

Evaluation of snowpack O₃ and NO_x exchange at Summit, Greenland, in a single-column chemistry-climate model

B. Seok¹, L. Ganzeveld², D. Helmig¹, R. Honrath³, B. Van Dam¹, J. Hueber¹, C. Toro³, L. Kramer³

¹ Institute of Arctic and Alpine Research
University of Colorado
Boulder, Colorado, USA



² Earth System Sciences Group
Wageningen University
Wageningen, The Netherlands



³ Atmospheric Sciences Program
Michigan Technological University
Houghton, Michigan, USA



Modeling objectives

- To develop & evaluate a process-based representation of snowpack O₃ and NO_x exchanges at Summit, Greenland, for implementation in global chemistry-climate models
- To determine key O₃ and NO_x chemical reactions in the snowpack
- To better describe the connections between air-snow O₃ and NO_x exchanges on the tropospheric O₃ budget at Summit

Model description

1D single-column model (SCM)

Based on

- ECHAM4 (General circulation model) & RACMO (Regional atmospheric climate model) physics
- ECHAM4 atmospheric chemistry scheme considering natural & anthropogenic emissions, gas-phase & cloud water chemistry, turbulent & convective tracer transport, and wet & dry deposition

Uses

- ECMWF (European center for medium-range weather forecast) reanalysis data for considering role of advection of wind, temperature, humidity, and liquid water content
- Free troposphere initial/observed concentrations for considering role of advection of long-lived tracers

Model has 60 atmospheric layers, 2 snowpack layers, and an ice layer (Fig 1).

Snowpack module uses a 2-layer scheme (Fig 1) based on a well-tested 2-layer canopy model scheme (Ganzeveld *et al.* 2002).

Pros/cons of a 2-layer snowpack

Pros

- Analytically solves transport between each layer
- Less code, slightly easier to debug
- Faster calculation speed; advantageous when module is integrated into a 3D model

Cons

- Lacks resolution; too simple?
- May miss out capturing some processes that can only be observed at higher resolution

Model validation

Model initialization

- Initialized snowpack [NO₃⁻] and J_{NO₃-NO_x} using average values reported in Honrath *et al.* 2002
- Snow surface microtopography for taking into account of windpumping effects: surface relief height, length, width = 0.23, 2.2, 1.3 m (based on Liao and Tan 2008)
- Ice pack temperature, 263 K (from measurements)
- Bulk snow density, 0.3 g/cm³ (from measurements)
- Albedo, 0.89 (from measurements)

Micrometeorology validation

To properly simulate mass flux, the micrometeorology in the model needs to be correct. The model is able to predict the micrometeorology at Summit fairly well (correlation coefficient $r > 0.75$, Fig 2). Simulated maximum temperatures are overestimated, whereas simulated outgoing longwave radiation is underestimated. This requires further investigation.

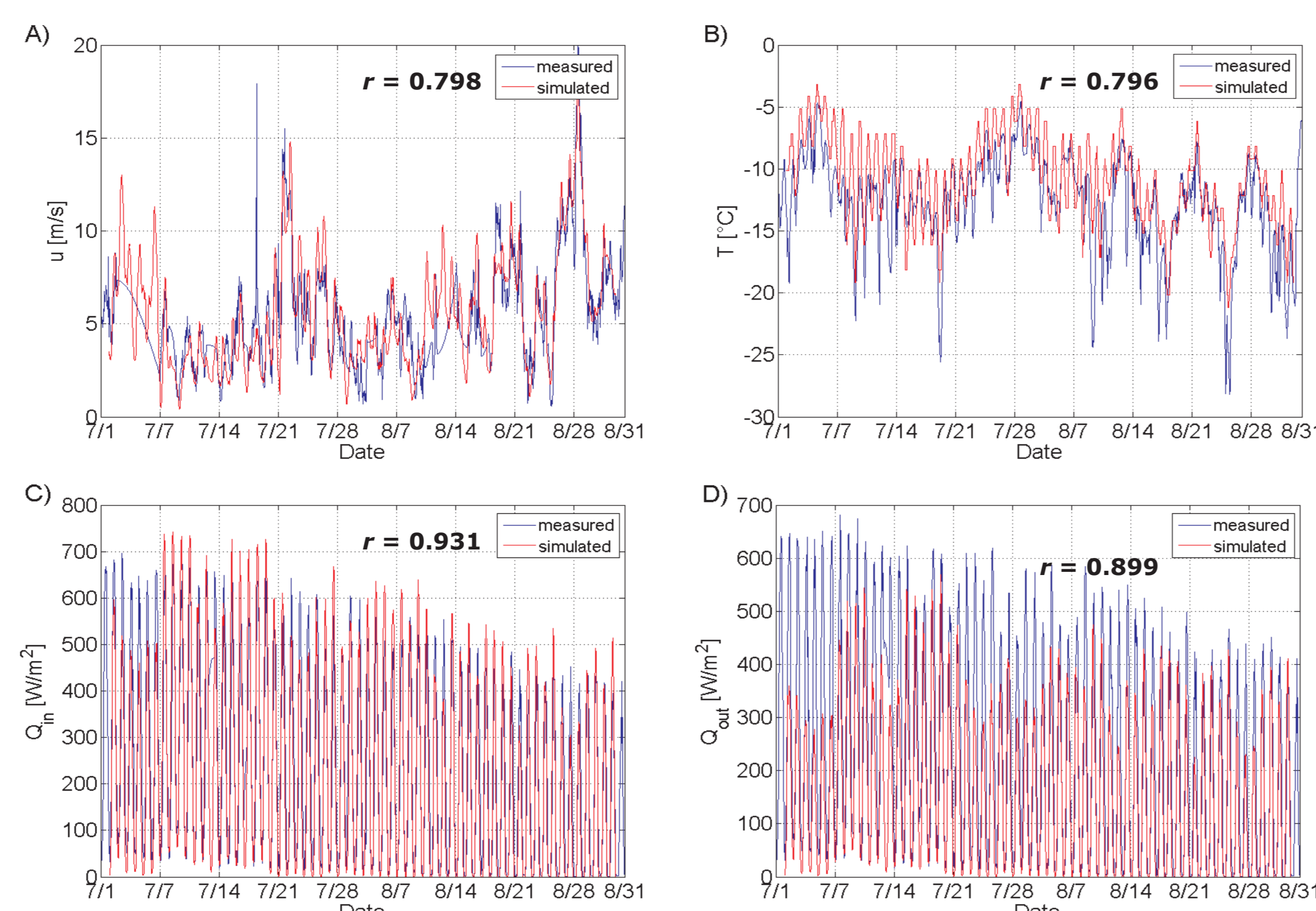


Fig 2. Comparing simulated results with measurements from the field. A) Wind speed at 8.5 m above the snow surface. B) Temperature at 2 m above the snow surface. C) Incoming shortwave radiation. D) Outgoing shortwave radiation. The r value is the linear correlation coefficient between the measured and the simulated.

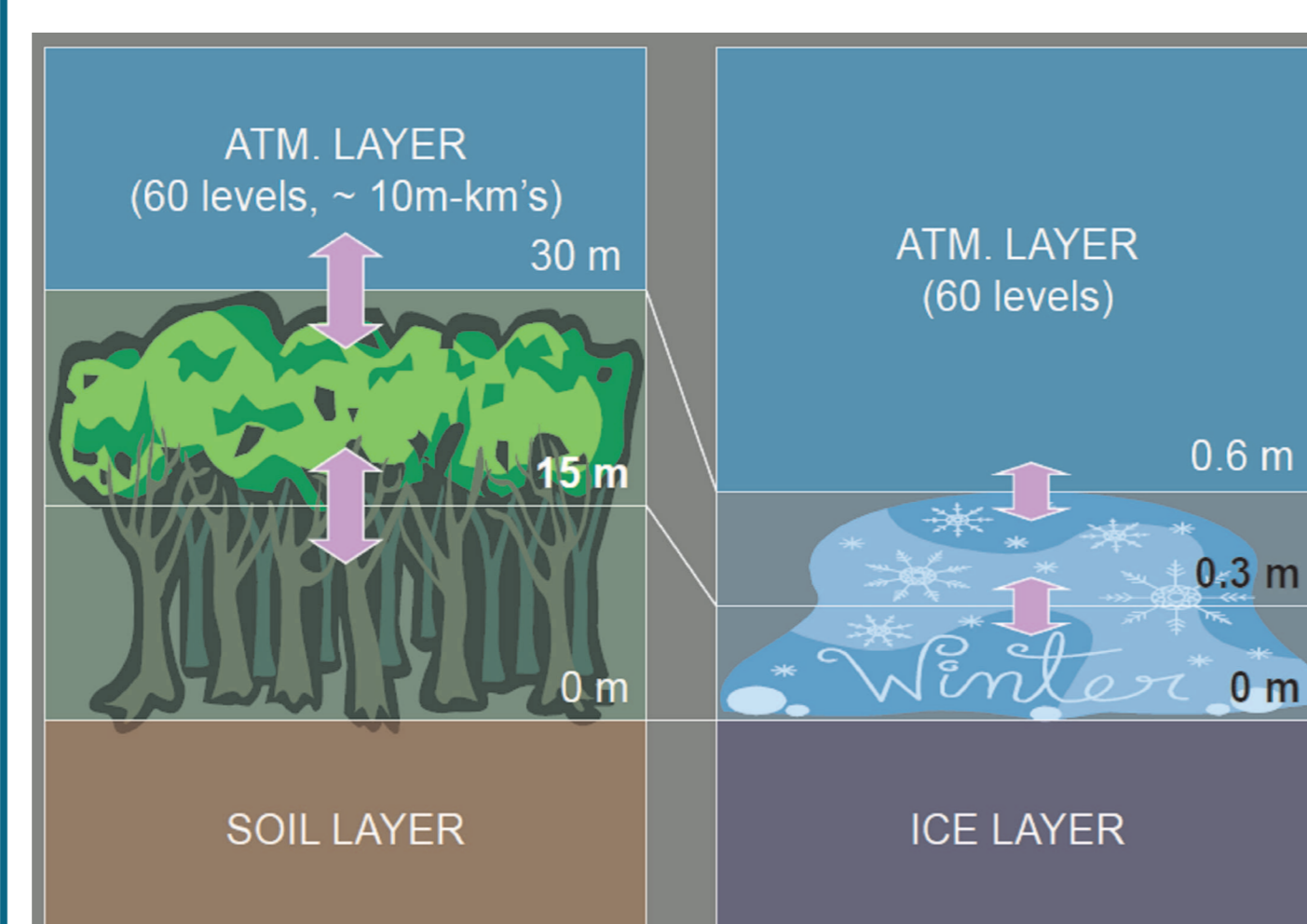


Fig 1. Layout of snowpack module (right) is based on a 2-layer canopy model scheme by Ganzeveld *et al.* 2002 (left). The total snowpack thickness is 0.6 m and is divided into 2 layers of equal thickness, 0.3 m. Transport (pink arrows) between each layer is solved analytically.

Chemistry validation

Conducted 2 experiments

- Tested if snowpack [NO₃⁻] and J_{NO₃-NO_x} initialized using values from Honrath *et al.* 2002 would result in proper order of magnitude [NO] & [NO₂] in the snow
- Tested if NO_x chemistry (gas-phase only) is sufficient enough to explain most of the O₃ removal in snow (Hypothesis: NO-O₃ titration)

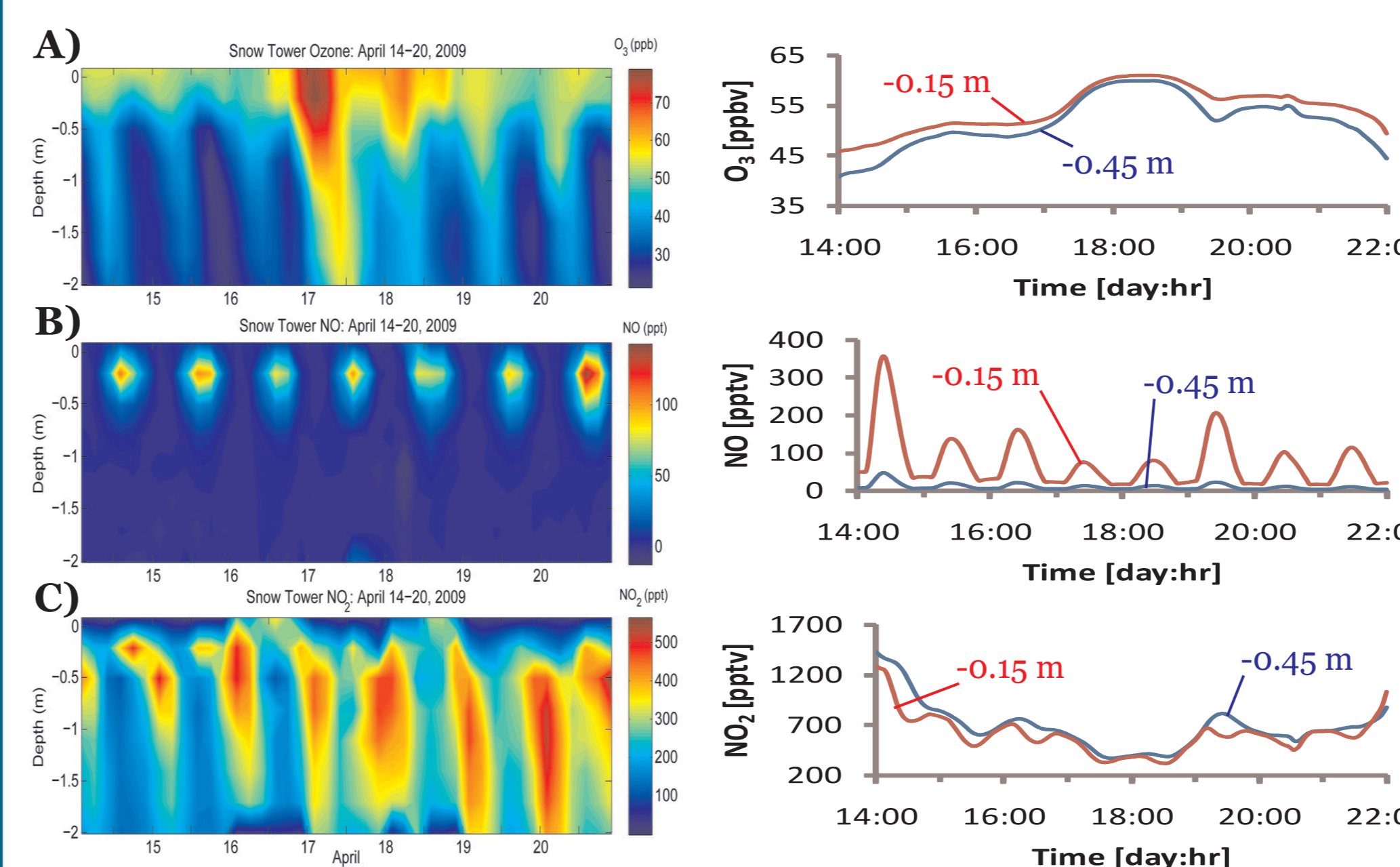


Fig 3. Measured and simulated O₃, NO, NO₂ concentrations in the snowpack in April 14-20 (22 for model), 2009. The color contour plots on the left are measured concentrations in the snowpack. The line plots on the right are simulated concentrations in the snowpack at depths 0.15 and 0.45 m from the snow surface.

Initializing the snowpack [NO₃⁻] and J_{NO₃-NO_x} using values reported in Honrath *et al.* 2002 overall gives good results. The model simulates the observed high [O₃] in the upper snow layer (Fig 3a). Diurnal signals of [NO] in the snowpack were captured in the simulation (Fig 3b). The higher [NO₂] concentrations at -0.45 m relative to at -0.15 m was also properly simulated (Fig 3c). However, the model underestimated [O₃] while it overestimated [NO] and [NO₂].

Table 1 provides an estimate of how much gas-phase NO_x-O₃ chemistry alone explains for the observed O₃ removal. Simulation with only NO_x-O₃ chemistry explains ~10% of observed ozone gradient. The other 90% requires an additional sink (e.g. sticking or quasi-liquid layer chemistry [QLL] not yet incorporated) at each snow grain surface (referred to as substrate-scale removal, SSR). SSR have been scaled to 0.0005 cm/s to reproduce observed O₃ gradient using the snow surface area [SSA] index on the order of 10² m², this can be compared with the bulk snowpack removal rate, but it does not result in proper fluxes suggesting that further evaluation of turbulent and diffusion transport is needed.

This implies that NO_x-O₃ chemistry plays a minor role in O₃ destruction in the snow and that there are other sinks that contribute significantly to the snowpack uptake of O₃, such as halogen, QLL, organics, and other yet unknown physical and chemical processes. Combining the imposed SSR and NO_x-O₃ chemistry in the model run results in bulk snowpack O₃ V_d within range of -0.01 to 0.01 cm/s in Spring at Summit reported by Helmig *et al.* (2009).

Work cited

Ganzeveld LN, *et al.* (2002) JGR 107 (D16) • Helmig D, *et al.* (2009) GRL 36 (L08809) • Honrath RE, *et al.* (2002) AE 36 (15-16) • Liao W, Tan D. (2008) ACP 8 (23)

Table 1. Average simulated and measured O₃ gradient, ΔO₃ = [O₃]_{8.5 m} - [O₃]_{0.15 m}, and its resulting bulk snowpack O₃ deposition velocities, V_d, for April 14-20, 2009. Substrate-scale removal rate, SSR, represent additional sinks in the snowpack, not yet incorporated in the model, to result in simulated ΔO₃ that was close to observed ΔO₃.

	Measured	Simulated		
		NO _x -O ₃ chem. + SSR	Only SSR (=0.0005 cm/s)	Only NO _x -O ₃ chem.
ΔO ₃ [ppbv]	7.50	7.38	6.76	0.74
V _d [cm/s]	≤ 0.01 *	2.1×10 ⁻⁴	1.9×10 ⁻⁴	0.23×10 ⁻⁴

* from Helmig *et al.* 2009

By evaluating O₃ tendencies (the rate of change of [O₃] over time at a given point in space), the drivers of O₃ removal in the snow can be determined.

Fig 5 shows that net O₃ tendencies is driven by turbulence. Therefore, proper simulation of micrometeorology is key! However, chemistry becomes important when contribution from turbulence is low.

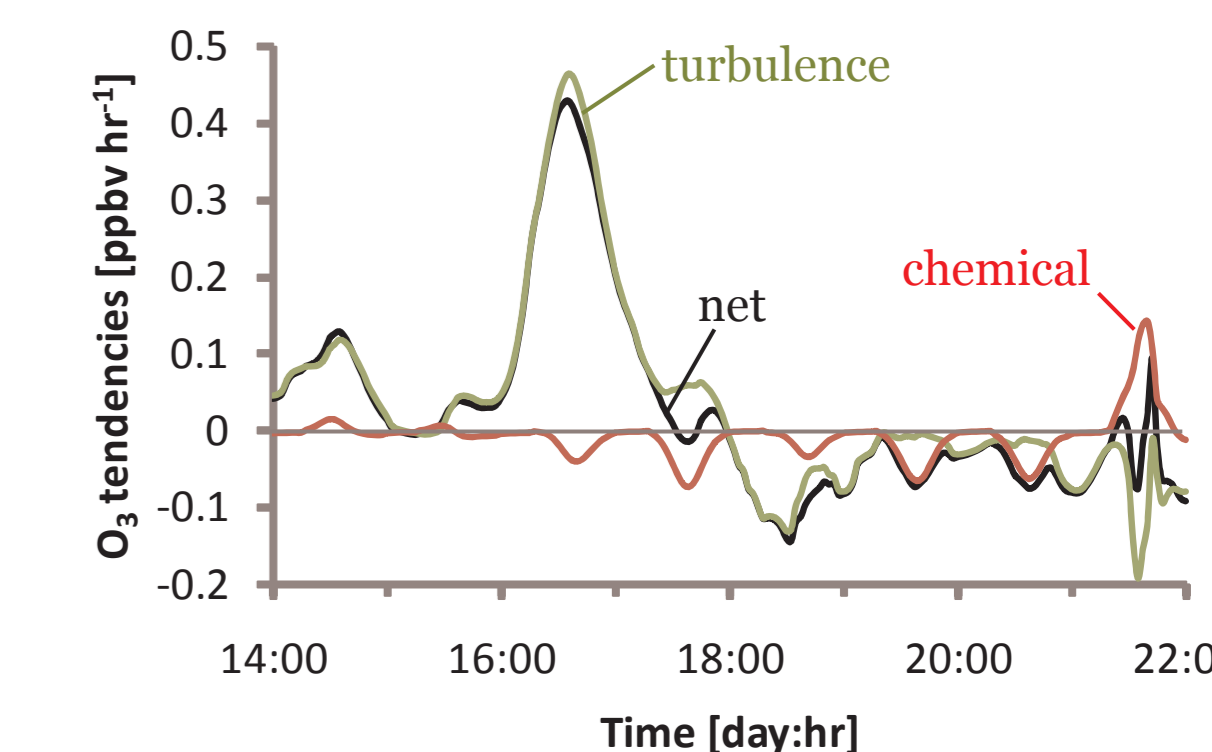


Fig 5. Processes that drive O₃ tendencies at 8.5 m above the snow.

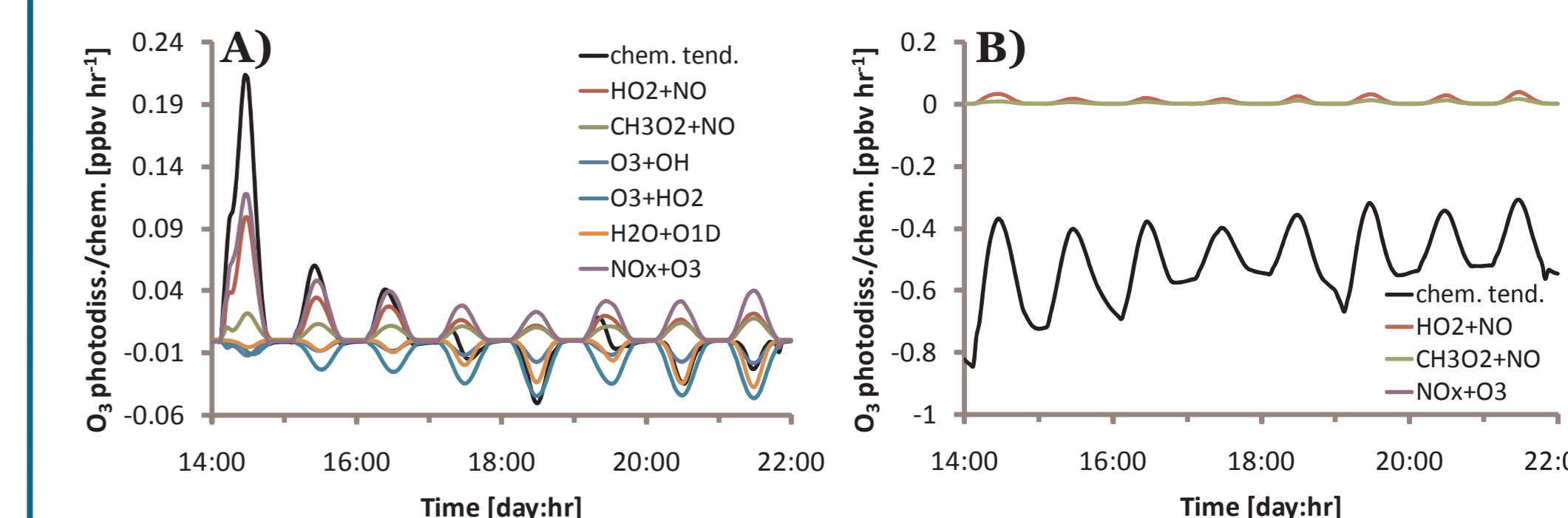


Fig 6. Chemical reactions that drive the chemical processes of the O₃ tendencies A) above the snowpack at 8.5 m and B) at -0.15 m from the snow surface.

Within the currently considered chemical processes of O₃ tendencies, the NO_x-O₃ reaction mechanism dominates the net chemical tendency in and above the snowpack (Fig 6). Above the snowpack, the NO_x-O₃ reaction mechanism plays a role in O₃ production (Fig 6a). In the snowpack, NO_x-O₃ reaction mechanism is an O₃ sink (Fig 6b, the NO_x-O₃ line is under the chem. tend. line).

Conclusions and outlook

- NO_x gas-phase chemistry alone fails to explain O₃ uptake to the snow
- Need to investigate the impact of heterogeneous (QLL) chemistry based on the aqueous phase chemistry scheme of the model
- Assess the role of other ozone sinks in the snowpack, possibly O₃ destruction by halogens
- Evaluate physical sorption process
- Further validate boundary layer structure and photolysis rates

Acknowledgements

We thank Jennie Thomas for invaluable discussion on our model features: wind-pumping and importance of "wet" chemistry (QLL). We thank the National Science Foundation, Office of Polar Programs, for funding this research.

