



*Supplement of*

## **Ozone in the boreal forest in the Alberta Oil Sands Region**

**Xuanyi Zhang et al.**

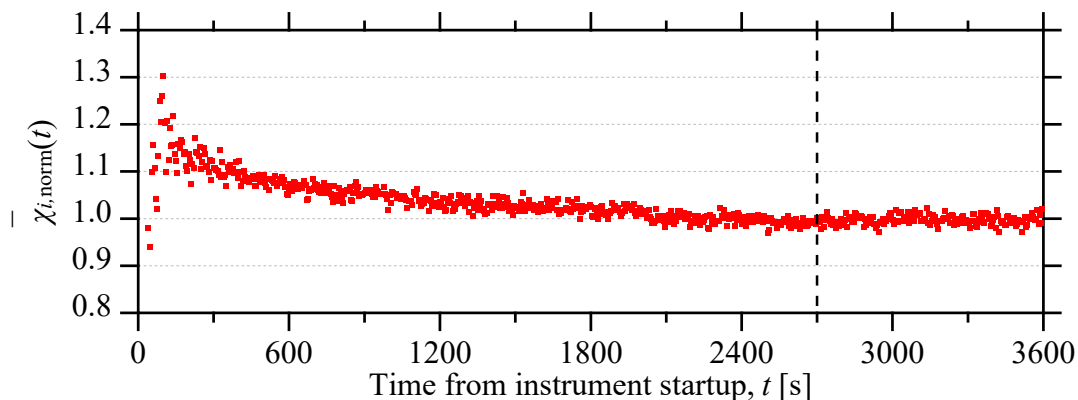
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# Supplement of Ozone in the boreal forest in the Alberta oil sands region

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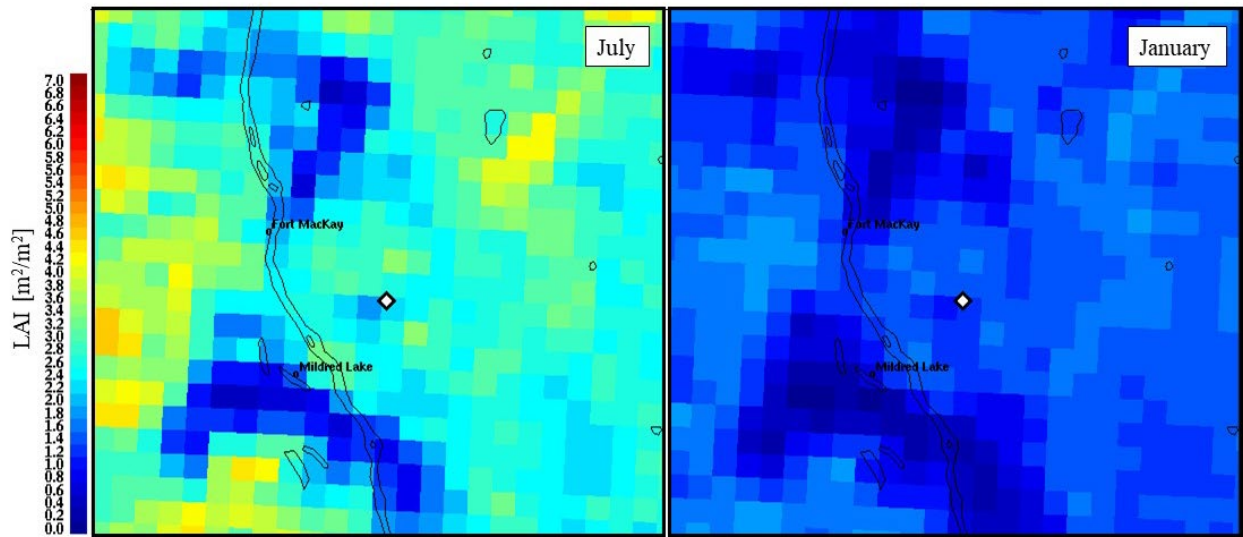
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**Figure S1:** Normalized ensemble mean ozone mixing ratio recorded by the 2B Model 205 analyzers to demonstrate the time to stabilization of the measurements. The time ( $t$ ) is the elapsed time from when the instrument is activated (every 6 hours for a 1-hour duration). The normalized ensemble means mixing ratio,  $\bar{\chi}_{i,\text{norm}}(t) = \left[ \frac{1}{n} \int_1^n \chi(t, i) / \bar{\chi}_t(i) di \right]$ , where  $\chi(t, i)$  is the measured mixing ratio at elapsed time  $t$  for the 1-hour time period  $i$  (with  $n = 448 = 56 \text{ days} \times 4 \text{ periods per day} \times 2 \text{ analyzers}$ ) and  $\bar{\chi}_t(i) = \frac{1}{T} \int_0^T \chi(t, i) dt$  with  $T = 1 \text{ hour}$ . The dashed line shows the time (at 45 minutes) after which the truncated mean (within  $\pm 3$  standard deviations) is calculated.

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**Figure S2:** LAI maps of the surrounding area (grid size is  $2.5 \times 2.5 \text{ km}^2$ ) from optimized MODIS data for months July (left) and January (right). Diamond marker shows the site location.

### Text S1: Additional Sensitivity Analysis

To test the model sensitivity to some of the assumptions, model statistics are generated from modified model runs compared to the base run with  $[\text{NO}] = 0.1$  ppb and a surface deposition rate of  $v_d = 4 \text{ mm s}^{-1}$  (config. #1). Tests include modifications to the value of the constant NO value, modification of the ozone upper boundary condition (at the highest model level of 1 km), the temperature profile above the canopy (a lapse rate of  $0 \text{ K m}^{-1}$  is compared to the assumed adiabatic lapse rate of  $0.098 \text{ K m}^{-1}$  used in the base case), use of a more transparent canopy (with a light extinction coefficient of  $k = 0.31$  compared with the base case of  $k = 0.68$ ), the choice of the height  $z_l$  used to normalize the canopy diffusion coefficient as  $K(z_l)$  ( $z_l = 42 \text{ m}$  compared with the base case of  $z_l = 23 \text{ m}$ ), a doubling of the isoprene and monoterpene emissions from the pine trees, and increased LAI (two values of 2 and  $3.5 \text{ m}^2 \text{ m}^{-2}$ ).

Table S1 lists the statistics for the base case and the modified runs. Modeled ozone output at a height of 22 m is compared to measurements from the same height. As discussed in Section 2.4, the model is highly sensitive to the NO input value. The input value of 0.05 ppb was determined through an optimization procedure to minimize the RMS error in the base case. The test results in Table S1 demonstrate that decreasing the NO amount by a factor of 5 (to 0.01 ppb) results in an overestimation of ozone (ratio of 1.45), while decreasing NO by a factor of 2 (0.10 ppb) results in an underestimation of ozone (ratio of 0.84). While decreasing NO lowers the  $R^2$  value relative to the base case, increasing NO results in a higher  $R^2$  value (0.548) due to a stronger diurnal variation in ozone levels.

Lowering the ozone upper boundary condition to 50 ppb reduces the RMS error (to 9.7 from 10.7 ppb) and raised the  $R^2$  value (to 0.449 from 0.423), but this causes the model to underpredict the ozone by an average of 13%. Conversely, increasing the upper boundary ozone to 70 ppb results in an overprediction of 12%, increases the RMS error (12.9 ppb), and decreases the  $R^2$  (0.402). Hence there appears to be some sensitivity to this variable with a trade-off between better diurnal variation in the model with less ozone versus an average underprediction relative to the observed average.

Changing the temperature profile above the canopy, the light extinction coefficient, or the height ( $z_l$ ) that is used to normalize the in-canopy  $K$  parameterization (following M17) does not have a significant effect on the statistics, although the  $R^2$  values are slightly higher (ranging from 0.424 to 0.434 for all these cases, compared to 0.423 for the base case). Doubling the basal emission rates of isoprene and monoterpenes or increasing the LAI has no significant effect (<2%) on any of the statistics. We note that a doubled isoprene emission rate corresponds to the warm conifer classification of Guenther et al. (1995) and can hence be considered realistic values. Changing the model maximum height from 1 km to 500 m results in a 30% average overestimation (due to the closer proximity of the canopy-top boundary condition to the measurement height) and a higher RMS error (15.1 ppb); however, the  $R^2$  value is slightly improved (0.469 from 0.424). In summary, these results demonstrate that the model is relatively insensitive to the choice of parameter values within the range of values investigated here (with the exception of input NO mixing ratio). The sensitivity analyses of this and the previous section suggest that the 1D model results depend most strongly on the assumed NO concentrations and the magnitude of the coefficients of vertical diffusivity ( $K$ ). Height dependent observations of both NO and turbulent kinetic energy ( $e$ ) as well as  $\text{O}_3$  are therefore recommended for future studies of this nature.

**Table S1:** Model statistics with modified parameters for 2-day model runs. Ratio of averages (modeled/observed), RMS error, and coefficient of correlation ( $R^2$ ) are shown. The base case is run with a constant ozone mixing ratio of  $[\text{NO}] = 0.05$  ppb, an upper boundary condition  $[\text{O}_3] = 60$  ppb at the 1 km model top, a lapse rate of  $dT/dz = -9.8 \text{ K km}^{-1}$  above 29 m, a canopy light extinction coefficient of  $k = 0.68$ ,  $z_l = 23$  m, and LAI = 1.17 m. The modeled isoprene and monoterpene emission rates are doubled as a sensitivity test. A model version is tested with a 0.5 km maximum model height. All runs include an ozone surface deposition of  $v_d = 4 \text{ mm s}^{-1}$ .

Model Run	Ratio	RMS [ppb]	$R^2$
Base case (Config. #2)	1.00	10.7	0.423
$[\text{NO}] = 0.01$ ppb	1.45	14.7	0.347
$[\text{NO}] = 0.10$ ppb	0.84	11.4	0.548
$[\text{O}_3] = 50$ ppb at 1 km	0.87	9.7	0.449
$[\text{O}_3] = 70$ ppb at 1 km	1.12	12.9	0.402
$dT/dz = 0$ for $z > h_c$	0.96	10.4	0.434
$k = 0.31$	1.00	10.7	0.424
$z_l = 42$ m	0.98	10.7	0.431
Double iso/mono rates	0.99	10.7	0.428
LAI = 2	0.99	10.7	0.426
LAI = 3.5	0.98	10.8	0.428
Model height of 500 m	1.30	15.1	0.459