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Reproducing Arctic springtime tropospheric ozone and mercury depletion events in an outdoor mesocosm sea ice facility

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Text S1. NO_x chemistry on ozone loss within the in-tube air

In this experiment, we studied the ozone loss (ΔO_3) by comparing between different locations (the ambient air vs. in-tube air; the UV-transmitting tube vs. UV-blocking tube). For ΔO_3 within the in-tube air (the ambient air vs. in-tube air), the ambient air can be considered as a control group while the in-tube air is the experimental group that examines the influence from sea ice and acrylic tube. Since the tube was open to the ambient environment, we consider similar air mass for both the ambient air and in-tube air, including NO_x from urban signal that was already present in the background ambient air. This assumption is also supported by overall similar O_3 trends observed between the ambient air and in-tube air (see Fig. 3 and Fig. S4). In this case, NO titration (mainly produced from urban signal) would equally affect O_3 dynamics in the ambient air and in-tube air, which is an offset process when studying ΔO_3 via the comparison between the ambient air and in-tube air. Thus, such ΔO_3 should not be affected by variations of NO_x in the background ambient air. Since the ΔO_3 within the in-tube air examines the influence from sea ice, NO_x production via snowpack photochemistry may be important, yet this process is considered negligible due to the low concentrations of nitrite and nitrate found in surface ice and saline snow samples. Then, NO_x that may influence O_3 dynamics is only expected from urban signal (the background ambient air) and should have little influence on the ΔO_3 within the in-tube air. We believe our general assumption that variations of NO_x in the background ambient air do not affect ΔO_3 obtained from comparisons is sound.

The assumption that the air mass between the ambient air and in-tube air was similar is challenged when there was a sudden and rapid disturbance (e.g., occasional use of vehicles within the facility). In this case, the vehicle exhaust signal was readily captured in the ambient air while the in-tube air was less affected due to a lack of rapid air mixing. During daytime, O_3 can be produced from photochemical oxidation of hydrocarbons in the vehicle exhaust or NO_2 photochemistry. This increased O_3 signal (within 20 minutes from the vehicle use) could be immediately observed as a lesser extent of O_3 depletion in the ambient air at the beginning of the disturbance, whereas such O_3 increase was not necessarily captured in the in-tube air due to a lack of rapid air mixing. This condition would overestimate ΔO_3 and result in those abnormal high values out of the general ΔO_3 trend observed around 12:00 on 6 and 9 March (shaded areas in Fig. S4). NO produced from on-site use of vehicles could subsequently cause small-scale O_3 depletion in both the ambient air and in-tube air. However, during each day, the ΔO_3 was observed before

the sharp increase of NO_x and continued until sunset, indicating that daytime NO_x production due to on-site use of vehicles was not the main driver for ΔO_3 within the in-tube air.

The role of NO_x chemistry in depleting O_3 can be qualitatively estimated by the behavior of NO/NO_2 ratio when the total amount of NO_x remains stable and without high concentrations of volatile organic compounds. The ratio would decrease if the NO + O_3 reaction proceeds to any substantial extent, otherwise it would increase (Finlayson-Pitts and Pitts, 2000). In Fig. S5, typical daytime ΔO_3 periods (5, 11 and 14 March) are provided, which shows a distinct behavior of NO_x chemistry: the NO/NO_2 ratio increased on 5 and 14 March whereas it decreased on 11 March, while NO_x concentration stayed at a relative stable level during the daytime ΔO_3 span. Although based on the experimental design, ΔO_3 obtained by comparisons should not be affected by NO_x in the background ambient air. If we assume NO_x chemistry-driven O_3 depleting process does contribute to ΔO_3 within the in-tube air, the contribution from NO_x chemistry in causing ΔO_3 would be expected on 11 March and some other processes (e.g., Br chemistry) would have contributed to ΔO_3 on 5 and 14 March. Such examinations are carried out on each daytime ΔO_3 period when NO_x measurements were available (3 to 16 March), and the potential NO_x contribution (decreasing NO/NO_2 ratio) was only observed on 3 and 11 March.

Furthermore, when we compare O_3 between the UV-transmitting and UV-blocking tubes, we consider both in-tube air masses are similar and background NO_x would affect both to a similar extent whereas the only variable being examined is the UV radiation. Thus, NO_x photochemistry, initiated by UV radiation, might contribute to ΔO_3 between two tubes. This influence, if possible, is expected to occur throughout the arcylic tube and regardless of the sea ice presence. Not observing a universal ΔO_3 throughout the acrylic tube (Fig. 5) or above the water surface (Fig. 8) indicates NO_x chemistry plays a minor role in ΔO_3 between two tubes as well.

In conclusion, ambient O_3 dynamics is associated with NO concentrations, especially when ambient O_3 depletions during night were observed with NO peaks (Fig. S3). However, ΔO_3 obtained from comparisons should not be attributed to variations of NO_x in the background ambient air by the experimental design and the in-situ NO_x production via snowpack photochemistry is considered negligible. Thus, NO_x produced either from the urban signal or snowpack photochemistry has limited influence on the ΔO_3 obtained from comparisons. Since the

general diurnal pattern of ΔO_3 within the in-tube air cannot be explained by NO_x chemistry, we believe Br chemistry is most likely the main driver for ΔO_3 reported in this study.

Reference:

Finlayson-Pitts, B. J., and Pitts Jr, J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications. Elsevier, https://doi.org/10.1016/B978-0-12-257060-5.X5000-X, 2000.

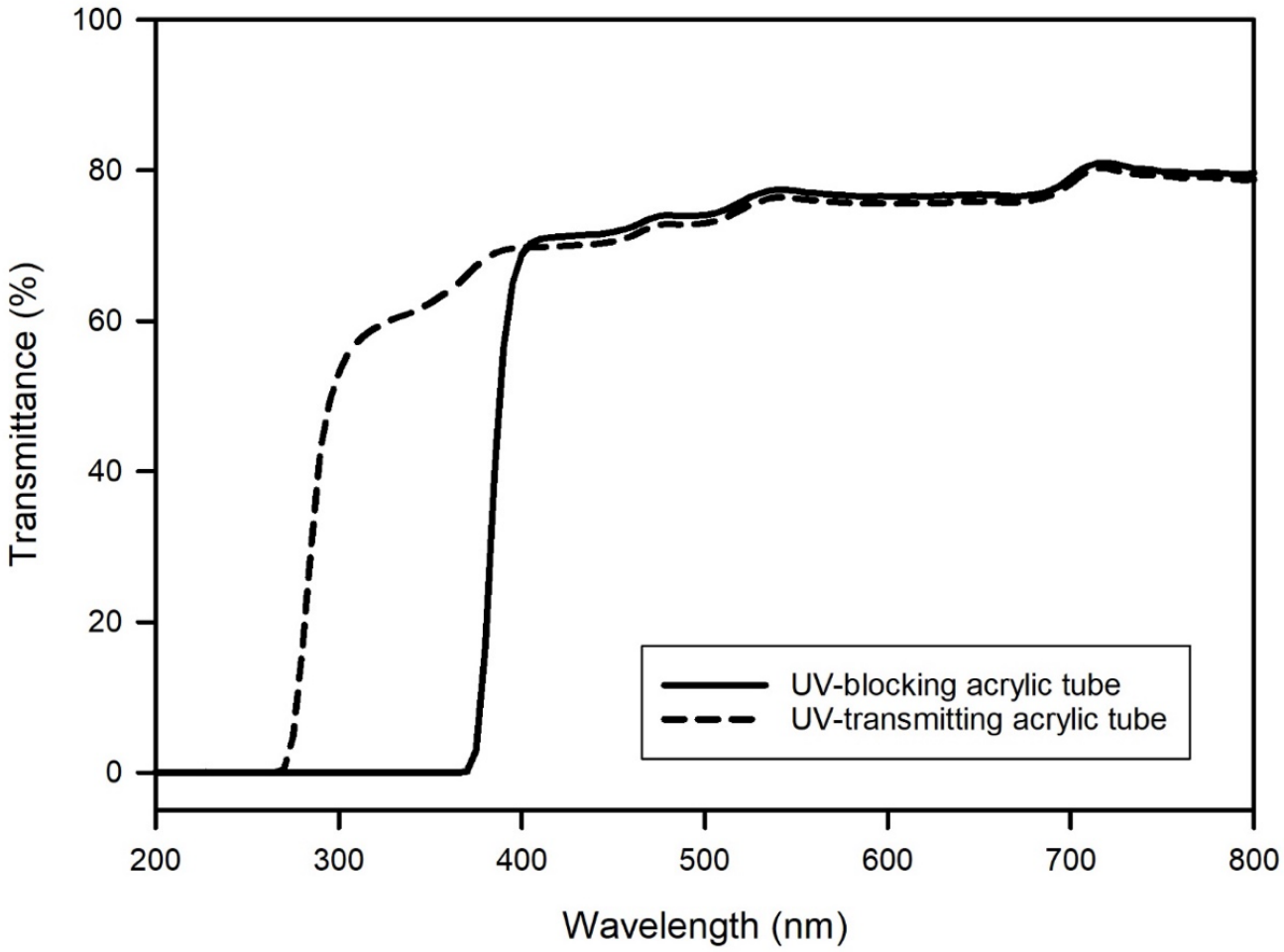

Figure S1. Light transmittance of the two acrylic tubes used in the experiments.

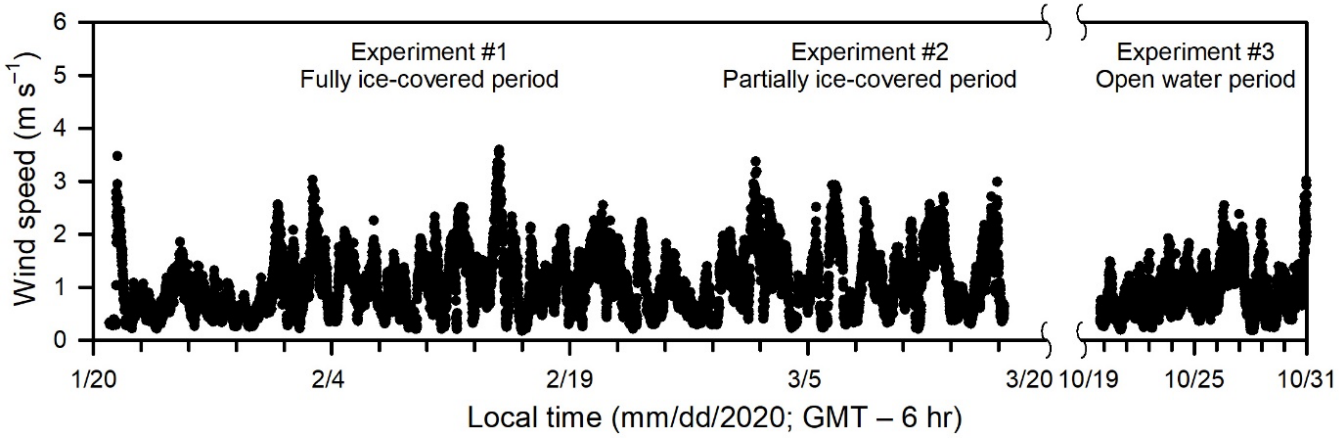

Figure S2. Temporal changes of wind speed measured at 1.5 m above the ice surface.

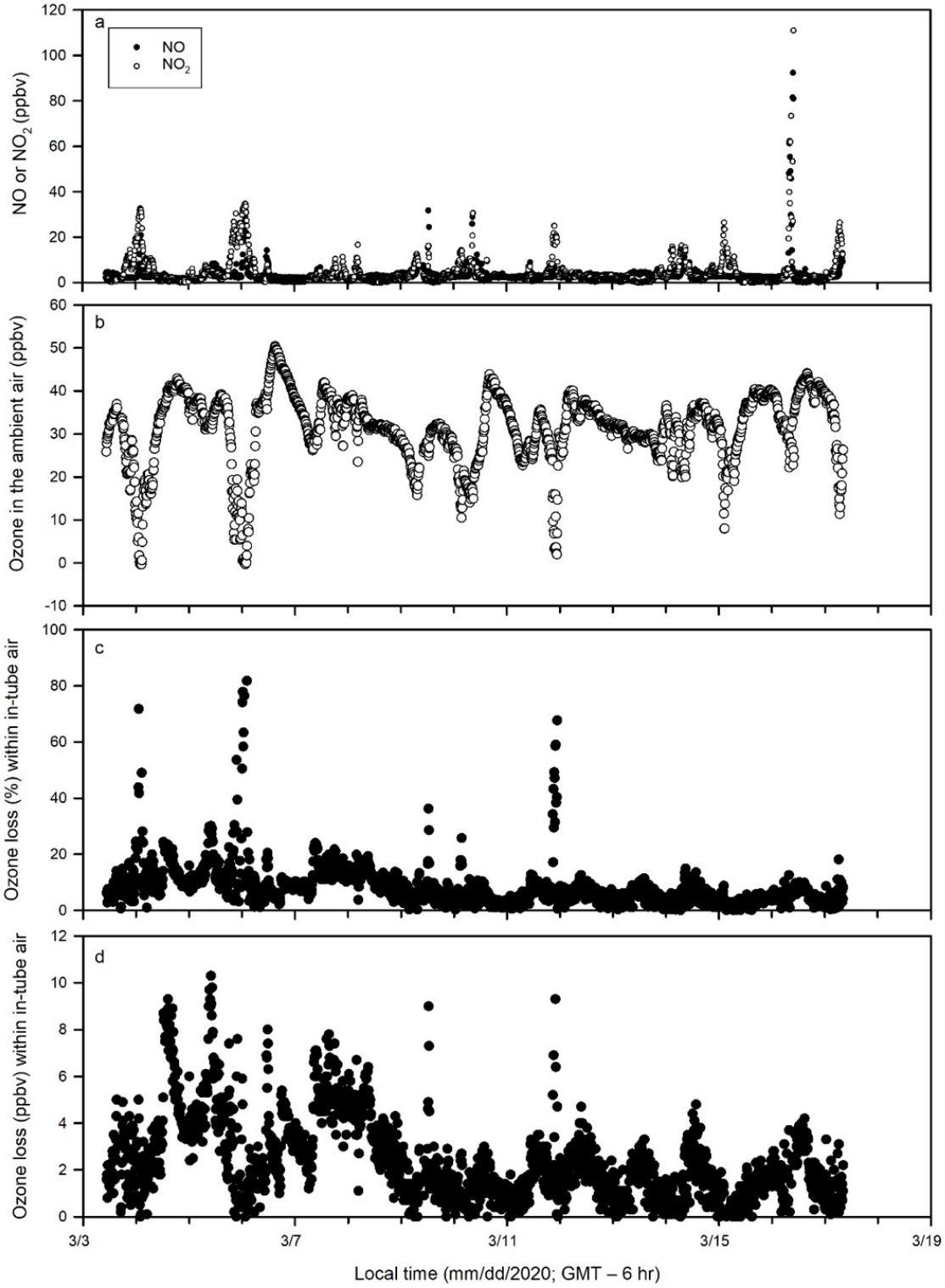

Figure S3. Temporal changes of a) NO_x ($NO + NO_2$) in the ambient air, b) ozone in the ambient air, c) ozone loss (%), and d) ozone loss (ppbv) (measured as the difference between the ambient air and in-tube air) during Experiment #2.

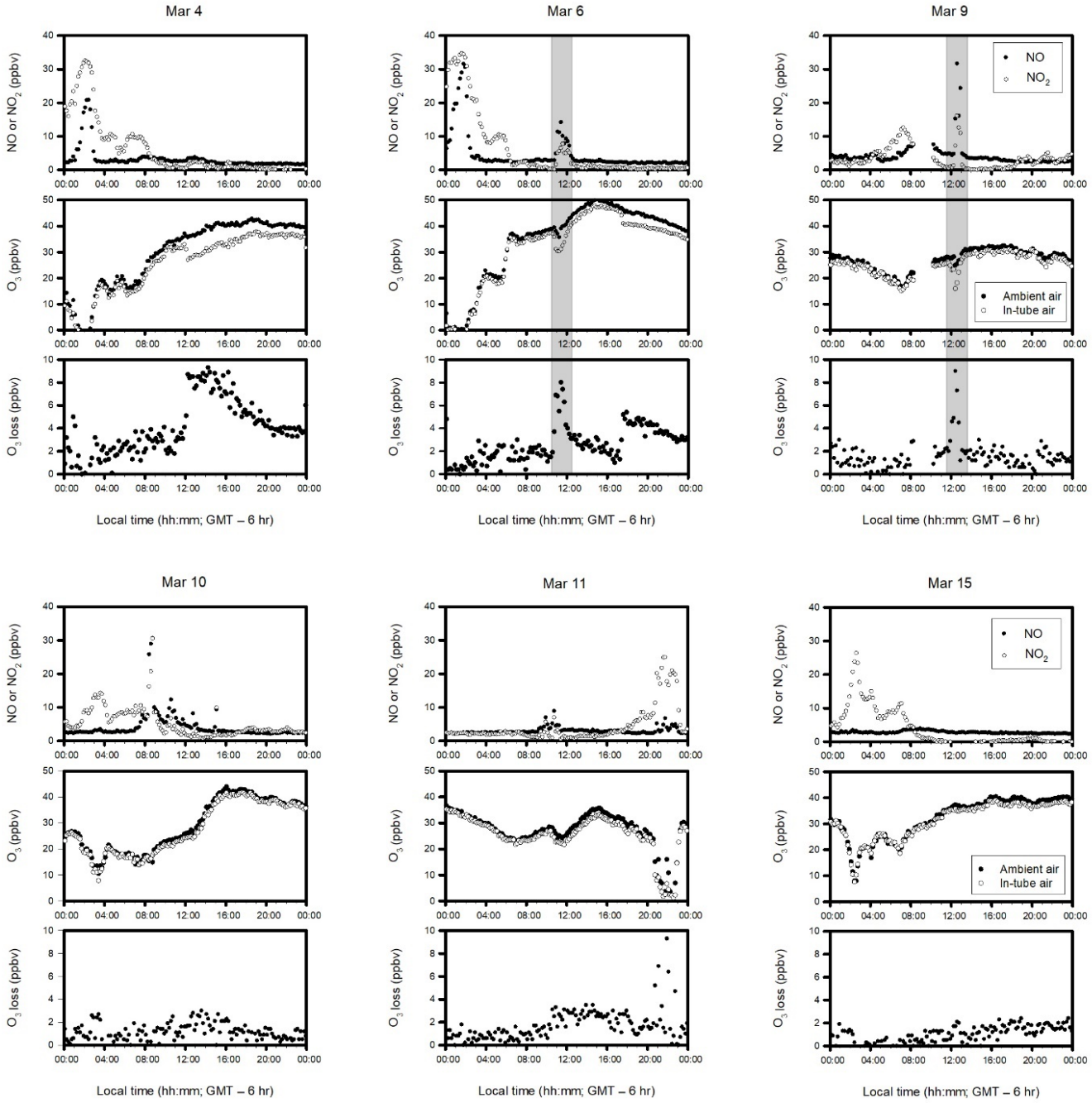

Figure S4. Temporal changes of O_3, NO, NO_2, and O_3 loss within the in-tube air (measured as the difference between the ambient air and in-tube air) during each major ambient O_3 depletion event of Experiment #2.

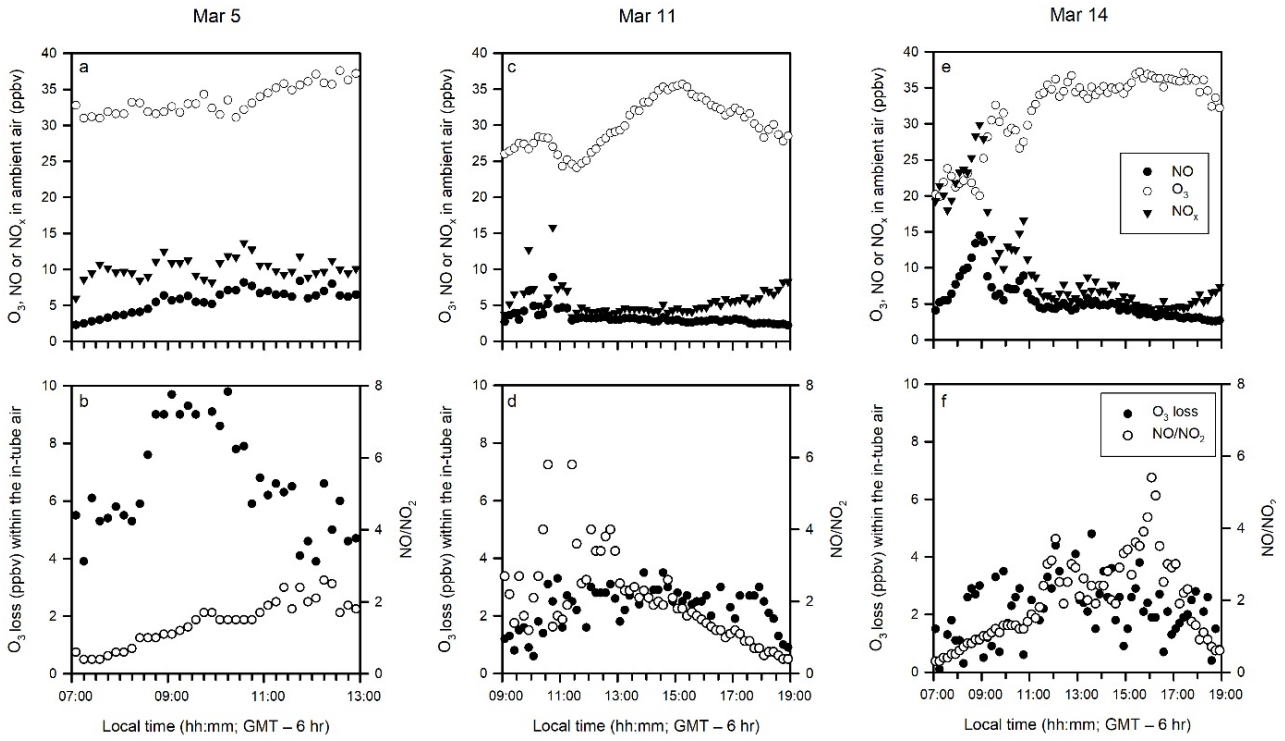

Figure S5. Temporal changes of ambient O_3, NO, NO_x, and O_3 loss within the in-tube air (measured as the difference between the ambient air and in-tube air) and NO/NO_2 ratio during the daytime O_3 span on 5 March (a, b), 11 March (c, d), and 14 March (e, f).

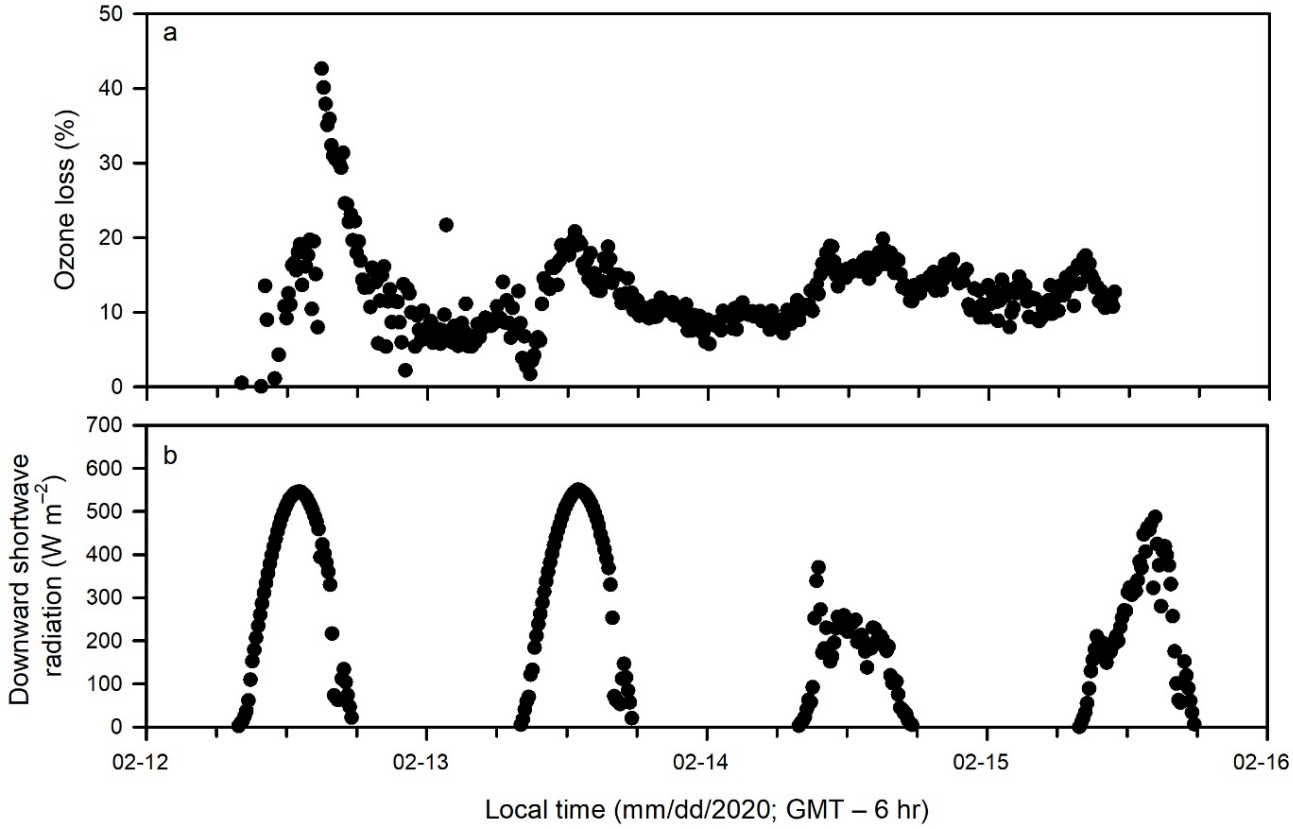

Figure S6. Temporal changes of a) ozone loss (%) between the UV-transmitting and UV-blocking tubes, and b) downward shortwave radiation during Experiment #1.