

Comments on 'Possible contribution of triboelectricity to snow–air interactions'

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There have been numerous new discoveries of chemical activity at the snow–atmosphere interface over the last 20 years. These observations have stimulated an increasing body of research on snow chemical systems. The findings from this research have led to a general consensus that photochemical processes are the determining control of this snow chemistry. Traditional gas-phase chemical reactions have fallen short of fully explaining observed behaviour. Heterogeneous and quasi-liquid layer chemistry has been postulated to play a role in accounting for the discrepancies. The Tkachenko and Kozachkov^[1] article is therefore a timely presentation of new ideas for further elucidating snowpack chemical mechanisms. In the following discussion we present recent data relevant to testing hypothesis proposed by Tkachenko and Kozachkov.^[1]

Some of the hypotheses presented in this paper build upon data from measurements of ozone (O₃) in interstitial air of the deep, glacial snowpack at Summit, Greenland, that were presented in our previous work.^[2] These experiments reported on positive O₃ atmosphere–snowpack gradients, i.e. depleted O₃ within the snowpack, and their dynamical behaviour dependent on environmental conditions. We have since taken this research to other locations and further investigated the dependencies of O₃ within snow on a variety of parameters. A particular interest of this new research was to further investigate snowpack chemistry in environments with different snowpack conditions (year-round dry, polar snow; seasonal mid-latitude snowpack; snow over permafrost; snow over frozen freshwater lakes). We have also conducted a further 2 years of experiments at Summit,^[3] where the measurement depth in the snowpack was

increased to 2.5 m and experiments were extended year round to include winter observations. Another environment with polar year-round snowpack over glacial ice was investigated at South Pole, Antarctica.

From the comparison with these other sites it has become obvious that the Summit snowpack is somewhat unique in that (1) O₃ levels within the snowpack are generally higher than observed at other locations, and (2) interstitial air O₃ shows a much more dynamic dependence on time of day and season than at the other locations that we have investigated. This behaviour might be in agreement with some hypotheses presented by Tkachenko and Kozachkov as they propose that O₃ production by the triboelectrical effect would be most pronounced at sites characterised by a thick, glacial snowpack, low humidity, periodic high wind speeds, and low temperatures^[1]; all conditions that are typical for Summit.

Our series of experiments have shown that different processes dominate snowpack chemistry in non-glacial snowpack. For example, one definite influence on O₃ reactions in seasonal, midlatitude snowpack is the role of NO emitted from microbial processes in the subnival soil.^[4,5] These influences were evident at a high alpine site at Niwot Ridge, CO, in the Rocky Mountains^[4]; snowpack under a canopy at the University of Michigan Biological Station (B. Seok, D. Helmig, M. W. Williams, C. Vogel, P. Curtis, unpubl. data); and snowpack over permafrost at Toolik Field Station, AK (B. Van Dam, D. Helmig, R. Honrath, L. Kramer, C. Toro, unpubl. data).

For the Summit snowpack, Helmig et al. noted that O₃ atmosphere–snowpack concentration gradients show three



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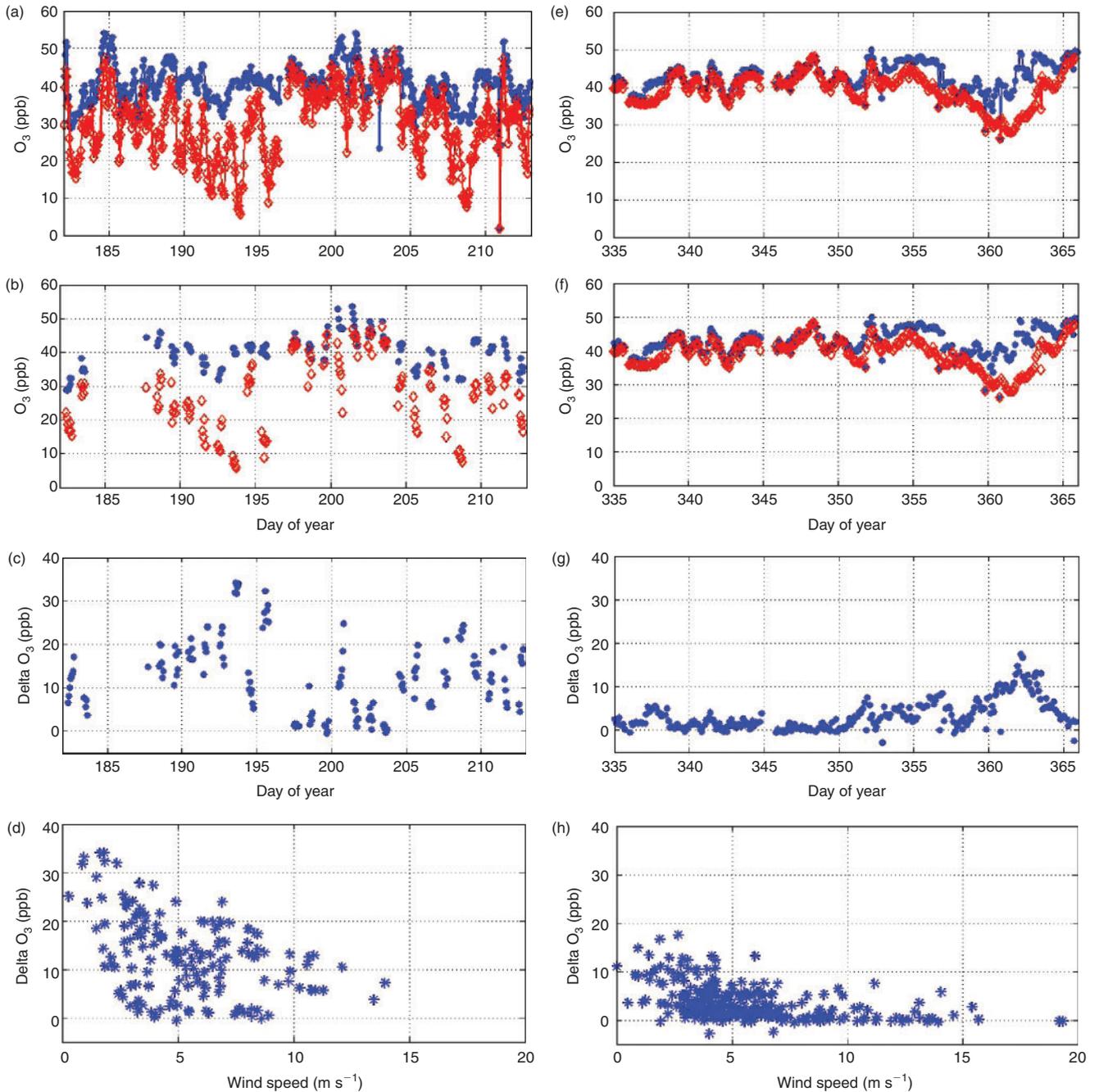


Fig. 1. The left column (a–d) show summertime ozone data for Summit station. The right column shows wintertime data (e–h). (a–b) and (e–f) show ozone measurements above and within the snowpack (blue dots indicate ambient air measurements and red diamonds indicate snowpack measurements), where (b) shows data filtered for high radiation ($>400 \text{ W m}^{-2}$) in summer and low radiation ($<4 \text{ W m}^{-2}$) in winter. (c) and (g) plot ozone gradients (ambient – snowpack) for these 1-month periods. (d) and (h) show the relationship between this ozone gradient and wind speed.

characteristic features: (1) diurnal cycles; (2) seasonal variations; and (3) a dependency on wind speed.^[2] Tkachenko and Kozachkov propose that the electrification of snow under the influence of wind initiates various free radical processes that can result in O_3 production in the snow.^[1] This theory is used to explain the third characteristic listed above. Tkachenko and Kozachkov claim that the decrease of the gradient seen under high winds is primarily a result of ozone production in the snowpack driven by the triboelectricity of snow under wind and that this produced ozone compensates for the loss from photochemical destruction.^[1]

To address this hypothesis we re-examined data from our 2008–10 snowpack chemistry experiment at Summit. Fig. 1a–d show summer data from July 2009 and Fig. 1e–f show winter data from December 2009. All data shown are filtered for clean air conditions (eliminating potentially polluted air from the direction of main camp). Figs 1a and 1e show the absolute concentrations of O_3 above the snow surface (blue dots) and within the snowpack (red diamonds). In July, the snowpack O_3 measurements are from air sampled at a depth of 0.25 m, and in December, the snowpack measurements are from a depth of 0.30 m.

Fig. 1b and 1f show the same data except filtered for radiation. For July, we only looked at cases when radiation was high, greater than 400 W m^{-2} , and in December, we only considered cases in darkness, i.e. when radiation was less than 4 W m^{-2} , Figs 1c and 1g show the ozone atmosphere–snowpack gradient time series (calculated from the ambient O_3 measurement minus the snowpack O_3 measurement) for these filtered data. These data clearly illustrate that the measured atmosphere–snowpack O_3 gradient is significantly larger during the higher radiation summer conditions (compared to low radiation conditions in winter). During summer $>80\%$ of the ambient ozone levels are destroyed inside the snowpack during late afternoon hours. Lastly, Figs 1d and 1h show the O_3 gradient v. wind speed measured from our meteorological tower at a height of 7 m. Both summer and winter data illustrate the dependence of the atmosphere–snowpack gradient on wind speed. The highest positive gradients occur under low winds, both during the summer and winter conditions. Under no measured conditions are negative gradients (higher O_3 within the snowpack) recorded.

According to Tkachenko and Kozachkov, ‘ozone production under wind occurs in quantities that are comparable with its photochemical loss and this is the reason why the concentration gradient decreases’.^[1] From this statement it would be expected that O_3 production from triboelectrification under windy conditions would compensate for the up to 80% ozone loss observed in the summer. Taking this one step further, one would expect that during the darkness of winter (when photochemical ozone destruction is absent) under windy conditions this triboelectrification-initiated ozone production would supersede the ozone loss, and that this ozone production should result in an ozone enhancement inside the snowpack. The wintertime data presented in Fig. 1e–h, however, do not show any O_3 enhancement within the snow. Even under the highest wind conditions, ozone in air below the snow surface remains consistently below ambient air levels. Consequently, there is no evidence for any O_3 production occurring within the snow under any wind conditions. Clearly these data do not support the hypothesis proposed by Tkachenko and Kozachkov.^[1] Therefore, our hypothesis remains that snowpack ventilation by wind pumping is the cause of decreased O_3 gradients during high winds. Support for this explanation has also been shown in other work,^[6] where wind pumping effects on other trace gas gradients and fluxes in the seasonal snowpack of Niwot Ridge, CO, were investigated.

Further elucidation of several points raised by the Tkachenko and Kozachkov paper^[1] would be beneficial to advance further

discussion. First, the paper unfortunately does not describe to what depth within the snowpack the proposed corona discharge-initiated ozone production mechanism would penetrate, and whether the vertical scale of these electrical effects within the snowpack is similar to what we show in the observational data from Summit. Second, the authors propose several reactions relating to O_3 within the snow under the influence of corona discharge. These proposed reactions include both an ozone source (reactions 7–9 in Tkachenko and Kozachkov^[1]) and an ozone sink (reaction 11^[1]), yet the article neglects to comment on the interplay between these proposed ozone sources and sinks.

The Tkachenko and Kozachkov^[1] publication provides interesting thoughts that may initiate further stimulating discussion among polar snow scientists. We hope that further experimental evidence can be provided to address the role of triboelectricity to snow–air interactions as proposed by these authors.^[1]

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