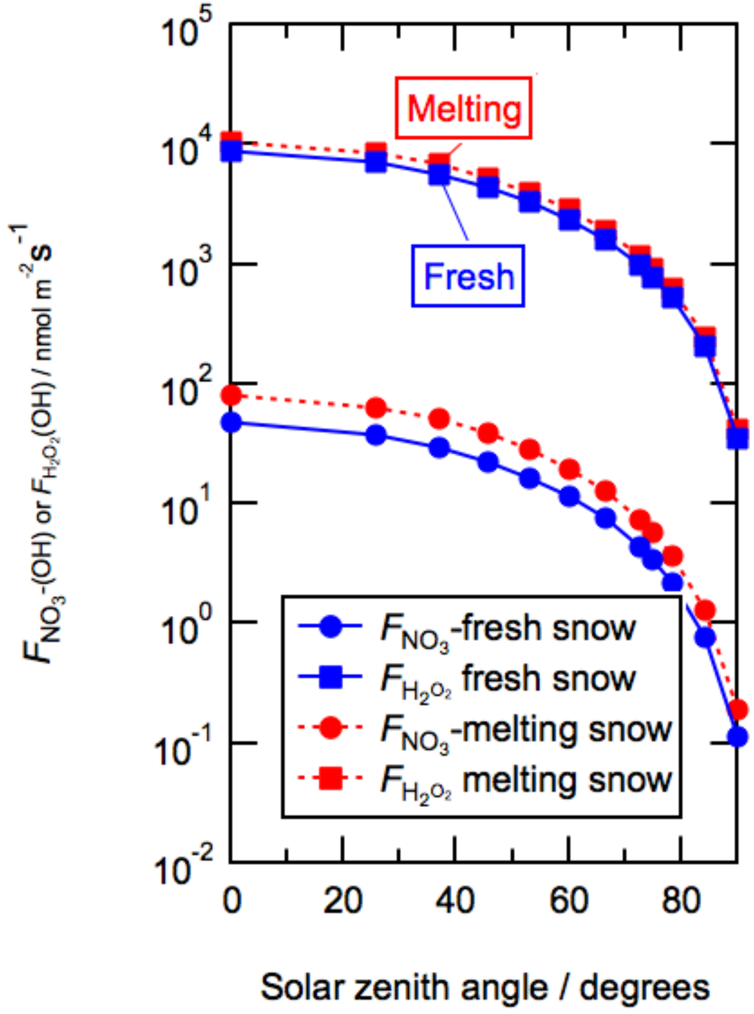
Is photochemistry at the snow surface a reliable measure of the total snowpack photochemistry?

“Is photochemistry at the snow surface a reliable measure of the total snowpack photochemistry?”

NO



Surface photolysis rates



Depth-integrated production rates

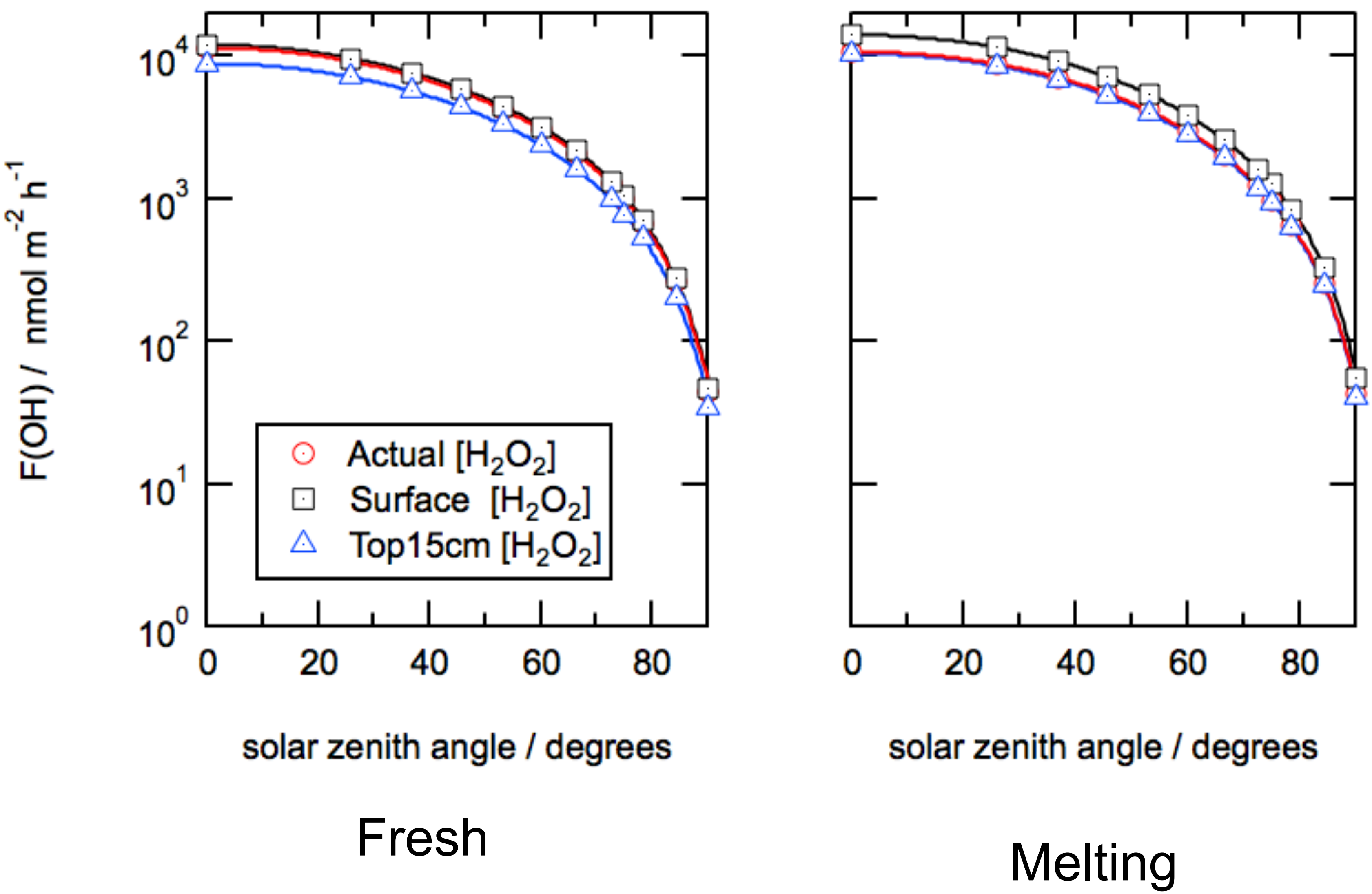
“Is the concentration-depth dependence of photolysing chemical important?”

“Is the concentration-depth dependence of photolysing chemical important?”

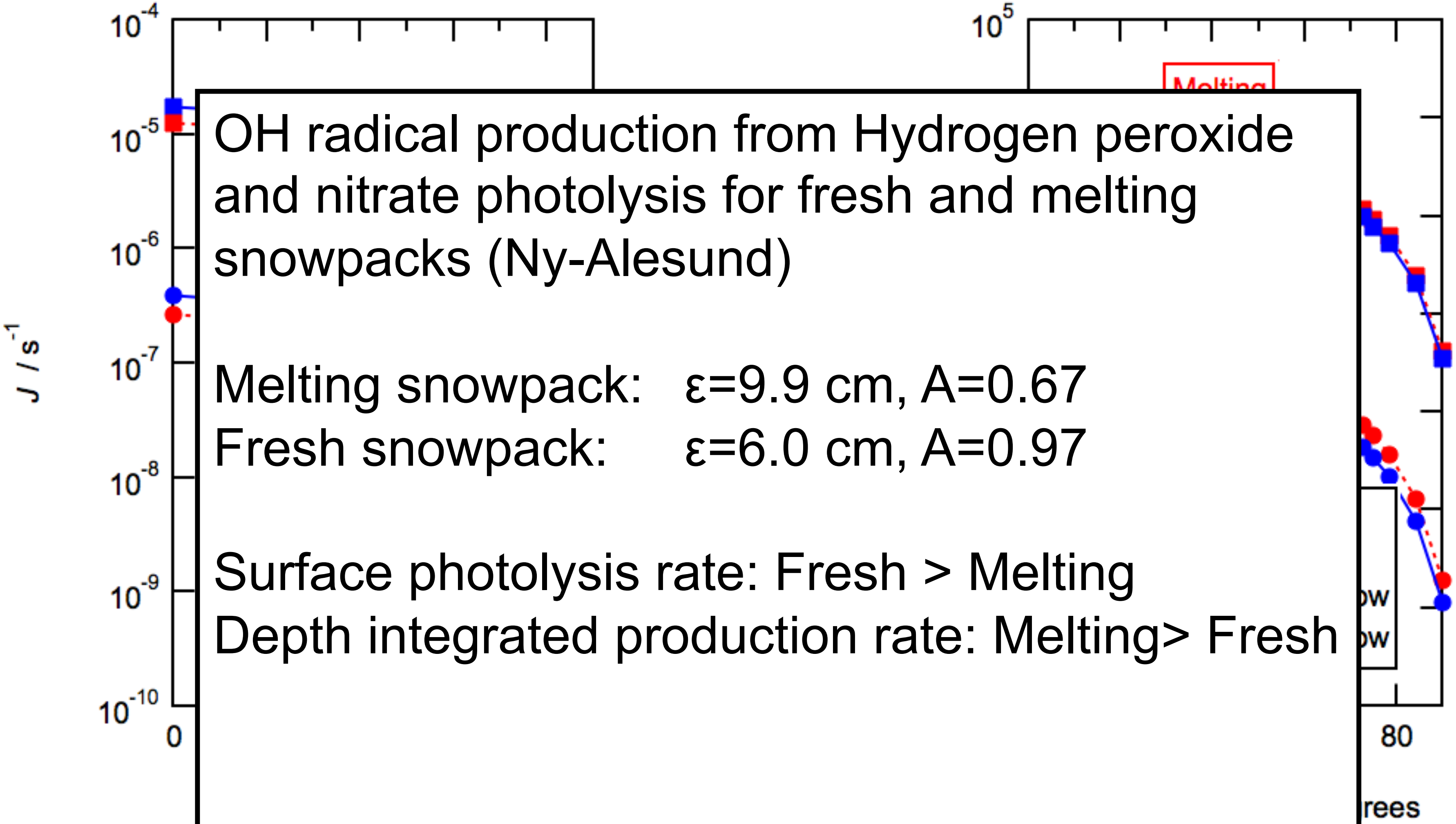
Usually not

Concentration vs light dependence

- The concentration-depth profile of nitrate or hydrogen peroxide can be often approximated to surface values.
- The irradiance in the snowpack decreases exponentially with depth changing many orders of magnitude
- Concentration changes perhaps an order of magnitude.



F(OH) / nmol m^{-2} h^{-1}
10^4
10^3
10^2
10^1
10^0
Actual [H_2O_2]
Surface [H_2O_2]
Top15cm [H_2O_2]
0
20
40
60
80
solar zenith angle / degrees
Fresh
0
20
40
60
80
solar zenith angle / degrees
Melting



OH radical production from Hydrogen peroxide and nitrate photolysis for fresh and melting snowpacks (Ny-Alesund)

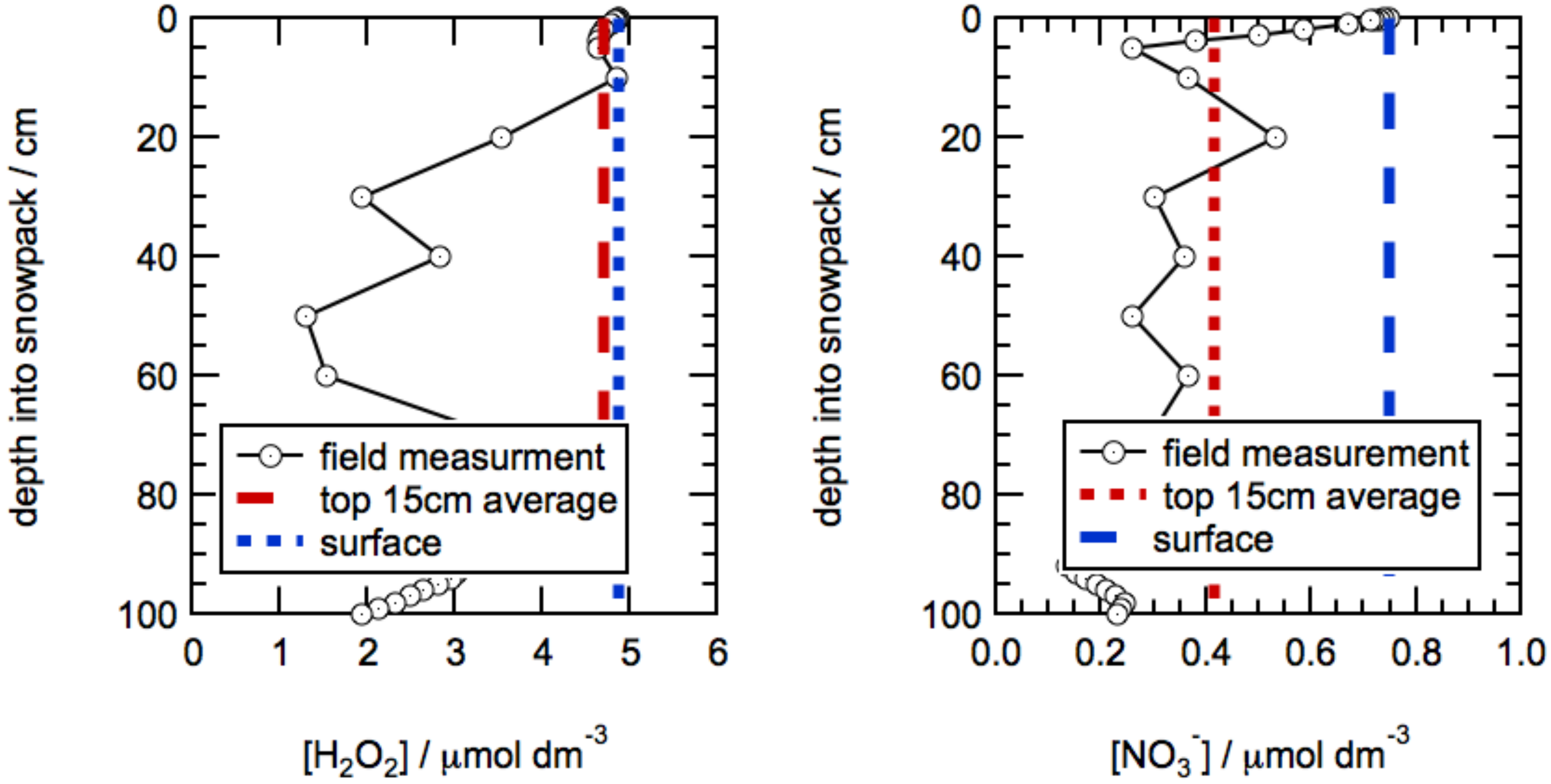
Melting snowpack: ε=9.9 cm, A=0.67

Fresh snowpack: ε=6.0 cm, A=0.97

Surface photolysis rate: Fresh > Melting

Depth integrated production rate: Melting> Fresh

Surf … oduction rates

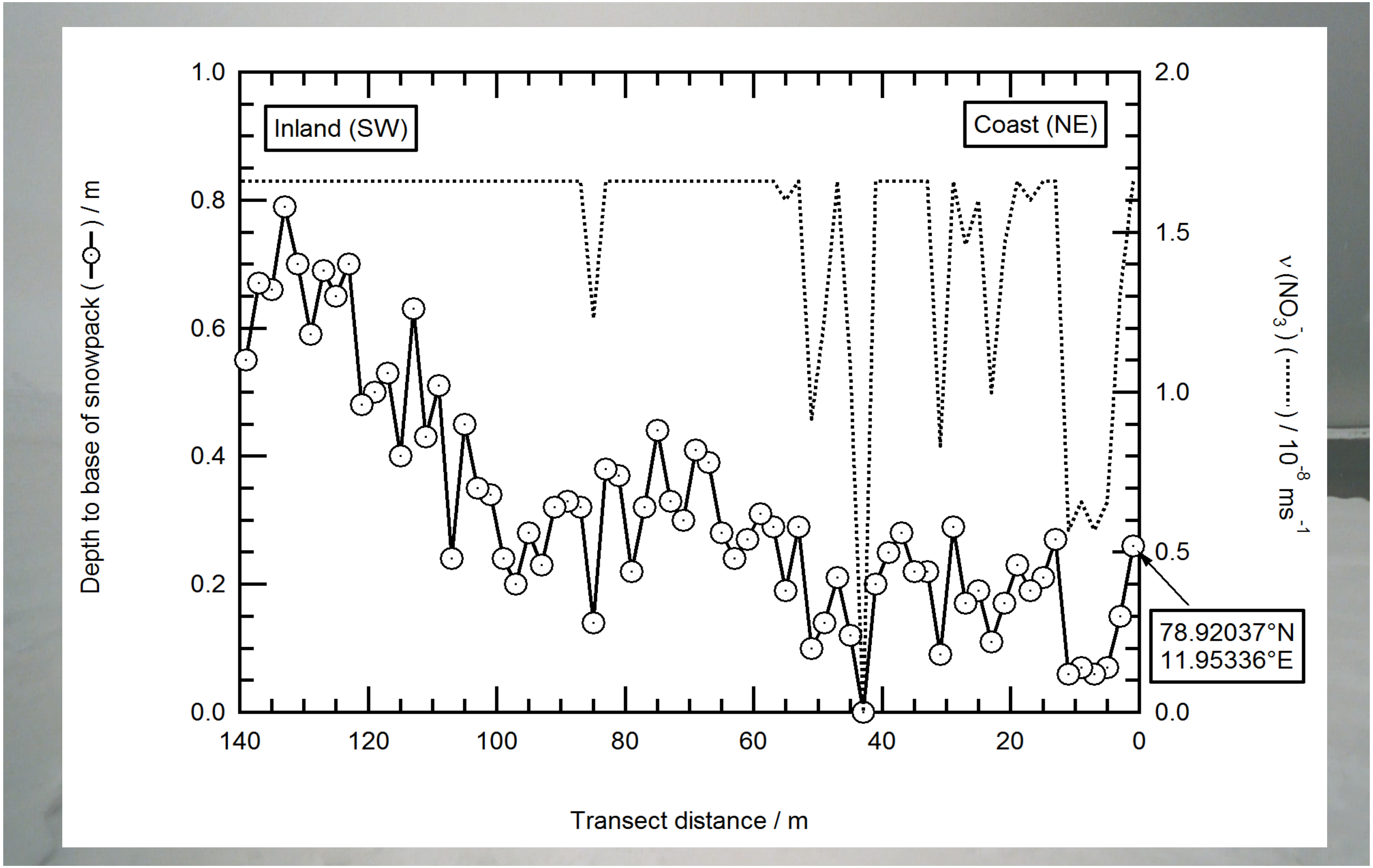


depth into snowpack / cm
0
20
40
60
80
100
0
1
2
3
4
5
6
[H2O2] / μmol dm-3
field measurment
top 15cm average
surface
depth into snowpack / cm
0.0
0.2
0.4
0.6
0.8
1.0
[NO3-] / μmol dm-3
field measurement
top 15cm average
surface

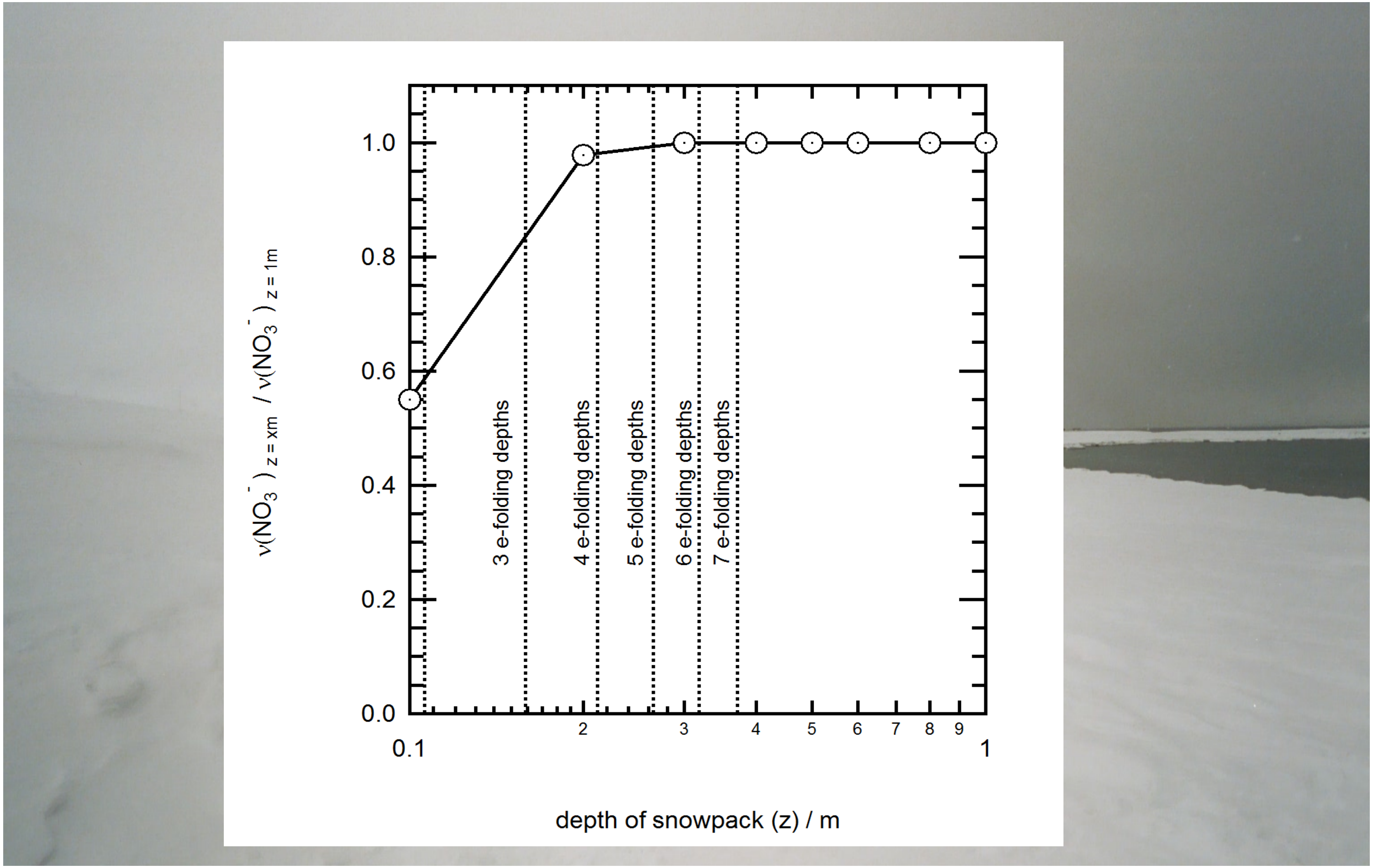
“Is the Snowpack Thickness important for photochemistry?”

“Is the Snowpack Thickness important for photochemistry?”

YES



Inland (SW)
Coast (NE)
Depth to base of snowpack ( ) / m
$v(NO_3^-)$ ( ) / 10^{-8} ms^{-1}
Transect distance / m
78.92037°N
11.95336°E
1.0
0.8
0.6
0.4
0.2
0.0
2.0
1.5
1.0
0.5
0.0
140
120
100
80
60
40
20
0



1.0
0.8
0.6
0.4
0.2
0.0
0.1
2
3
4
5
6
7
8
9
1
3 e-folding depths
4 e-folding depths
5 e-folding depths
6 e-folding depths
7 e-folding depths
$\nu(NO_3^-)_{z = xm} / \nu(NO_3^-)_{z = 1m}$
depth of snowpack (z) / m